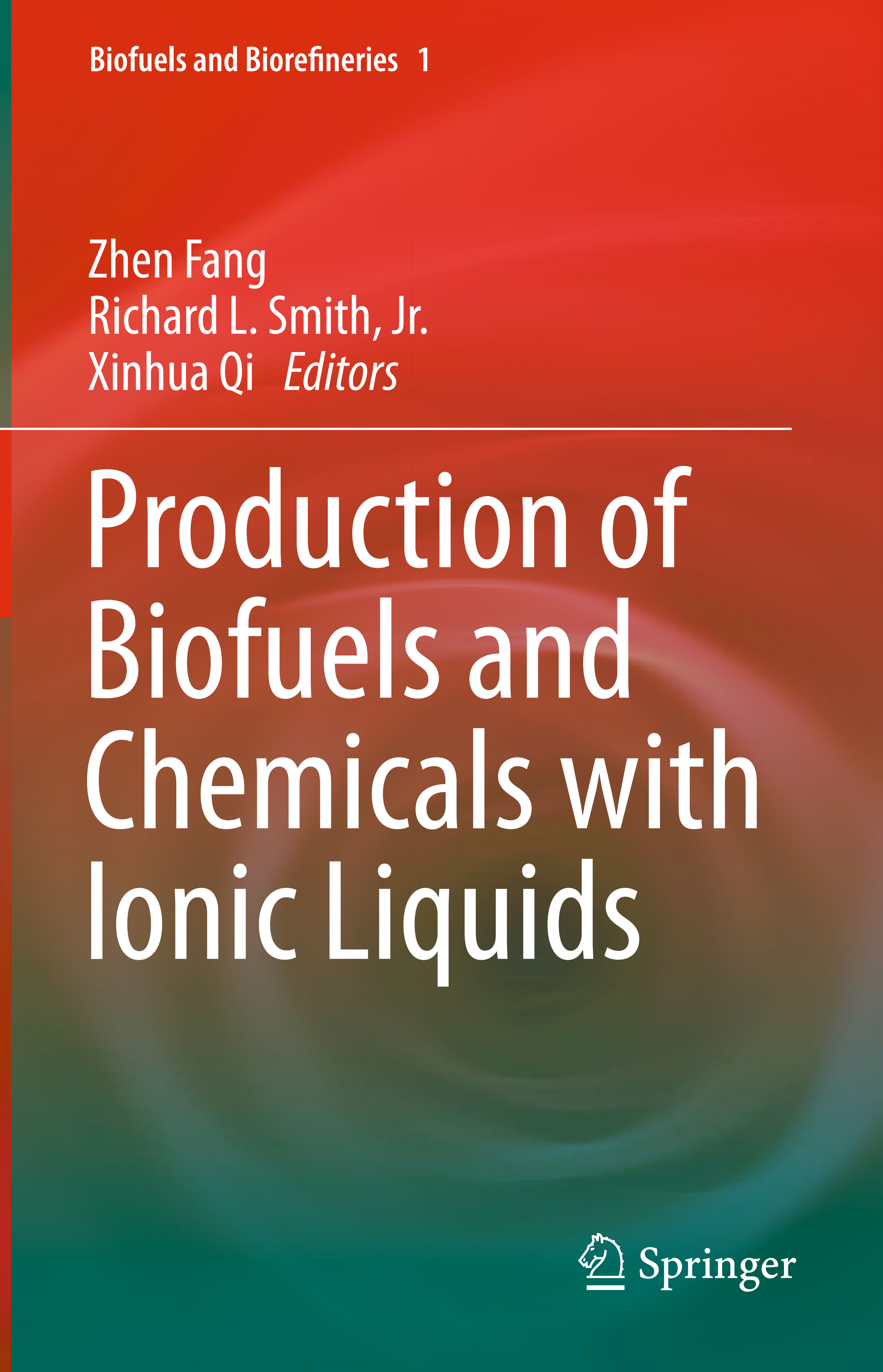

Biofuels and Biorefineries 1

Zhen Fang
Richard L. Smith, Jr.
Xinhua Qi *Editors*

Production of Biofuels and Chemicals with Ionic Liquids

Springer

Biofuels and Biorefineries

Volume 1

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Book Series in Biofuels and Biorefineries aims at being a powerful and integrative source of information on biomass, bioenergy, biofuels, bioproducts and biorefinery. It represents leading global research advances and opinions on converting biomass to biofuels and chemicals; presents critical evidence to further explain the scientific and engineering problems in biomass production and conversion; and presents the technological advances and approaches for creating a new bio-economy and building a clean and sustainable society to industrialists and policy-makers.

Book Series in Biofuels and Biorefineries provides the readers with clear and concisely-written chapters on significant topics in biomass production, biofuels, bioproducts, chemicals, catalysts, energy policy and processing technologies. The text covers areas of plant science, green chemistry, economy, biotechnology, microbiology, chemical engineering, mechanical engineering and energy studies.

Series description

Annual global biomass production is about 220 billion dry tons or 4,500 EJ, equivalent to 8.5 times the world's energy consumption in 2008 (532 EJ). On the other hand, the world's proven oil reserves at the end of 2011 amounted to 1652.6 billion barrels, which can only meet 54.2 years of global production. Therefore, alternative resources are needed to both supplement and replace fossil oils as the raw material for transportation fuels, chemicals and materials in petroleum-based industries. Renewable biomass is a likely candidate, because it is prevalent throughout the world and can readily be converted to other products. Compared with coal, the advantages of using biomass are: (i) it is carbon-neutral and sustainable when properly managed; (ii) it is hydrolysable and can be converted by biological conversion (e.g., biogas, ethanol); (iii) it can be used to produce bio-oil with high yield (up to 75%) by fast pyrolysis because it contains highly volatile compounds or oxygen; (iv) biofuel is clean because it contains little sulfur and its residues are recyclable; (v) it is evenly distributed geographically and can be grown close to where it is used, and (vi) it can create jobs in growing energy crops and building conversion plants. Many researchers, governments, research institutions and industries are developing projects to convert biomass (including forest woody and herbaceous biomass) into chemicals, biofuels and materials and the race is on to create new "biorefinery" processes. The development of biorefineries will create remarkable opportunities for the forestry sector, biotechnology, materials and the chemical processing industry, and it will stimulate advances in agriculture. It will help to create a sustainable society and industry based on renewable and carbon-neutral resources.

Zhen Fang • Richard L. Smith, Jr. • Xinhua Qi
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ISSN 2214-1537 ISSN 2214-1545 (electronic)
ISBN 978-94-007-7710-1 ISBN 978-94-007-7711-8 (eBook)
DOI 10.1007/978-94-007-7711-8
Springer Dordrecht Heidelberg New York London

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Preface

Interest in biofuels and value-added chemicals that can be produced from biomass is increasing daily as societies look to sustainable sources of energy. Ionic liquids are used for the pretreatment and chemical transformation of biomass due to their unique ability for dissolving lignocellulosic materials. Although there are many books on the topic of either biomass conversion or ionic liquids, the unique feature of this book is that it links biomass conversion with ionic liquids and chemicals such that processing, chemistry, biofuel production, enzyme compatibility and environmental treatment are covered for conceptual design of a biorefinery. This book is the first book of the series entitled *Biofuels and Biorefineries*.

This book consists of 12 chapters contributed by leading world-experts on biomass conversion with ionic liquids. Each chapter was subjected to peer-review and carefully revised by the authors and editors so that the quality of the material could be improved. The chapters are arranged in five parts:

Part I: Synthesis and Fundamentals of Ionic Liquids for Biomass Conversion (Chaps. 1, 2, and 3).
Part II: Dissolution and Derivation of Cellulose and Fractionation of Lignocellulosic Materials with Ionic Liquids (Chaps. 4, 5, and 6).
Part III: Production of Biofuels and Chemicals in Ionic Liquids (Chaps. 7, 8, and 9).
Part IV: Compatibility of Ionic Liquids with Enzymes in Biomass Treatment (Chaps. 10 and 11).
Part V: Ionic Liquids for Absorption and Biodegradation of Organic Pollutants in Multiphase Systems (Chap. 12).

Chapter 1 introduces the fundamentals of ionic liquids related to biomass treatment. Chapter 2 gives an outline of design and synthesis of ionic liquids for cellulose dissolution and plant biomass treatment. Chapter 3 overviews the recent advances made with choline-chloride (ChCl) not only for the activation of biomass but also for its conversion to value-added chemicals. Chapter 4 summarizes approaches to design of ionic liquids that have good capability for dissolving cellulose and discusses factors for realizing efficient room-temperature dissolution of cellulose dissolution and subsequent enzymatic hydrolysis. Chapter 5 provides a comprehensive overview about the use of ionic liquids for the chemical derivatization of cellulose. Chapter 6 reviews the current state of knowledge and process development in the area of ionic liquid fractionation of wood, and reports findings on factors that control the solubility of wood in ionic liquids. Chapter 7 provides an overview on the biodiesel production in ionic liquids, ionic liquids-catalyzed biodiesel production, ionic liquids-modified enzymes for biodiesel production, purification of bio-alcohols with ionic liquids, and prospects. Chapter 8 focuses on catalytic transformations of biomass into fuels and chemicals in ionic liquids. Chapter 9 describes the efficient methods for producing the platform chemical, 5-hydroxymethylfurfural with ionic liquids. Chapter 10 covers the biocompatibility issues of ionic liquids, for example, biocatalysts in ionic liquids media, the effect of ionic liquids properties on the activity and stability of enzymes, approaches to enhance the activity and stability of enzymes in the ionic liquids containing medium, and rational design of ionic liquids for use with enzymatic reactions. Chapter 11 focuses on the application of enzyme technology in ionic liquids. Chapter 12 introduces the potential of ionic liquids for hydrophobic organic pollutants absorption and biodegradation in multiphase systems.

This book reviews many aspects of the ionic liquids techniques necessary for efficient development of biomass resources. The text should be of interest to students, researchers, academicians and industrialists in the area of ionic liquids and biomass conversion.

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Acknowledgements

First and foremost, we would like to thank all the contributing authors for their many efforts to insure the reliability of the information given in the chapters. Contributing authors have really made this project realizable.

Apart from the efforts of authors, we would also like to acknowledge the individuals listed below for carefully reading the book chapters and giving constructive comments that significantly improved the quality of many aspects of the text:

Dr. Leigh Aldous, the University of New South Wales, Australia;
Dr. Agnieszka Brandt, Imperial College London, UK;
Prof. Johann Görgens, Stellenbosch University, South Africa;
Prof. Yanlong Gu, Huazhong University of Science and Technology, China;
Prof. Mohd Ali Hashim, University of Malaya, Malaysia;
Prof. Noriho Kamiya, Kyushu University, Japan;
Dr. Takao Kishimoto, Toyama Prefectural University, Japan;
Dr. Jong Min Lee, Nanyang Technological University, Singapore;
Dr. Sang Hyun Lee, Konkuk University, South Korea;
Prof. Jean-Marc Lévêque, Université de Savoie, France,
Dr. Ruigang Liu, Chinese Academy of Sciences, China;
Prof. Rafael Luque, Universidad de Córdoba, Spain;
Dr. Patrick Navard, Ecole des Mines de Paris/CNRS, France;
Dr. Vladimír Raus, Academy of Sciences of the Czech Republic;
Prof. Robin D. Rogers, The University of Alabama, USA.;
Prof. Roger A. Sheldon, Delft University of Technology, The Netherlands;
Prof. Run-Cang Sun, Beijing Forestry University;
Dr. Yugen Zhang, Institute of Bioengineering and Nanotechnology, Singapore;

We are also grateful to Ms. Becky Zhao (senior editor) and Ms. Abbey Huang (editorial assistant) for their encouragement and assistant with the guidelines during preparation of the book.

Finally, we would like to express our deepest gratitude towards our family for their kind cooperation and encouragement, which helped us in completion of this project.

Fangzhen
Richard L Smith, Jr.
Xinhua Qi

Zhen FANG, August 1, 2013 in Kunming
Richard L. Smith, Jr., August 1, 2013 in Sendai
Xinhua Qi, August 1, 2013 in Tianjin

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Part IV Compatibility of Ionic Liquids with Enzyme in Biomass Treatment

Part V Ionic Liquids for Absorption and Biodegradation of Organic Pollutant in Multiphase Systems

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Part I

Synthesis and Fundamentals of Ionic Liquids for Biomass Conversion

Chapter 1
Fundamentals of Ionic Liquids

Junli Xu, Qing Zhou, Xinxin Wang, Xingmei Lu, and Suojiang Zhang

Abstract Ionic liquids (ILs) are composed of cations and anions that exist as liquids at relatively low temperatures (<100 °C). They have many attractive properties, such as chemical and thermal stability, low flammability, and immeasurably low vapor pressures. This review provides a summary of the fundamental structural features of ionic liquids, the physical properties, and their applications as solvents for biomass.

Keywords ILs • Properties • Cellulose • Biomass

1.1 Introduction

The energy crisis has caused great pressure on the economic development and environmental sustainability worldwide, resulting in renewable energy, such as, solar, wind, and biomass, receiving significant attention [1]. Especially, as a resource of fuel and chemicals, biomass is developed greatly due to its large potential and universality as an energy resource. Biomass pretreatment is a key procedure for efficient processing. Biomass pretreatment was first conducted with acid or alkali, as well as some organic solvents. Gradually, considering the environmental and economic influence, ionic liquids (ILs) were introduced for biomass

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Z. Fang et al. (eds.), *Production of Biofuels and Chemicals with Ionic Liquids*,
Biofuels and Biorefineries 1, DOI 10.1007/978-94-007-7711-8_1,

pretreatment and biomass conversion with ILs was followed since ILs have many unique and excellent properties.

This part aims to briefly introduce the definition of ILs, the structures and classification of ILs, meanwhile, the properties of ILs will be discussed in detail, including melting point, viscosity, density, and thermal stability. Then the history, advantage and current status of ILs applied to cellulose/biomass, the quantities and kinds of ILs are used in dissolution and separation of cellulose from biomass are also summarized.

1.2 Overview

Ionic liquids (ILs), are organic compounds containing salts with many attractive properties like extremely low vaporization pressure and melting point, excellent thermal stability and wide liquid ranges [2–5]. ILs have widely been used in many areas, for example, chemical synthesis, catalysis, biocatalysts and electrochemical devices [6–10]. ILs can be chosen to have different anions and cations so that one can form IL with the desired properties. Especially, some kinds of ILs with special functional groups have been designed for application in many industrial processes, such as imidazolium-based ILs, phosphonium-based ILs, amino-based ILs, acid-based ILs, and biodegradable ILs [11].

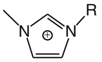
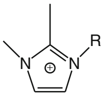
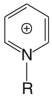
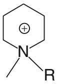
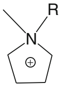
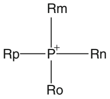
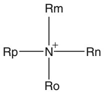
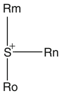
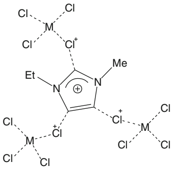
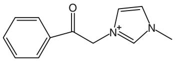
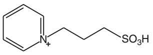
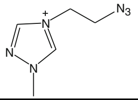
Lignocellulosic biomass is an abundant plant material and widely available, so that it has attracted much attention for conversion to fuels and chemicals [12, 13]. The main components of biomass are cellulose, hemicelluloses, lignin and other extractives. However, the complex structure of biomass makes its chemical degradation and biological conversion difficult to realize [14]. Pretreatment to disrupt the structures is necessary and a key procedure for biomass utilization.

Cellulose, as an important component of biomass, is composed of thousands of β- (1–4) – linked glucose units [15], which form many intermolecular or intramolecular hydrogen bonds [16]. Cellulose is widely treated with several organic solvents, such as N, N-dimethylformamide/nitrous tetroxide (DMF/N_2O_4) [17], N, N-dimethylacetamide lithium chloride (DMAc/LICl) [18], N-methylmorpholine (NMMO) [19] and dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) [20]. These traditional solvents suffer from volatility, toxicity, and solvent recovery issues [21, 22], so novel solvents, such as ILs, have received attention for cellulose dissolution in recent years. Cellulose dissolution with present ILs dates back to 2002 [23], before which, a solvent system for dissolving cellulose was discovered by Graenacher [24].

1.2.1 The Structures and Classification of ILs

There are a large number of ILs that can be produced theoretically, while the synthesized and reported ones are very limited [25]. By the end of 2009, more than 1,800 available ionic liquids which were composed of 714 different cations and 189 different anions have been reported in the book named ionic liquid: physicochemical properties have reported [26]. According to our current ionic liquids

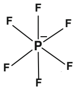
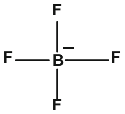
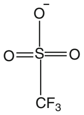
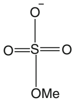
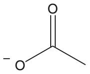
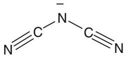
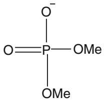
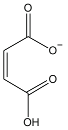
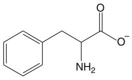
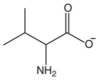
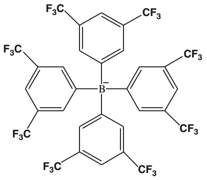
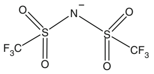
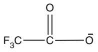
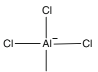
Table 1.1 Common used cations of ILs

Types	Cations	Structures
Imidazolium based cations	1-alkyl-3-methylimidazolium	
	1-alkyl-2, 3-dimethylimidazolium	
Pyridinium based cations	1-alkylpyridinium	
	1-alkyl-1-methylpyridinium	
Pyrrolidinium based cation	1-alkyl-1-methylpyrrolidinium	
Phosphonium, ammonium, sulfonium based cations	Tetraalkylphosphonium	
	Tetraakylammonium	
	Trialkylsulfonium	
Metal based cations	M = Co^{2+}, Ni^{2+}	
Functionalized cations	1-phenylethanoyl-3-methylimidazolium	
	N-propane sulfuricpyridiniumdihydrogen	
	1-methyl-4-(2-azidoethyl)-1, 2, 4-triazolium	

database, there are more than 2,300 kinds of ILs, including varieties of 229 anions, 907 cations. In these ILs, the most common used cations are imidazolium, pyridinium, piperidinium, tetraalkylphosphonium, tetraalkylammonium, trialkylsulfonium and metal based, functional cations, the cations are listed in Table 1.1.

However, the generally used ions are either inorganic or organic, for example, hexafluorophosphate, bis (trifluoromethylsulfonyl) imide, tetrafluoroborate, trifluoromethanesulfonate, dicyanamide, halide, formate, acetate, and alkyl-phosphate and so on (Table 1.2).

Table 1.2 Common used anions of ILs

Entry	Anions	Structures
1	Hexafluorophosphate	
2	Tetrafluoroborate	
3	Trifluoromethanesulfonate	
4[a]	Methyl sulfate	
5	Acetate	
6	[N $(CN_2)]^-$ chloride/bromide/iodide	
7	Chloride/bromide/iodide	Cl^-, Br^-, I^-
8[a]	Dimethyl phosphate	
9	Hydrogen maleate	
10	Tyrosine	
11	Valine	
12[b]	Tetrakis [3, 5-bis (trifluoromethyl) phenyl] borate	
13[c]	bis(trifluoromethanesulfonyl)amide	
14	Trifluoroacetate	
15[d]	$AlCl_4$-	

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[a] the methyl also could be changed into ethyl et al.

[b] the other borate and borane anions are fluoroacetoxyborate, bis(oxalato)borate, alkyl carborane et al.

[c] the similar anions are bis(perfluoroethylsulfonyl)amide, 2,2,2-trifluoro-N-(trifluoromethanesulfonyl) acetamide, tris(trifluoromethanesulfonyl)methanide.

[d] the similar metal salts based anion like $FeCl_4$-.

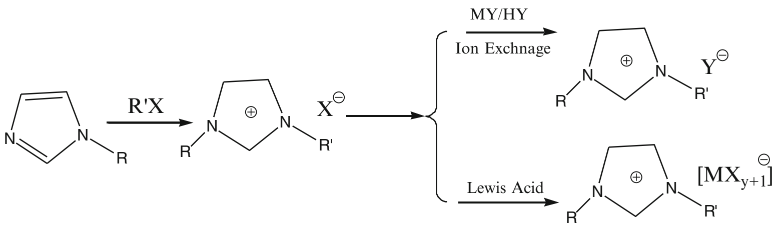
1.3 Synthesis of ILs

The synthetic routs are greatly related to the structures and composition of ILs, such as metathesis, protic synthesis, halogen free synthesis and other special methods, in this review, the synthesis procedures are summarized into one step method, two step method, enhanced methods and others especial methods, such as the synthetic method of chiral ILs.

1. One step method
   The ILs synthesized in one step method are mainly produced by the nucleophilic solvents reacting with the alkyl halide or esters, and the tertiary amine neutralized with acid. For example, the alkylimidazole halide, quaternary ammonium halide, alkyl sulfate, alkyl phosphate and neutralization reaction [27–31]. The alkylimidazole based ILs are synthesized according to Eq. 1.1.

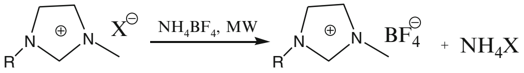
$$\mathrm{Rim} + \mathrm{R}'\mathrm{X} \rightarrow \left[\mathrm{RR}'\mathrm{im}\right]\mathrm{X} \qquad (1.1)$$

2. Two step method
   In the two step method, the alkylimidazole halide was first synthesized, then the halide was changed to targeted anions by complex reaction,metathesis reaction, ions exchange and electrolytic method. Many common used ILs are produced with this method, for examples, the [Bmim][$FeCl_3$], [Bmim][PF_6], $[Bmim]_2[SO_4]$ and [bpy][NO_3] [32–36]. The synthetic routs are shown in the Eq. 1.2.



(1.2)

3. Enhanced methods
   In the synthesis process, microwave or ultrasonic are used to enhance the reaction to increase the reaction and conversion rate. For example, the [Bmim][BF_4] is synthesized in the route as shown in Eq. 1.3 [37].



(1.3)

4. The synthetic method of chiral ILs [38, 39]
   Chiral ILs have more unique properties than that of common ILs, which combining the advantages of chiral material and ILs, and the chiral materials or asymmetric synthesis are both used in the procedure. For example, the chiral

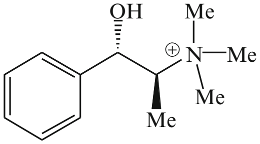
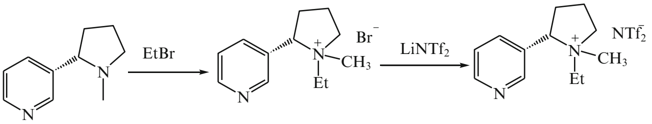


Fig. 1.1 (1S, 2R)-(+)-N, N-dimethylephdrinium

Table 1.3 Companies that produce ILs

Entry	Classification	Companies	Website
1	Range of ILs	Merck	http://www.merck.de/de/index.html
		Sigma-Aldrich	http://www.sigmaaldrich.com/united-states.html
		CAS	http://www.casact.org/
2	Imidazolium ILs	BASF	http://www.basf.com/group/corporate/us/en/
		io-li-tec	http://www.iolitec-usa.com/
3	Phosphonium ILs	Cytec	http://www.cytec.com/index.htm
4	Typically functional ILs	Frontier Scientific	http://www.frontiersci.com/
		Linzhou Keneng Materials Technology Co. Ltd.	http://lzkn.atobo.com.cn/
5	Ammonium ILs	Bioniqs	http://www.ipgroupplc.com/

compound (1S, 2R)-(+)-N, N-dimethylephdrinium cation(Fig. 1.1) can be used to synthesized ephedrinium based chiral ILs [39], and the nicotine based chiral ILs are synthesized according to the Eq. 1.4 [40, 41].



(1.4)

Now ILs are applied in a variety of fields, so many companies that produce and sale ILs are occurred all over the world. The common companies that produce ILs are listed in Table 1.3.

1.4 Characterization and Purification

After the ILs synthesis, the characterizations are followed to confirm the structures and purities. Nuclear magnetic resonance (NMR) spectrometry, Fourier transform infrared spectroscopy (FT-IR), the X-ray diffraction (XRD), elementary analysis (EA) and mass spectroscopy (MS) are common used techniques in ILs analysis. The

NMR included ^{1}H NMR and ^{13}C NMR, together with the FT-IR are widely to confirm the desired structures and functional groups of ILs. Meanwhile, the EA and MS are usually used to detect the ILs purities.

The common impurities are water, metathesis byproducts, sorbents and chemical drying agents, especially the water, which almost exit in all kinds of ILs, the water in ILs has various effects on the ILs applications, for the water sensitive reaction, the water removal is very necessary, while, sometimes a little amount of water in ILs may enhance the reaction, so the water content in ILs can be controlled by evaporated or vacuum drying according to the ILs applications. Some halide salts, alkali metals and heavy metal precipitation as byproducts in ILs, some of them are reduced by passing the ILs through silica gel [42], the precipitations are common filtered by millipore filters. In addition, some other methods, such as sorbents, distillation, zone melting and clean synthetic routes are also developed to obtain more pure ILs [39]. Sometimes the color of ILs would be dark when the reaction temperature is high, activated carbon is introduced to use in ILs discoloration. Meanwhile, the ILs those are solid at room temperature would be recrystallized to get better quality.

The separation and purification methods of ILs can be decided by different water solubility of ILs. The cation and anion composed of ILs both influence the water solubility of ILs, of course, the increased alkyl chain (n) length of the cation decreases the water solubility of ILs, and $n = 10$ is a boundary of liquid and solid phase of ILs. With a short alkyl chain cation, the ILs containing halide, acetate, sulfate, or phosphate are generally liquids insoluble with water, while the ILs with BF_4 or PF_6 are mostly water-immiscible [39].

1.5 Physicochemical Properties of ILs

ILs used in cellulose and biomass pretreatment has attracted much interest due to their excellent properties, such as the low melting point, high thermal stability and solvation capacity, especially the hydrogen-bonds among the cations and anions [43]. Moreover, the promising diversity of ILs suggests that appropriate ILs will be non-volatile polar solvents for carbohydrate dissolution and biomass pretreatment.

1.5.1 Melting Point

The melting point of a compound represents the lower limit of the liquid range and together with thermal stability defines the temperature window in which it can be used as a solvent [44].

The melting point is defined as the temperature of equilibrium between solid and liquid state in thermodynamic. Since the change of the Gibbs free energy equals zero at the equilibrium, the melting point (T_m) is defined as follows [45]:

$$T_m = \frac{\Delta H}{\Delta S} \tag{1.5}$$

Recently, many researchers study the effect of structural features on melting point because the melting point is an important factor for employment of ILs as a reaction media. Factors influencing in ILs melting point are charge, size and the distribution of charge on the constituent ions. For the same class of ILs, small changes in the shape of the uncharged, covalent regions of the ions need to be considered [46]. For example, the melting point of imidazolium based ILs is influenced by four factors: electron delocalization, H-bonding ability, the symmetry of the ions, and van der Waals interactions. Both alkyl substitutions on the cation and ion asymmetry have been shown to interfere with the packing efficiency of ions in the crystalline lattice [47]. Researchers are always try to find that how the chemical structure affects the melting point by many different measuring methods. The following trends can be concluded from open literature:

1. The sizes and shapes of cations of ILs are important factors influencing the melting points of ILs. In general, as the size of the cation increases, the melting point of the salts decreases.
2. With increasing the size of the anion, the melting point of the salts decreases, which reflects the weaker columbic interactions in the crystal lattice. For instance, from Cl^- to $[BF_4]^-$ to $[PF_6]^-$ to $[AlCl_4]^-$, the melting points of the sodium salts decrease from 801 to 185 °C with increasing thermochemical radius of the anion [47].
3. With the same anion, symmetry of the alkyl substitution also affects the melting point of ILs. Generally, highly asymmetric alkyl substitution has been identified as important for obtaining high melting point. For example, the melting point of [Mmim]Cl is 124.5 °C while the melting point of [Bmim]Cl is 65 °C.
4. The alkyl chain length of cations also affect melting point of ILs. For example, as for 1-alkyl-3-methylimidazolium tetrafluoroborate, with an increase in the alkyl chain length (up to $n = 8$), the melting point decrease, where n is the number of carbon atoms. But the melting point of ILs increases gradually with increasing chain length when $n > 8$. The same condition occurs in 1-alkyl-3-methylimidazoliumbis (trifyl) imide [46].
5. For ILs in which the only difference is the degree of branching within the alkyl chain at the imidazolium ring, higher degree of branching within the alkyl chain, higher melting point of ILs.

Owing to their unique properties, ILs are widely used as a kind of versatile solvents in biomass separation/conversion. Most ILs used for biomass pretreatment have low melting points, so that they are liquid at room temperature, the melting points of the ILs listed in Fig. 1.2 are all lower than 350 K [26]. That’s because

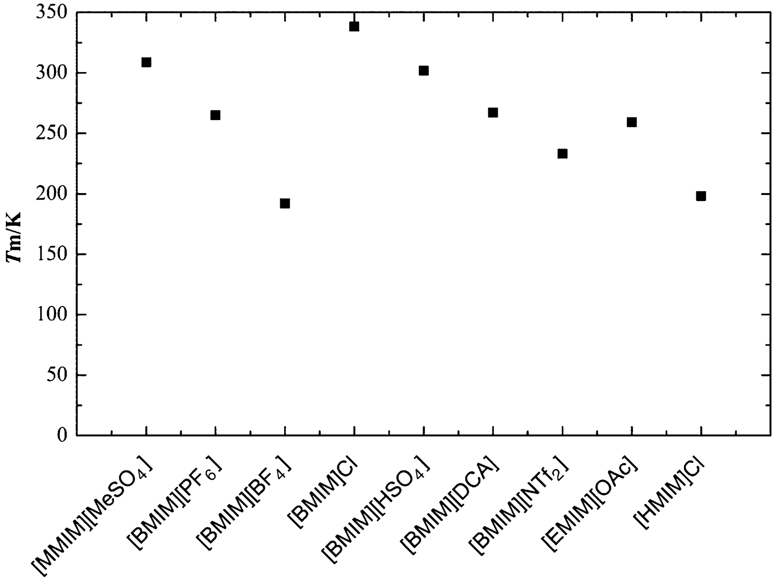


Fig. 1.2 The melting points of ILs used for biomass pretreatment

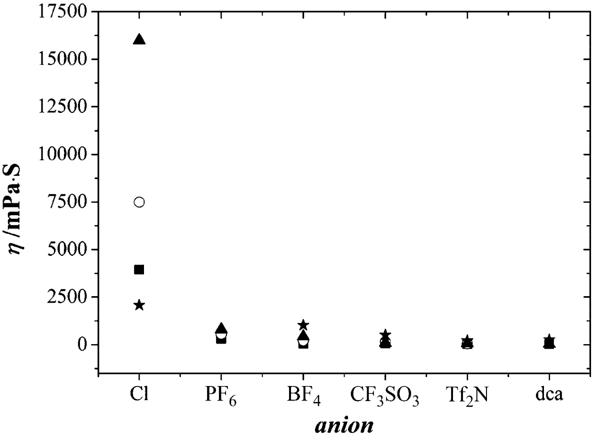
lower melting points of ILs make them easy to handle and are known as a technical advantage on the recyclability of the solvents. In recent years, some new types of ILs that have lower melting points and a sufficient polarity to further process carbohydrates have been claimed to replace chloride-based ILs [48]. These ILs are formate, acetate or phosphate salts with imidazolium based cations. They have been proven to be potential solvents to dissolve cellulose under mild condition.

1.5.2 Viscosity

Viscosity is one of the most important physical properties when considering ionic liquid applications. The viscosities of many ILs are much higher than most organic solvents at room temperature. Generally, the viscosity of ILs is 10–1,000 mPa s. A low viscosity is generally desired to use IL as a solvent, to minimize pumping costs and increase mass transfer rates while higher viscosities may be favorable for other applications such as lubrication or use in membranes [49]. Viscosity can be fitted with the Vogel-Tammann-Fulcher equation although it usually follows a non-Arrhenius behavior. Viscosities of ILs remain constant when the shear rate increases so that they have Newtonian and non-Newtonian behaviors [44].

The viscosity of ILs is usually affected by the kind of the anion, cation and substituents on the cation and anion of the imidazolium-based ILs. Generally, for ILs with the same anion, the alkyl substituents on the imidazolium cation is larger,

Fig. 1.3 Effect of anion on the viscosities of ILs. ■: $[\mathrm{BMIM}]^+$ based ILs at 303.15 K; ○: $[\mathrm{HMIM}]^+$ based ILs at 298.15 K; ▲: $[\mathrm{P}_{6,6,6,14}]^+$ based ILs at 303.15 K; ★: $[\mathrm{OMIM}]^+$ based ILs at 298.15 K



the viscosity of ILs is higher. For example, for the 1-alkyl-3-methylimidazolium hexafluorophosphate and bis((trifluoromethyl)sulfonyl)imide series ($[\mathrm{Rmim}][\mathrm{PF}_6]$ and $[\mathrm{Rmim}][\mathrm{Tf}_2\mathrm{N}]$), viscosity increases with increasing the number of carbon atoms in the linear alkyl group [50]. Furthermore, branching of the alkyl chain in 1-alkyl-3-methylimidazolium salts usually result in lower viscosity. Finally, a reduction in van der Waals interactions can also attribute to the low viscosity of ILs bearing polyfluorinated anions. Hydrogen bonding between counter anions and symmetry can also affect viscosity. In short, the viscosity of ILs based on the most common anions decreases in the order $\mathrm{Cl}^- > [\mathrm{PF}_6]^- > [\mathrm{BF}_4]^- > [\mathrm{TfO}]^- > [\mathrm{Tf}_2\mathrm{N}]^- > [\mathrm{dca}]^-$ (shown in Fig. 1.3) [26, 51–53].

The impurities in the ILs greatly affect their viscosities [4]. In one study [54], a series of ILs were prepared and purified by many kinds of techniques. Then their impurities were analyzed and physical properties were evaluated. The results showed that chloride concentrations of up to 6 wt% were found for some of the preparative methods whereas chloride concentrations of between 1.5 and 6 wt% increased the observed viscosity by between 30 and 600 %. Studies also found that the non-halo aluminate alkylimidazolium ILs absorbed water rapidly from the air. As little as 2 wt% (20 mol%) water could reduce the viscosity of $[\mathrm{BMIM}][\mathrm{BF}_4]$ by more than 50 %. Therefore, purities and handling should be carefully considered when viscosities of ILs are measured.

Owing to the widely application of ILs, the experimental measurement and theoretical modeling of viscosities of ILs and mixtures are essential in the development and design of processes [55]. There are several models used for the prediction of ILs viscosities.

Abbott [56] proposed a theoretical model for prediction of viscosities by modifying the “whole theory”. In that model, 11 ILs mainly based on imidazolium at three temperatures (298, 303 and 364 K) were investigated. The model had low reliability despite its theoretical interpretation and therefore it has limited application for practical processes.

Han et al. [57] proposed a QSPR method for prediction of the viscosity of imidazolium based ILs. In that work, a database of 1,731 experimental data values at various temperatures and pressures were used for 255 ILs, that included 79 cations and 71 anions. As for the viscosity of imidazolium-based ILs, the cation-anion electrostatic interactions have important effects.

The most useful viscosity estimation models for complex molecules are those based on group contributions. The methods usually use some variation of temperature dependence proposed by de Guzman [58].

The Orrick–Erbarmethod [59] proposed employs a group contribution technique to estimate the A and B parameters in the following equation [49]:

$$\ln\frac{\eta}{\rho M} = A + \frac{B}{T} \tag{1.6}$$

Where the η and ρ are the viscosity in mPa · s units and density is in g · cm^{-3} units, respectively.

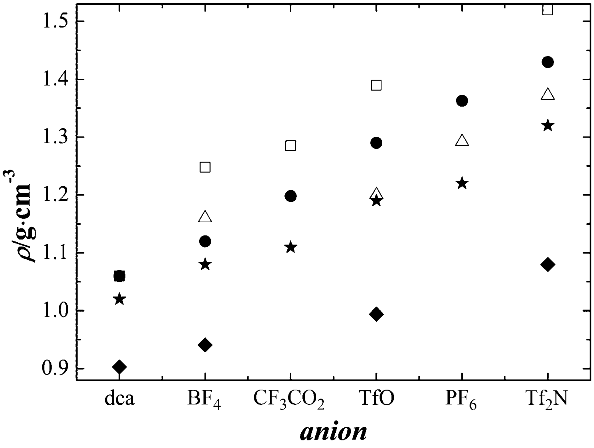
Viscosities calculated by the following method are in good agreement with experimental literature data. The model could predict the viscosity of new ILs in wide ranges of temperature and could be extended to a larger range of ILs as data for these become available. It is also shown that an Orrick–Erbar-type approach was successfully applied to estimate of the viscosity of ILs by a group contribution method.

In 2002, it was reported that ILs can dissolve biomass materials [23]. Viscosity plays a role in cellulose solvation, because it considered that ILs with low viscosity are more efficient and easier to handle in dissolving cellulose [60]. When an IL has a low viscosity, cellulose can be dissolved at room temperature. For example, microcrystalline cellulose was dissolved at a lower temperature in 1-ethyl-3-methyl imidazolium methylphosphonate [EMIM][CH_3PO_4] in compared with 1-ethyl-3-methylimidazolium dimethylphosphate [EMIM][$(CH_3)_2PO_4$] [61]. However, viscosities of ionic liquids are not the only important parameter in biomaterial dissolution. In 1-benzyl-3-methylimidazolium chloride [$PhCH_2MIM$]Cl, researchers have found that it was a rather powerful solvent no matter its dicyanamide anion, the cation-anion pair resulted in reasonably low viscosity [62]. Nevertheless, it was found that ILs containing alkyloxy or alkyloxyalkyl groups have low viscosities and that they are beneficial for dissolving cellulose. Especially, a powerful solvent for cellulose has been found to be 1-(3, 6, 9-trioxadecyl)-3-ethylimidazolium acetate [Me$(OEt)_3$-Et-Im][OAc] (in Table 1.6) [63].

1.5.3 Density

Many density correlations of ILs have been reported because it is an important fundamental property [49]. IL database, such as The UFT/Merck Ionic Liquids Biological Effects Database, IUPAC Ionic Liquids Database and Tohoku Molten

Fig. 1.4 Effect of anion on the densities of ILs. □: $[EMIM]^+$ based ILs at 298.15 K; ●: $[BMIM]^+$ based ILs at 298.15 K; △: $[HMIM]^+$ based ILs at 298.15 K; ★: $[OMIM]^+$ based ILs at 298.15 K; ◆: $[P_{6,\,6,\,6,\,14}]^+$ based ILs at 293.15 K



Salt Database, provide up-to-date information on densities of ILs [26]. Generally, imidazolium-based ILs are widely used as solvents for ILs applications owing to their excellent physical properties, such as low viscosities and high thermal and aqueous stability. Their densities are more available in the open literature than other properties ILs.

The usual densities of ILs vary between 1.12 $g \cdot cm^{-3}$ ($[(n\text{–}C_8H_{17})(C_4H_9)_3N][(CF_3SO_2)_2N]$) and 2.4 $g \cdot cm^{-3}$ (a 34–66 mol% $[(CH_3)_3S]Br/AlBr_3$ ionic liquid) [64, 65]. However, large cations have densities lower than water, such as aliquat (in Table 1.6), since their long alkyl chains have higher flexibility. From IPE IL database [26], the densities of most ionic liquids tend to have low sensitivity to variations in temperature. Furthermore, the impact of impurities on densities is much less dramatic than for viscosities.

One can make some conclusions on the cation effect and also to study the effect of alkyl chain length on the density and derived properties. Gardas et al. [66] found that as the alkyl chain length in the pyrrolidinium cation increases, the density of the corresponding IL decreases, similar to that observed for imidazolium-based ILs [67]. Generally, the order of increasing density for ILs with a common cation is $N(CN)_2^- < BF_4^- < CF_3CO_2^- < CF_3SO_3^- < PF_6^- < Tf_2N^-$ (shown in Fig. 1.4) [26, 53, 69]. The higher densities of Tf_2N^--containing ILs arise from the much higher mass of the anion [68].

Since it is difficult to measure densities of all ILs at different conditions, it is necessary to find a method to estimate densities of ILs. So far, a large amount of models about prediction of densities of ILs have been proposed in the open literature. The common models are group contribution methods (GCMs), quantitative structure property relationships (QSPRs) and artificial neural networks (ANNs) [70]. For instance, Lazzús [71] used the method of ANNs to estimation the density of imidazolium-based ionic liquids at different temperature and pressure. The method has a better estimation results, but it is not convenient to be used in prediction.

Table 1.4 The decomposition temperatures of ILs used in dissolving cellulose

Name of ILs	Abbreviation	Decomposition temperature/K
1-Butyl-3-methylimidazolium tetrafluoroborate	$[BMIM][BF_4]$	680.15 [26]
1-Butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide	$[BMIM][NTf_2]$	675.15 [26]
1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate	$[BM_2IM][BF_4]$	671.15 [75]
Trihexyltetradecyl phosphonium dicyanamide	$[P_{6,6,6,14}][dca]$	668.15 [26]
1-Butyl-3-methylimidazolium hexafluorophosphate	$[BMIM][PF_6]$	663.15 [26]
1,3-Dimethylimidazolium Methylsulfate	$[MMIM][MeSO_4]$	649.15 [79]
1-Butyl-3-methylimidazolium hydrogen sulfate	$[BMIM][HSO_4]$	603.15 [80]
1-Allyl-3-methylimidazolium chloride	[AMIM]Cl	558.95 [81]
1-Butyl-3-methylimidazolium carboxybenzene	$[BMIM][(C_6H_5)COO]$	552.75 [26]
1-Butyl-3-methylimidazolium chloride	[BMIM]Cl	527.15 [26]
1-Hexyl-3-methylimidazolium chloride	[HMIM]Cl	526.15 [26]
1-Ethyl-3-methylimidazolium acetate	[EMIM][OAc]	493.15 [82]
1-Butyl-3-methylimidazolium formate	[BMIM][dca]	473.15 [83]

The volumetric properties for the ILs can be estimated by the values of density. For example, $[C_nMIM][BF_4]$ ($n = 2, 3, 4, 5, 6$) are common ILs, many researchers have previously reported many properties in wide ranges of temperature. We can plot of values of in ρ against T, a straight line was obtained for given IL, and its empirical linear equation is [72]

$$\mathrm{Ln}\rho = b - \alpha T \tag{1.7}$$

Where b is an empirical constant, the negative value of slope, $\alpha = -(\partial \ln\rho/\partial T)_p$, is thermal expansion coefficient of the IL $[C_nMIM][BF_4]$.

We can also obtain the molecular volume (V_m) of ILs. The value of V_m was calculated using the following equation [72]

$$V_m = M/(N\rho) \tag{1.8}$$

Where M is molar mass of ILs, N is Avogadro's constant.

1.5.4 Thermal Stability

Compared with organic solvents, most ILs have relatively high thermal stability. The decomposition temperatures reported in the open literature are generally >200 °C, and they are liquid state in a wide range of temperatures (from 70 to 300–400 °C). The decomposition temperatures of ILs that dissolving cellulose are listed in Table 1.4.

Many literature works have investigated the thermal stability of ILs on imidazolium and anion structures. The onset of thermal decomposition is similar for the different cations but appears to decrease as the anion hydrophilicity increases. Ngo et al. [73] found that the thermal stability of the imidazolium-based ILs increases with increasing linear alkyl substitution. Owing to the facile elimination of the stabilized alkyl cations, the presence of nitrogen substituted secondary alkyl groups decreases the thermal stability of ILs. They also found that the stability dependence on the anion is $[PF_6]^- > [Tf_2N]^- \sim [BF_4]^- >$ halides. Fox et al. [74] found that the alkyl chain length does not have a large effect on the thermal stability of the ILs.

However, the thermal stability of ILs has been revised [4]. The range of thermal stability of ILs published in the open literature is overstated. The decomposition temperature of ILs calculated from fast thermo gravimetric analysis (TGA) scans in a protective atmosphere and does not imply a long-term thermal stability below those temperatures [44]. Fox and his group have done some nice study on the thermal stability of ILs [74–76]. Compared with the data from both isothermal and constant ramp rate programs for the decomposition of 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF_4]) under N_2, they found that isothermal TGA experiments may be the more appropriate method for evaluating the thermal stabilities of ILs [75]. Based on TGA pyrolysis data of 1, 2, 3-trialkylimidazolium room temperature ILs, They also found that although the calculated onset temperatures were above 350 °C, significant decomposition does occur 100 °C or more below these temperatures.

Singh et al. [77] analyzed the thermal stability of imidazolium based ILs [BMIM][PF_6] in a confined geometry. They found that [BMIM][PF_6] in confined geometry starts at an earlier temperature than that for the unconfined ILs. The loss of alkyl chain end groups of [BMIM] cation of ILs assign to the early decomposition by using a phenomenological ‘hinged spring model’. The idea of ‘hinged spring’ model is that the imidazolium ring is supposed to be ‘hinged’ to the SiO_2 matrix pore walls by surface oxygen interacting with the C-H group of the imidazolium ring.

Researchers have reported a new method to study the changes that occur during thermal aging of ILs. The method is potentiometric titration, which is precise, low-cost and quick analytically. To a small extent, they found that imidazolium salts start to decompose at much lower temperatures than those obtained from thermo gravimetric analysis by using this method. They also concluded that the stability of ILs is also influenced by water, except by their composition, such as anion type and alkyl substituent at the imidazolium ring. For instance, 2 wt% of water in ILs could bring about increased degradation of [BMIM]Cl at 140 °C. Furthermore, [BMIM][BF_4], [EMIM][CH_3SO_3], [BMIM][CH_3SO_3] and [BMIM][Tf_2N] are completely stable at 140 °C for 10 days [78]. Finally, from these data, long-term stability of ILs is a complicated problem with obvious and serious implications for their use as solvents media of chemical reactions.

1.6 Solubility of Cellulose/Biomass in ILs

Many kinds of materials can be dissolved in ILs, such as the metal salts, gases, carbohydrates, sugar alcohols, cellulose and even the biomass [36, 84, 85]. In this chapter, cellulose dissolution with various ILs would be discussed.

Cations and anions play an important role in the cellulose dissolution process [23]. The soluble ability of cellulose in ILs can be modified by changing the cations or anions. Anions that form hydrogen bonds with hydroxyl groups are effective for cellulose dissolution, small size and alkalinity of anions promote to increase cellulose soluble ability, for example, halide, acetate, formate and dialkyl phosphate [22, 61, 86]. Different imidazolium, pyridinium and pyrrolidinium-based cations are commonly used in cellulose dissolution together with the anions above mentioned. Cellulose soluble ability decreases in the ILs with length of the alky chain. Meanwhile, alkyl chains or anions with hydroxyl groups tend to be adverse to the cellulose dissolution in ILs due to the increase of hydrogen-bond acidity of ILs [22].

The Kamlet-Taft polarity parameters, for example, β is the hydrogen-bond basicity parameter, α is the measure of the hydrogen-bond acidity, which express the ability to donate and accept hydrogen bonds, respectively, and π^* is the parameter of the interactions through dipolarity and polarizability. The parameters α and β are similar to the acid and base characteristics according to the definition, while, the α and β are not completely consistent with the acidity and alkalinity of ILs in all conditions, the α and β emphasize the acceptance ability of hydrogen-bond. As for ILs, β has been the most useful parameter in predicting the solubility of cellulose in different ILs with various anions [87, 88].

With ILs, the higher β and dipolarity caused the better ability to dissolve cellulose [22]. With the cation $[\text{Bmim}]^+$, some anions showed different trends for dissolving cellulose due to the increasing hydrogen-bond acceptance ability, for example, the β value of some anions are in an order of $\text{OAc}^- > \text{HCOO}^- > (\text{C}_6\text{H}_5)\text{COO}^- > \text{H}_2\text{NCH}_2\text{COO}^- > \text{dca}^-$, and the cellulose solubility was about 16 wt% in [Bmim][OAc] ($\beta = 1.161$), which was higher than those in [Bmim][HCOO] ($\beta = 1.01$), $[\text{Bmim}][(\text{C}_6\text{H}_5)\text{COO}]$ ($\beta = 0.98$) [8, 89–92]. For a given cation, the effect of anions on cellulose dissolution changes greatly, this result may contribute to the formula weight of ILs, which means that the cellulose dissolution is close to the mass percent in the given ILs.

The Kamlet-Taft parameters of selected ILs and examples of used in dissolving cellulose and biomass pretreatment are as followed in Table 1.5, and the properties of ILs examples and applications in biomass are shown in Table 1.6. Common ILs used for cellulose/biomass pretreatment are shown with details in Table 1.7.

Table 1.5 Kamlet-Taft parameters of selected ILs [61, 93–96]

ILs	α	β	π*
[BMIM][$MeSO_3$]	0.44	0.77	1.02
[BMIM][$MeSO_4$]	0.55	0.67	1.05
[BMIM][HSO_4]	–	0.67	1.09
[BMIM][$MeCO_2$]	0.47	1.20	0.97
[BMIM][$N(CN)_2$]	0.54	0.59	1.05
[BMIM][Me_2PO_4]	–	1.12	–
[BMIM]Cl	0.44	0.84	1.14
[AMIM]Cl	0.46	0.83	1.17
[Bmim][OAc]	0.57	1.16	0.89
[Bmim][HCOO]	–	1.01	–
[Bmim][(C6H5)COO]	–	0.98	–
[EMIM][OAc]	–	1.074	–
[EMIM][$(MeO)HPO_2$]	0.52	1.00	1.06
[EMIM][$(MeO)MePO_2$]	0.50	1.07	1.04
[EMIM][$(MeO)_2PO_2$]	0.51	1.00	1.06
[AMIM][HCOO]	0.48	0.99	1.08
[AEIM][HCOO]	0.47	0.99	1.06
[TMIM][HCOO]	0.46	0.99	1.06
[BMIM][OTf]	0.63	0.48	0.97
[BMIM][PF_6]	–	0.44	–

π* stands for the parameter of the interactions through dipolarity and polarisability

1.7 Conclusion and Prospects

ILs have many intriguing properties, such as low vapor pressure, high chemical and thermal stability, wide electrochemical window, non-flammability, wide liquid range and recognition ability of biomaterials. They are applied in a variety of fields, including extraction, organic synthesis, catalysis/biocatalysts, materials science, electrochemistry and separation technology. Furthermore, because ILs have ionic nature, they may interact with charged groups in the enzyme, either in the active site or at its periphery, causing changes in the enzyme's structure.

ILs are promising solvents, for reaction and separation, offers tremendous possibilities for the development of sustainable industry, advanced materials and chemicals. Up to date, cellulose dissolution with ILs has been well developed. And the problems of ILs like high cost, which is obstacle to the industrial scale of ILs application, and the future researches trends and orient of ILs in cellulose/biomass applications, such as the binary systems including complex ILs or solvents, additives and catalysts, will be described more clearly.

The recycle of ILs in an efficient way is also should be well developed. The process of dissolving cellulose or biomass applications in ILs should be optimized to reduce the loss of cellulose or biomass. Binary and ternary system of ILs perhaps will be more efficient for the dissolution of cellulose/biomass, meanwhile, the large scale of synthesis and functional design of ILs with high stabilities and low viscosities will be developed. Considering of the environmental effect and special purposes, bio-degradable ILs and chiral ILs, acid or base enhanced ILs with lower

Table 1.6 Physical properties of ILs that dissolve cellulose

No.	Name	Abbreviation	Viscosity/ (mPa · s)	Density/ (g · cm^{-3})	Biomass
1	1,3-Dimethylimidazolium methylsulfate	[MMIM][MeSO$_4$]	72.91^a [97]	1.32725^a [97]	Softwood, kraft lignin, maple wood flour [87]
2	1-Allyl-3-methylimidazolium formate	[AMIM][HCOO]	66^a [98]		Cellulose [98]
3	1-Allyl-3-methylimidazolium chloride	[AMIM]Cl	821^a [99]	1.1660^a [99]	Southern pine powder, Norway spruce sawdust, spruce, fir, beech, chestnut, maple wood flour, cellulose, maple [62, 112, 113]
4	1-Butyl-3-methylimidazolium hexafluorophosphate	[BMIM][PF$_6$]	450^a [100]	1.369^a [101]	Does not dissolve [23, 114]
5	1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF$_4$]	233^a [102]	1.213^a [103]	Does not dissolve [23, 114, 116]
6	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[BM$_2$IM][BF$_4$]	780^a [104]	1.2^a [104]	Softwood kraft lignin [115]
7	1-Butyl-3-methylimidazolium chloride	[BMIM]Cl	3950^b [26]	1.08^a [26]	Cellulose, lignin, wood, xylan [23, 62, 112, 114, 116–119]
8	1-Butyl-3-methylimidazolium hydrogen sulfate	[BMIM][HSO$_4$]	1572^c [80]	1.32^d [80]	Pine sapwood, debarked mixed willow stems, miscanthus [94]
9	1-Butyl-3-methylimidazolium formate	[BMIM][HCOO]	38^a[105]		Sugars, starch and cellulose [63]
10	1-Butyl-3-methylimidazolium thiocyanate	[BMIM][SCN]	51.7^a [106]	1.06979^a [106]	Pulp cellulose [63]
11	1-Butyl-3-methylimidazolium dicyanamide	[BMIM][dca]	37^a [104]	1.06^a [104]	Avicel, cellulose [22, 63]
12	1-Butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide	[BMIM][NTf$_2$]	54.5^a [107]	1.433^a [103]	Avicel [63]
13	1-Butyl-3-methylimidazolium carboxybenzene	[BMIM][(C$_6$H$_5$)COO]			Avicel [22]
14	1-Ethyl-3-methylimidazolium dialkybenzenesulfonate	[EMIM][ABS]			Sugarcane plant waste [120, 121]
15	1-Ethyl-3-methylimidazolium acetate	[EMIM][OAc]	91^a [104]	1.03^a [104]	Spruce, beech, chestnut, maple wood flour, red oak, southern yellow pine, kraft lignin, cellulose [23, 114, 118, 120]

(continued)

Table 1.6 (continued)

No.	Name	Abbreviation	Viscosity/ (mPa · s)	Density/ (g · cm^{-3})	Biomass
16	1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]		1.1400^a [108]	Wheat straw, cellulose [61, 122]
17	1-Ethyl-3-methylimidazolium xylene sulfonate	[EMIM][XS]			Kraft wood lignin [120]
18	1-Hexyl-3-methylimidazolium Chloride	[HMIM]Cl	716^a [109]	1.03^a [109]	Cellulose dissolving pulps [114]
19	1-Hexyl-3-methylimidazolium trifluoromethanesulfonate	[HMIM] [CF_3SO_3]	160^a [104]	1.2^a [104]	Softwood kraft lignin [115]
20	N,N-Dimethylethanolammonium Acetate	[MM(EtOH)NH] [OAc]		0.8247^a [110]	Cellulose filter paper cotton [88]
21	Tetrabutylamimonium formate	[TBA][HCOO]			Cellulose [63]
22	1,8-Diazabicyclo[5.4.0]undec-7-enium hydrochloride	[HDBU]Cl			Cellulose [123]
23	1,8-Diazabicyclo[5.4.0]undec-7-enium formate	[HDBU][HCOO]			Cellulose [123]
24	1,8-Diazabicyclo[5.4.0]undec-7-enium acetate	[HDBU][OAc]			Cellulose [123]
25	1,8-Diazabicyclo[5.4.0]undec-7-enium thiocyanate	[HDBU][SCN]			Cellulose [123]
26	1,8-Diazabicyclo[5.4.0]undec-7-enium hydrogensufate	[HDBU][HSO_4]			Cellulose [123]
27	1,8-Diazabicyclo[5.4.0]undec-7-enium trifluoroacetate	[HDBU][TFA]			Cellulose [123]
28	1,8-Diazabicyclo[5.4.0]undec-7-enium methanesulfonate	[HDBU] [$MeSO_3$]			Cellulose [123]
29	1,8-Diazabicyclo[5.4.0]undec-7-enium lactate	[HDBU][Lac]			Cellulose [123]
30	1,8-Diazabicyclo[5.4.0]undec-7-enium tosylate	[HDBU][Tos]			Cellulose [134]

31	1,8-Diazabicyclo[5.4.0]undec-7-enium saccharinate	[HDBU][Sacch]			Cellulose [123]
32	1, 8-diazabicyclo [5.4.0] undec-7-enium bis(trifluoromethanesulfonyl)imide	[HDBU][NTf_2]			Cellulose [123]
33	8-Methyl-1,8-diazabicyclo[5.4.0]undec-7-enium hydrogensulfate	[MDBU][HSO_4]			Cellulose [123]
34	8-Methyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride	[MDBU]Cl			Cellulose [22]
35	8-Octyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride	[ODBU]Cl			Cellulose [22]
36	1-Butyl-4-methylpyridinium hexafluorophosphate	[BMPy][PF_6]			Insoluble [115]
37	1-Butyl-4-methylpyridinium chloride	[BMPy]Cl			Avicel, spruce sulfite, pulp, Cotton linters, cellulose [22]
38	AMMOENG 110 formate	[Amm110] [HCOO]			Avicel [63]
39	AMMOENG 110 acetate	[Amm110][OAc]			Avicel [63]
40	Trihexyltetradecyl phosphonium dicyanamide	[P66614][dca]	378.0[a] [111]	0.898[a] [111]	Avicel [63]
41	AMMOENG 110 dicyanamide	[Amm110][dca]			Avicel [63]
42	Tetrabutylammonium formate	[Bu_4N][HCOO]			Avicel [63]
43	N,N,Ntriethyl-3,6,9-trioxadecylammonium acetate	[$Me(OEt)_3$-Et_3N] [OAc]			Avicel [63, 117]
44	Benzyldimethyl(tetradecyl)ammonium chloride	BDTACl			Spruce sulfite, avicel, pulp, cotton linters [124, 125]
45	1-(2-Hydroxyethyl)-3-methylimidazolium chloride	[EOHMIM]Cl			Not mentioned [126]
46	1-Allyl-2,3-dimethylimidazolium chloride	[AdMIM]Br			Avicel, spruce sulfite, pulp, cotton linters[63, 127]
47	1-(3,6,9-Trioxadecyl)-3-ethylimidazolium	[$Me(OEt)_3$-Et-Im][OAc]			Avicel [63]

[a]at 298.15K; [b]at 303.15K; [c]at 296.65K; [d]at 293.15K.

Table 1.7 Common ILs used for cellulose/biomass pretreatment

ILs	Material	Solubility	Conditions	Refs.
[BMIM]Cl	Cellulose	10 wt%	100 °C	[23][a]
	Cellulose	25 wt%	Microwave heating 3–5 s	[23][a]
	Southern yellow pine (<0.125 mm)	52.6 %	110 °C, 16 h	[128][b]
	Wood chips	Partially soluble	130 °C, 15 h	[62]
	Silk	9.51 % (w/w)	100 °C	[129]
	Bird feather	23 %	100 °C, 48 h	[130]
	Chitin	10 wt%	110 °C, 5 h	[131]
[AMIM]Cl	Cellulose	14.5 wt%	80 °C	[132]
	Ball-milled Southern pine powder	8 wt%	80 °C, 8 h	[62]
	Norway spruce sawdust	8 wt%	110 °C, 8 h	[62]
	Pine	26 wt%	24 h	[133]
	Southern pine TMP	5 wt%	130 °C, 8 h	[62]
[EMIM][OAc]	Cellulose/lignin	4 wt%	75 °C, 1 h	[137]
	Southern yellow pine (<0.125 mm)	98.5 %	110 °C, 16 h	[128][b]
	Red oak (0.125–0.250 mm)	99.5 %	110 °C, 16 h	[128][b]
	Aspen wood	5 wt%	120 C	[135]
	Energy cane bagasse	5 wt%	120 °C	[136]
[BMIM][PF_6]	–	Insoluble	Microwave	[23]
[Ch][AA]	Sugar Cane Bagasse	5 wt%	Magnetic stirrer	[134]

[a] 0.5–1.0 g of fibrous cellulose, 10 g [Bmim]Cl
[b] Wood load (0.50 g) in 10 g IL

viscosity, higher thermal stability would be designed and synthesized by calculating the structure-function relationship or predicting the properties with group contribution method or semi-rational formula.

Acknowledgements This research was supported financially by the Projects of International Cooperation and Exchanges NSFC (No. 21210006), Natural Science Foundation of Beijing of China (No.2131005, No.2132055) and National High Technology Research and Development Program of China (863 Program) (No. 2012AA063001).

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