

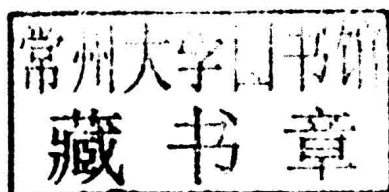
Advanced Topics in Ionic Liquids

Pablo Rickman



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Edited by **Pablo Rickman**



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Preface

In my initial years as a student, I used to run to the library at every possible instance to grab a book and learn something new. Books were my primary source of knowledge and I would not have come such a long way without all that I learnt from them. Thus, when I was approached to edit this book; I became understandably nostalgic. It was an absolute honor to be considered worthy of guiding the current generation as well as those to come. I put all my knowledge and hard work into making this book most beneficial for its readers.

This book presents an overview on latest advancements in the study and research of ionic liquids. Ionic liquids are a rapidly evolving field of study in physical chemistry, material science, technology and engineering. Use of ionic liquids for research in biology and natural resource domain has received significant attention. This book presents updated scientific developments in theoretical, specific and applied domains of ionic liquid. It encompasses the latest developments in ionic liquid research on basic properties, energy, fuels and biomass conversion. It is a valuable source of information for scientists, engineers and academicians engaged in the research related to ionic liquids.

I wish to thank my publisher for supporting me at every step. I would also like to thank all the authors who have contributed their researches in this book. I hope this book will be a valuable contribution to the progress of the field.

Editor

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List of Contributors

Fundamental Properties

A Comparative Study of Piperidinium and Imidazolium Based Ionic Liquids: Thermal, Spectroscopic and Theoretical Studies

Madhulata Shukla and Satyen Saha

Additional information is available at the end of the chapter

1. Introduction

Ionic liquids (ILs) comprise an extremely broad class of molten salts that are attractive for many practical applications because of their useful combinations of properties [1-3]. The ability to mix and match the cationic and anionic constituents of ILs and functionalize their side chains. These allow amazing tenability of IL properties, including conductivity, viscosity, solubility of diverse solutes and miscibility/ immiscibility with a wide range of solvents. [4] Over the past several years, room temperature ILs (RTILs) has generated considerable excitement, as they consist entirely of ions, yet in liquid state and possess minimal vapour pressure. Consequently, ILs can be recycled, thus making synthetic processes less expensive and potentially more efficient and environmentally friendly. Considerable progress has been made using ILs as solvents in the areas of monophasic and biphasic catalysis (homogeneous and heterogeneous).[5-6] The ILs investigated herein provides real practical advantages over earlier molten salt (high temperature) systems because of their relative insensitivity to air and water. [6-7] A great deal of progress has been made during last five years towards identifying the factors that cause these salts to have low melting points and other useful properties.[8] ILs are subject of intense current interest within the physical chemistry community as well. There have been quite a lot of photophysical studies in ionic liquids. [8] The most important properties of ionic liquids are: thermal stability, low vapour pressure, electric conductivity, liquid crystal structures, high electro-elasticity, high heat capacity and inflammability properties enable the use of ionic liquids in a wide range of applications, as shown in Figure 1. It is also a suitable solvent for synthesis, [5, 8, 9-12] catalysis [6, 8, 13] and purification. [14-18] It is also used in electrochemical devices and processes, such as rechargeable lithium batteries and electrochemical capacitors, etc.[19] Rechargeable Lithium

batteries are a ubiquitous energy device that is being worldwide in many types of portable electronic equipment, such as cellular phones, laptop computers, and digital cameras and many more devices.[20] Recently, it has been realized that variation of the type of cationic core is a very valuable approach to get more number of ILs.[8]

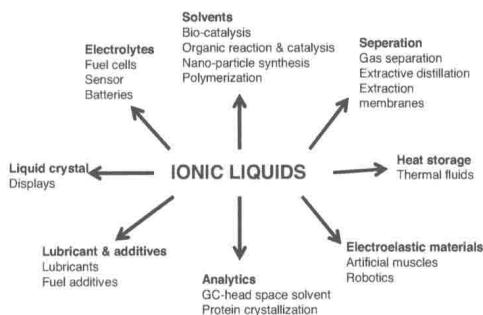


Figure 1. Applications of Ionic Liquids

A major difference between imidazolium salt on one hand and piperidinium salts on the other hand is that the positive charge is delocalized over the aromatic ring in imidazolium salt, whereas the positive charge is localized on the nitrogen atom of piperidinium salts. Next to imidazolium, piperidinium based ILs are the most popular and versatile. Several literatures are available on study of imidazolium based ILs, where x-ray crystallography studies [21-22], theory [23-28], viscosity [8], spectroscopic studies including IR and Raman spectra [27] have been discussed. In comparison to this, very few literatures exist related to piperidinium based ILs. During the last five years interest towards piperidinium based ILs has increased considerably. Cyclic alkyl quaternary ammonium (QA) cations, N-alkyl-N-methylpiperidinium (PIP_{1n} ; where 1 indicates CH_3 and n = number of carbon in another alkyl substitution) are class of cations whose room temperature ILs (RTILs) are very promising in the field of electrochemical applications due to their high thermal and electrochemical stabilities.[29-43] Recently, PIP_{1n} ILs found to be potentially useful for electrochemical applications due to their water immiscibility, high conductivities, thermal stabilities and wide electrochemical windows. For example, 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ($\text{PIP}_{14}\text{NTf}_2$; where, NTf_2^- : bis(trifluoromethylsulfonyl)imide anion) improves the stabilization of the chemical composition and structure of the sulphur cathode in Li/S cells during charge-discharge cycles. In the state of the art technologies of 4V-class rechargeable Li batteries, a mixture of organic aprotic solvents and LiPF_6 is generally used.[44] Recent studies have shown that the highly fluid and conductive 1, 3-dialkylimidazolium salts cannot be used as electrolyte for 4V-class Li batteries, because of very positive cathodic potential of the 1,3-dialkylimidazolium cations. [45-47] On the other hand, it was revealed that the ILs based on quaternary ammonium cations with the electrochemically stable and weak-

ly coordinating anion, NTf_2^- offer some promising properties.[48-50] These promising properties mainly include i) wide electrochemical windows on account of the low cathodic potential of the saturated QA cations and the high anodic potential of the NTf_2^- , ii) low viscosities on account of the high flexibility and good charge distribution of the NTf_2^- , and iii) wide stable liquid ranges on account of the low melting point and high thermal stability of the NTf_2^- salts.[51-54] The free NTf_2^- anion itself has several interesting features.[55] The negative charge can be expected to be delocalized over five atoms (four oxygen and the nitrogen), implicating a weak coordinating power. This is of vital importance in the applications where the formation of ion pairs would reduce the number of charge carriers and hence the ionic conductivity. The possibility of rotations around the two central S-N bonds would provide a mechanical flexibility resulting in a plasticizing effect of the polymer electrolyte, making the system more conductive due to the large internal mobility of the dissolved species. Both these effects have been observed for polymer electrolytes based on PEO/ LiNTf_2 [56-57] and PEO/alkaline salts.[58] As for example, $\text{PIP}_{1n}\text{NTf}_2$, have been recently proposed for high-voltage super capacitors and lithium batteries.[31-33, 36] Particularly $\text{PIP}_{13}\text{NTf}_2$ has been found to be useful for the use in Li-batteries [38] with a superior reversible discharge capacity of 340-350 mA-h/g with only a small irreversible capacity loss per cycle [59]. Despite this tremendous interest, the properties, molecular structure and theoretical calculation of PIP_{1n} cation based ILs have not been investigated in detail so far. As the properties of any material depends on the structure of molecules in different phases, it is important to understand the structural features of ILs in depth. In general, liquids are much less understood than gases and crystals. While structure in the gas phase can be accurately determined by electron diffraction or high-resolution rotationally-resolved spectroscopy, solid/crystal structure can be determined by X-ray or neutron diffraction. On the other hand, diffraction and spectroscopic techniques has limited applicability to elucidate liquids structure. Structural information available for liquids is thus much less. Thus theoretical calculations are of very much important in predicting the structure of different room temperature ionic liquids (RTILs). In particular, Density Functional Theory (DFT) calculation found to be very useful in predicting structure of various RTILs. [23-24, 27] DFT calculation also helps us to understand the interaction present among cation and anion in the molecule as well as the type of bonding present in the molecule. Magnetic moment, dipole moment and many other physical properties as well as wavelength of various electronic transition of ILs can also be calculated by DFT calculation. In this chapter we addressed the following very specific issues related to important class of piperidinium based ILs. Synthetic procedure for different piperidinium based ILs has been described and it was found that with variation of anion, cation being the same, physical state of ILs changes drastically.[23] Thermophysical properties of imidazolium and piperidinium based cation with similar anion has been compared briefly. Melting point, viscosity and cyclic voltammetry properties with variation of alkyl chain as well as variation of several anions has been reported for both types of cation. Further we have compared the optimized molecular geometry of bmimBr , bmimI and bmimNTf_2 ion pairs with PIP_{14}Br , PIP_{14}I and $\text{PIP}_{14}\text{NTf}_2$ respectively in gaseous phase using theoretical calculations. bmimBr and bmimI ILs, exist as solid of very low melting point or in liquid state [22], whereas its analogous piperidinium based ILs (PIP_{14}Br and PIP_{14}I respectively) exist in solid

having high melting point. In addition, the calculated vibrational frequency of the molecule gives us a strong base to analyze the experimental spectra and also the effect of interaction causing shifting in vibrational bands. Further, experimental IR frequencies of $\text{PIP}_{14}\text{NTf}_2$ and its correlation with theoretical (DFT and HF methods) vibrational frequencies have been reported.

2. Reagents and instrumentation

N-methylpiperidine (Sigma Aldrich, >99%), bromobutane, Iodobutane (Merck, Germany), bis(trifluoromethanesulfonyl)imide (Sigma Aldrich, >99%) were used as received for the synthesis. Acetonitrile (HPLC grade) was procured from Merck, Germany and were used after purification following standard procedures. UV-Visible spectra were measured by CARY 100 BIO UV-Visible Spectrophotometer, which has photometric linearity till absorbance 3.5. Infrared spectra were measured with Varian FTIR 3100 in the region $400\text{ cm}^{-1} - 3500\text{ cm}^{-1}$ using neat sample. 300MHz NMR (JEOL) was used to measure the ^1H NMR and ^{13}C NMR. Melting point of the synthesized samples were recorded using automatic digital melting point apparatus (Optimelt).

3. Experimental

3.1. Conventional preparation for ammonium cation based ILs

The general synthetic path for preparing ammonium based ILs is shown in Figure 2. The first step usually is a quaternization reaction, where an amine (NR_3) is alkylated with an appropriate alkylation reagent ($\text{R}'\text{X}$) e.g. alkyl halide, resulting in the corresponding IL. When an IL with a desired anion cannot be formed via this reaction, an anion exchange reaction is needed. A previously formed IL is used as precursor and the anion is changed by a metathesis reaction. This metathesis reaction can be performed by using a metal salt (MA).

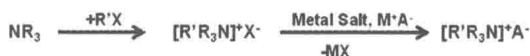


Figure 2. Synthetic path for preparing ammonium based ILs

3.2. Synthesis of 1-butyl-3-methylimidazolium halide (bmimX, where $\text{X}^- = \text{Br}, \text{I}$) and bmimNTf₂

Synthetic Procedure for bmimX and bmimNTf₂ have been reported by us earlier [24] Since we have used considerable less temperature than generally reported [60], the time required

for the reactions are also much higher. Nevertheless, this low temperature reaction has been found to provide much purer ILs.

3.3. Synthesis of N-butyl-N-methylpiperidinium halide (PIP_nX, where X = Br, I) and PIP₁₄NTf₂

3.3.1. Synthesis of N-butyl-N-methylpiperidinium bromide (PIP₁₄Br)

A general synthesis procedure for synthesizing PIP₁₄Br was reported in literature.[40] A modified form of that reported procedure is followed; instead of using high temperature, lower temperature (50 °C) is used with longer time of stirring. This excludes major possibilities of inclusion of impurities in ionic liquids. Scheme for the synthesis of PIP₁₄Br is shown in Figure 3. 20 mL of ethyl acetate was taken in 100 mL RB flask. To it 10 mL (82.3 mmol) N-methyl piperidine was added with stirring and then 9.7 mL (90.5 mmol) of bromobutane was added slowly with continuous stirring at 25 °C. Mixture was stirred for 16 h at RT in nitrogen atmosphere and then stirring was made at 50 °C for 3 h. The solution was washed with 150 mL dry distilled ethylacetate and remaining solvent was evaporated on a rotavapour. White solid product was kept under high vacuum at 50 °C for 3 h. (yield= 90%). Melting point (mp) found to be 241 °C. The product was confirmed by ¹H NMR (δ, ppm, 1.01 (t, 3H), 1.47 (q, 2H), 1.72 (8H), 3.63 (s, 3H), 3.66 (4H) and 3.81 (2H); IR: 569, 673, 904, 940, 1030, 1227, 1369, 1464, 2874 and 2959 cm⁻¹.

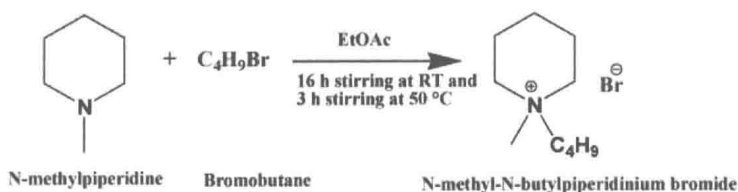


Figure 3. Scheme for the synthesis of PIP₁₄Br

3.3.2. Synthesis of N-alkyl-N-methylpiperidinium Iodide (PIP_nI)

A general synthesis procedure for synthesizing PIP_nI (where n=1, 3, 4, 6, 8) is shown in Figure 4. As above mentioned process, here also instead of using high temperature, RT is preferred with longer time of stirring to exclude the major possibilities of inclusion of impurities in ionic liquids. All the reactions were carried out with 1:1.1 molar ratios. 10 mL of Ethyl acetate was taken in 100 mL RB flask. To it 2 mL (16 mmol) N-methyl piperidine was added with stirring and then X mL (X mmol) of iodoalkane was added slowly with continuous stirring at 25 °C. Mixture was stirred for 24-48 h at RT in nitrogen atmosphere (except for PIP₁₁I, where stirring was done for 4 h only). The solution was washed with 150 mL dry distilled ethylacetate and remaining solvent was evaporated on a rotavapour. White solid product was kept under high vacuum for 3 h. Yield for PIP₁₁I = 100% and for rest of the

salt, it is found to 70%. Melting point (mp) found to be 181°C, 198°C, 124°C and 131°C for PIP₁₃I, PIP₁₄I, PIP₁₆I and PIP₁₈I respectively. The products were confirmed by ¹H NMR, ¹³C NMR and IR.

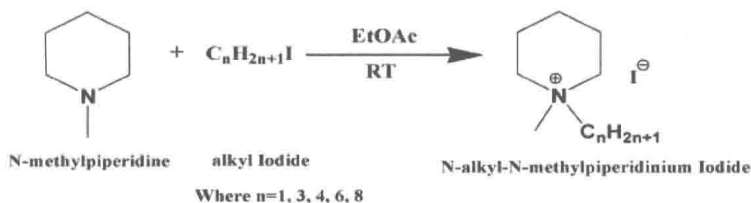


Figure 4. Scheme for the synthesis of PIP_{*n*}I

3.3.3. Synthesis of *N*-butyl-*N*-methylpiperidiniumbis(trifluoromethanesulfonyl)imide (PIP₁₄NTf₂)

PIP₁₄NTf₂ was done following the similar procedure as described in literature.[40] Scheme for preparation of PIP₁₄NTf₂ is shown in Figure 5. 4.6 g (19.5 mmole) of PIP₁₄Br was taken in a RB and to it 10 mL of triple distilled (TD) water was added. 6.1 g (21.4 mmole) LiNTf₂ dissolved in 10 mL TD water added to it. Stirring was done for 4 h. 150 mL dichloromethane (DCM) solvent was used to wash followed by the cold distilled water. DCM was evaporated on rotavapour and after that it was kept under high vacuum for 2 h at 60 °C. Light yellow colour liquid was obtained with a yield of 88%. This light yellow colored liquid was further dissolved in 10 mL of pure predistilled acetonitrile (ACN) and treated with activated celite for decolorization. Room temperature stirring was done for 4 h followed by filtration through a column packed with fresh charcoal and activated alumina. The resultant solution was evaporated on rotavapour at reduced pressure. Completely colorless liquid was obtained. The product was confirmed by ¹H NMR (δ , ppm, 1.01 (t, 3H), 1.44 (q, 2H), 1.74 (8H), 3.42 (s, 3H), 3.56 (4H) and 3.85 (2H) and IR: 570, 619, 1054, 1139, 1197, 1348, 1474, 2881 and 2966 cm⁻¹.

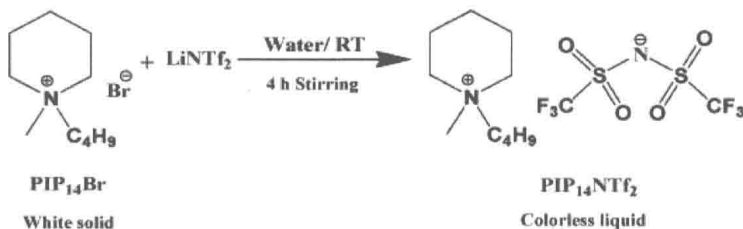


Figure 5. Scheme for the synthesis of PIP₁₄NTf₂