Chapter 2
Solubilization of Biomass Components with Ionic Liquids Toward Biomass Energy Conversions

Mitsuru Abe and Hiroyuki Ohno

Abstract Ionic liquids (ILs) are collecting keen interest as novel solvents for plant biomass, especially for cellulose. ILs have several unique properties and they dissolve cellulose under milder condition than existing procedures. Here, we give an outline of the development of biomass dissolving ILs together with their physico-chemical properties. Dissolution and/or extraction of not only cellulose but also lignin with ILs are overviewed. The extracted biomass is expected to be converted into other energies. For this purpose, energy-saving biomass treatment is inevitable, and ILs are one of the most potential media for this. This chapter will deliver further ideas on the design of ILs for cellulose dissolution or plant biomass treatment in the near future.

Keywords Ionic liquid • Polarity • Hydrogen bond • Cellulose • Lignin • Dissolution • Design of ions • Save energy

2.1 Introduction

Ionic liquids (ILs) are organic salts with melting point below 100 °C, and especially those with the melting point at and below room temperature are called "room temperature Ionic liquids" [1]. There are a few important properties required for solvents such as non-volatility, non-flammability, and thermal stability in a wide temperature range. Although there are many solvents that have some of these properties, there are few solvents that have all of the above-mentioned properties. ILs have unique properties different from molecular solvents. Many ILs have non-volatility, non-flammability, and stability in a wide temperature range. Furthermore, there is a potential chance to design new ILs through unlimited

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possibility of combination of ion pairs. ILs are accordingly known as “designer solvents”. It is easy to change their physico-chemical properties by the selection of suitable ions.

One of successful examples on the design of ILs is cellulose dissolution. Plant biomass is one example of a renewable and abundant natural material. These materials can be considered to be the embodied energy of sunlight and so is one possible method to produce energy on earth. Considering the limit of fossil fuels, there are increasing trials to convert plant biomass into user-friendly energy. There are many industrial plants for bioethanol production from corn starch or sugar cane in US and other countries. There are established methods to convert starch into sugar in our human life. However, since these processes compete with food industry, there are ethical concerns about the use of edible plant biomass as raw materials for fuel production [2]. Cellulosic biomass therefore is attracting attention as energy sources because they are inedible materials for human beings.

Cellulosic biomass essentially consists of cellulose, hemicellulose, and lignin. To obtain energy from cellulosic biomass with minimum given energy, following three steps are required, namely (1) extraction of cellulose from biomass, (2) hydrolysis of the cellulose into glucose or other oligosaccharides, and (3) oxidation or fermentation. However, cellulosic biomass is scarcely used for bioenergy production because of its very poor solubility in common molecular solvents. The chemical and physical stability of cellulose are known to be derived from many intra- and inter-molecular hydrogen bonds [3, 4]. Since ordinary molecular solvents have not enough power to dissolve cellulose, it is required to heat the mixture or stir it for a long time which is inefficient for energy conversion. The energy cost for dissolution and extraction processes for cellulose should be very low.

Many scientists recognize that ILs have great potential as solvents for cellulose and are paying particular attention to ILs as novel solvents for cellulose under mild conditions. Design of ILs to dissolve cellulose with low energy cost is therefore indispensable for energy conversion. Without this step, it is difficult to use cellulosic biomass as valuable materials as well as fossil fuel substitutes. The discussion in this chapter concentrates on the dissolution of biomass in ILs.

2.2 Chloride Type Salts for Cellulose Dissolution

Concerted attempts to dissolve cellulose do not have such a long history. The first reported study on cellulose dissolution using an ionic material was reported in 1934 by Graenacher and co-workers [5]. They used a mixture of amine and a pyridinium salt to dissolve cellulose. At this stage, pyridinium salt was not used as an IL but as an added salt. Thus, the “first” study of cellulose dissolution with ILs that was reported was by Swatloski et al. in 2002 [6]. They reported that 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) dissolved pulp cellulose. This IL dissolved 3 % cellulose at 70 °C, and 10 % cellulose at 100 °C. They also clarified that the cellulose dissolving degree was improved with a combination of IL soaking and

Table 2.1 Solubility of dissolving pulp cellulose in ionic liquids [6]

Ionic liquid	Method	Solubility (wt%)
[C4mim]Cl	Heat (100 °C)	10
	Heat (70 °C)	3
	Heat (80 °C) + sonication	5
	Microwave irradiation	25
[C4mim]Br	Microwave irradiation	5–7
[C4mim]SCN	Microwave irradiation	5–7
[C4mim][BF_4]	Microwave irradiation	Insoluble
[C4mim][PF_6]	Microwave irradiation	Insoluble
[C6mim]Cl	Heat (100 °C)	5
[C8mim]Cl	Heat (100 °C)	Slightly soluble

other physicochemical treatments such as sonication or microwave irradiation. On the other hand, tetrafluoroborate-type salts and hexafluorophosphate-type salts did not dissolve cellulose unlike [C4mim]Cl. The data shown in Table 2.1 provides that the properties of ILs that deeply affect the solubility of cellulose in the corresponding ILs.

[C4mim]Cl has a high melting point (T_m) of 73 °C and high viscosity, thus it is hard to use as a solvent at ambient condition [7, 8]. Heinze and co-workers reported that some chloride salts which have pyridinium or ammonium cations also dissolve cellulose (Scheme 2.1, Table 2.2) [8]. 3-Methyl-*n*-butylpyridinium chloride ([C4mpy]Cl) dissolved cellulose much better than [C4mim]Cl, and benzyldimethyl(tetradecyl)ammonium chloride (BDTAC) has a lower T_m (52 °C). Sometimes, the degree of polymerization of cellulose (DP) decreases after dissolution in ILs (see Table 2.2). In the case of energy conversion, changes in the DP are a less important factor. Some studies also require dissolving cellulose without lowering DP from the viewpoint of cellulose application. In both cases, the dissolution of cellulose under mild conditions is suitable considering efficient processing. Then there are some studies on reducing the T_m of these chloride salts. Physical chemistry tells us that small anions such as chloride anion interact strongly with cations due to higher charge density resulting high T_m of the salts. It is therefore important to design cations to lower the T_m. Mizumo et al. developed liquid state chloride salts using imidazolium cations having allyl group(s) [9]. Allyl group is effective to show conformational change or rotation of the group, that induces to lower the T_m of the imidazolium salt. They clarified that the adopting allyl groups into imidazoliulm cation is a valid way to lower the T_m of the chloride salts. After this report, Zhang and co-workers reported that one of room temperature ILs, 1-allyl-3-methylimidazolium chloride ([Amim]Cl), has a good ability to dissolve cellulose [10]. [Amim]Cl dissolved no cellulose at room temperature, but it dissolved cellulose at 60 °C under stirring. With increasing temperature, cellulose could be dissolved easily in [Amim]Cl.

With an increase in the variety of chloride type cellulose-dissolving ILs (CDILs), cellulose dissolving mechanisms as well as dominant properties of the ILs for cellulose dissolution have been gradually clarified. Those studies suggest that the chloride anion works dominantly to dissolve cellulose by breaking the hydrogen bonding networks of cellulose fibrils. Remsing and co-workers have

3-Methyl-N-butylpyridinium chloride Benzyldimethyl(tetradecyl)ammonium chloride

Scheme 2.1 Structure of chloride type ILs to dissolve cellulose under heating [8]

Table 2.2 Solubility of cellulose samples in ILs

Cellulose		Solubility of cellulose					
		[C4mim]Cl		[C4mpy]Cl		BDTAC	
Type	DP	%	DP[a]	%	DP[a]	%	DP[a]
Avicel	286	18	307	39	172	5	327
Spruce sulfite pulp	593	13	544	37	412	2	527
Cotton linters	1,198	10	812	12	368	1	966

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[a] After regeneration, DP: Degree of polymerization of cellulose, T_m of [C4mim]Cl, [C4mpy]Cl, and BDTAC was 73, 95, and 52 °C, respectively

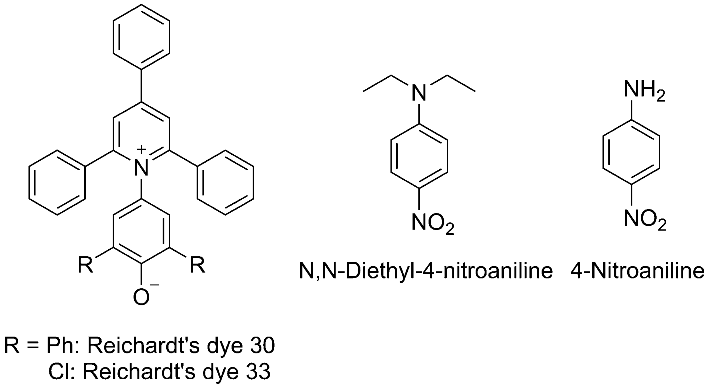
clarified that [C4mim]Cl makes hydrogen bonding between the carbohydrate hydroxyl protons and the chloride ions in a 1:1 stoichiometric ratio using ^{13}C and $^{35/37}$Cl NMR relaxation measurements [11]. The relaxation time of the imidazolium cation and chloride anion in [C4mim]Cl was analyzed as a function of concentration (wt%) of cellobiose as a model compound of cellulose. The relaxation time of the cation was almost constant regardless of cellobiose concentration. This means that there are no specific interaction between cations and cellobiose. On the other hand, there was a clear relationship between the $^{35/37}$Cl relaxation time and cellobiose concentration. This suggests that the chloride anion interacts strongly with the dissolved carbohydrate. They analyzed the interaction between the chloride anions and non-derivatized carbohydrates. This study clarified that the chloride ions interact in a 1:1 ratio with the carbohydrate hydroxyl protons.

Some simulation studies have also been reported on carbohydrate dissolution in dialkylimidazolium chloride-type ILs. Youngs and co-workers reported about the molecular dynamics simulations of glucose solvation by 1,3-dimethylimidazolium chloride [C1mim]Cl [12]. They found that the primary solvation shell around the glucose consists predominantly of chloride anions hydrogen bonding with the hydroxyl groups of glucose ring. This is the predominant interaction between glucose rings and chloride-type ILs. There is a small contribution of cations on the carbohydrate-IL interaction. Cations were however also found near the glucose, and a hydrogen at the 2-position of the imidazolium ring interacted with an oxygen atom of the secondary hydroxyl group of the glucose. A weak contribution of van der Waals force was also seen between the glucose and the cations. Even at high glucose concentrations (16.7 wt%), the anion-cation interactions and overall liquid structure of [C1mim]Cl were found not to be significantly changed. This means that the glucose is readily solubilized by the IL even under high concentration. Gross and co-workers reported on the thermodynamics of cellulose solvation in [C4mim]Cl [13]. All-atom molecular dynamics (MD) simulations were conducted to analyze the thermodynamic driving force of the cellulose dissolving process and to clarify the role of both anions and cations in the process. They suggested that the dissociated cellulose has higher potential energy in water than that in [C4mim]Cl. They suggested that the cellulose insolubility in water is mostly derived from the entropy reduction of the solvent. In addition, they also suggested that both the anion and cation of the IL interact with the glucan residues. In the case of Cl^- anions, they form hydrogen bonds with the hydroxyl groups of cellulose from either equatorial or axial directions. On the other hand, for the cations, the contact with cellulose along the axial directions was closer than that along the equatorial directions. They concluded that interacting with cellulose along axial directions and disrupting the cellulose fibrils is an important step of cellulose dissolution.

2.3 Carboxylate Type Salts with Low Melting Points and Low Viscosity

As described in the previous section, chloride type ILs have a strong ability to dissolve cellulose, and it is predominantly attributed to the anion to form hydrogen bonding with the hydroxyl groups of cellulose. However, most chloride salts have both a high melting point and high viscosity. These properties are not suitable for the improvement of cellulose solubilization. Various attempts have been made to reduce the melting point of chloride-based ILs, as discussed above. Despite the prepared chloride salts being in their liquid state at room temperature, heating is necessary to dissolve cellulose. Since the necessity of the continuous heating requires an excessive amount of energy consumption, this leads the increase in the total cost of the cellulose treatment process. It is therefore strongly desired to develop novel ILs to dissolve cellulose with low energy cost. Design of anion structure is required because there is a limitation to overcome the problem by only optimization of cations of chloride-based salts.

To design novel CDILs, we should have an analytical method to evaluate the hydrogen bonding basicity of ILs, because chloride type ILs dissolve cellulose through making favorable hydrogen bonds with hydroxyl groups of cellulose. The analysis of physicochemical properties of ILs is essential for the design of CDILs. There are many ways to investigate or predict the proton accepting ability, in other words, hydrogen bond basicity. For example, Hansen solubility parameters [14], COSMO-RS [15], and the Kamlet-Taft parameters [16, 17] are known as useful empirical or semi-empirical polarity scales. Especially, it is known that Kamlet-Taft parameters are very useful, which requires three solvatochromic dyes



Scheme 2.2 Structure of prove dyes for Kamlet-Taft parameter measurements [16]

(Scheme 2.2). From the shift of the absorption maximum wavelength of the individual dye molecules shown in Scheme 2.2, three Kamlet-Taft parameters such as α, β, and π values are calculated. These three parameters, α, β, and π values represent hydrogen bond acidity, hydrogen bond basicity, and polarizability, respectively [16, 17]. Since ILs are conductive materials, it is not easy to determine the polarity with conventional electrochemical methods. Considering this, Kamlet-Taft parameters are quite useful to evaluate the polarity of ILs.

Brandt and co-workers compiled the correlation between cellulose dissolving ability and the Kamlet-Taft β value of several ILs (Fig. 2.1) [18]. Although the plotted data were measured at different conditions (*e.g.* different temperature, dissolution time, degree of polymerization (DP) of cellulose, moisture content, purity of ILs, etc.), there is a certain correlation between cellulose solubility and the β value of the ILs. ILs with β value of less than 0.6 have no power to dissolve cellulose under any condition. The ILs having a β value of more than 0.6 start to dissolve cellulose and solubility increases with an increase of their β value. Here, it should be noted that the β value is not only the factor to govern the cellulose solubility. There are still many ILs that cannot solubilize cellulose in spite of their larger β value [19]. Other factors such as α value and ion structure should also be considered for the design of cellulose solvents. Although the β value does not entirely determine the cellulose dissolving ability, it is a useful design parameter for CDILs.

According to the data compiled by Ohno and co-workers, a series of carboxylate salts (Scheme 2.3) were confirmed to have strong hydrogen bond basicity (Table 2.3) [20]. Since there are a wide variety of carboxylic acid derivatives, carboxylate anions have been selected as good anions to construct CDILs [21].

From the structures listed in a patent by Swatloski and co-workers, BASF reported that imidazolium ILs bearing acetate anions are effective for the dissolution of cellulose [22]. Since 1-ethyl-3-methyl-imidazolium acetate ([C2mim]OAc) is less toxic, and less viscous, this IL is a favorable solvent for cellulose. Fukaya and

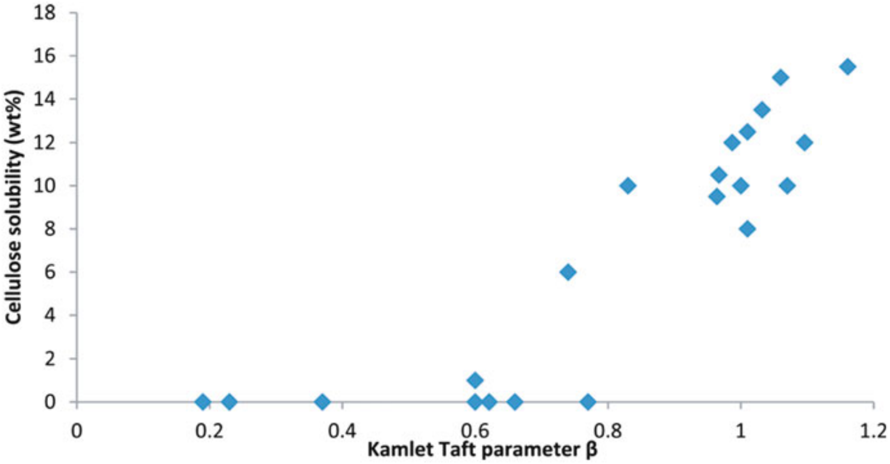


Fig. 2.1 Cellulose solubility in [C2mim] and [C4mim] type ILs as a function of the Kamlet-Taft *β* value of the ILs. The *plotted data* were measured under different conditions (Reproduced from Brandt et al. [18] with permission from The Royal Society of Chemistry)

$[C_4mim][RCOO]$ $[Amim][HCOO]$

R = H : [HCOO], C_nH_{2n+1} (n = 1~3) : $[C_nCOO]$, $C(CH_3)_3$: $[t\text{-}C_4COO]$

Scheme 2.3 Structure of carboxylate type salts (Reprinted with permission from Ohno and Fukaya [20], Copyright (2009) The Chemical Society of Japan)

Table 2.3 Kamlet-Taft parameters of a series of [C4mim] carboxylate-type salts

	Kamlet-Taft parameters		
Anion	*α*	*β*	*π**
[HCOO]	0.56	1.01	1.03
$[C_1COO]$	0.55	1.09	0.99
$[C_2COO]$	0.57	1.10	0.96
$[C_3COO]$	0.56	1.10	0.94
[*t*-C_4COO]	0.54	1.19	0.91
Cl	0.47	0.87	1.10

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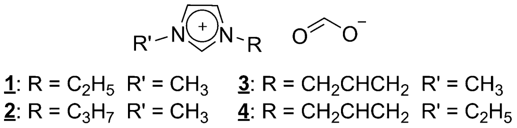
co-workers also reported that a series of carboxylate-type ILs for cellulose dissolution [23]. They suggested that 1-allyl-3-methylimidazolium formate ([Amim] formate, IL<u>**3**</u> in Scheme 2.4) is a good solvent to dissolve cellulose. This ionic liquid shows no melting temperature but low glass transition temperature (−76 °C) and low viscosity (66 cP at 25 °C) (Table 2.4). The hydrogen bond basicity of IL<u>**3**</u>



1: R = C_2H_5 R' = CH_3 **3**: R = CH_2CHCH_2 R' = CH_3
2: R = C_3H_7 R' = CH_3 **4**: R = CH_2CHCH_2 R' = C_2H_5

Scheme 2.4 Structure of formate salts with imidazolium cations which have different length of alkyl chains (Reprinted with permission from Fukaya et al. [23], Copyright (2006) American Chemical Society)

Table 2.4 Physicochemical properties and Kamlet-Taft parameters of the ILs

					Kamlet-Taft parameters		
IL	T_g (°C)[a]	T_m (°C)[a]	T_d (°C)[b]	η (cP) (at 25 °C)	α	β	π^*
1	[c]	52	212	[d]	[d]	[d]	[d]
2	−73	c	213	117	0.46	0.99	1.06
3	−76	c	205	66	0.48	0.99	1.08
4	−76	c	205	67	0.47	0.99	1.06
[Amim]Cl	−51	c	256	2,090	0.46	0.83	1.17
[C4mim]Cl	[c]	66	262	[d]	0.44[e]	0.84[e]	1.14[e]

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[a] Temperature at signal peak

[b] Temperature for 10 wt% loss under N_2 gas

[c] Not observed

[d] Not measured

[e] Measured under a supercooled state

was higher than that of chloride salts. The IL**3** was confirmed to have a good ability to dissolve cellulose under mild condition. It solubilized 10 wt% cellulose at 60 °C though [Amim]Cl required 100 °C to dissolve the same concentration of cellulose (Fig. 2.2).

After the appearance of these carboxylate type CDILs, many studies were reported about the cellulose dissolving mechanism by carboxylate salts. Remsing and co-workers analyzed the solvation mechanisms of acetate and chloride type salts, such as [C4mim]Cl, [Amim]Cl, and 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) using $^{35/37}Cl$ and ^{13}C NMR relaxation [24]. The $^{35/37}Cl$ and ^{13}C relaxation rates of anions showed a strong dependency on the carbohydrate concentration in the ILs having acetate or chloride anions. Especially, in the case of [C2mim][OAc], with the increase of carbohydrate concentration, the reorientation rate of the anion decreased faster than that of cations. They suggested that the interactions between the cations and carbohydrates are nonspecific, and concluded that the solvation mechanism was almost the same regardless of the structure of the anions.

Zhang and co-workers also analyzed the interaction between [C2mim][OAc] and cellobiose, a repeating unit of cellulose (Scheme 2.5), using ^{1}H-NMR spectroscopy [25]. The acetate anion made hydrogen bonds with hydroxyl groups of cellobiose, and the imidazolium cation also interacted with the oxygen atom of

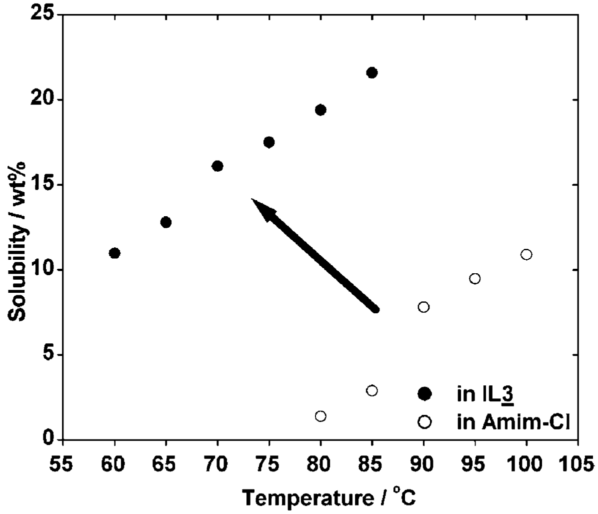
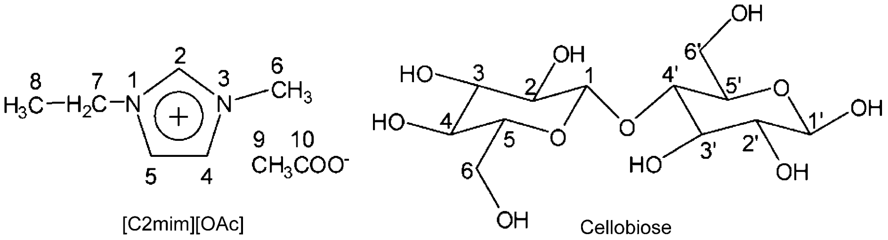


Fig. 2.2 Cellulose solubility as a function of temperature in IL3 and [Amim]Cl (Reprinted with permission from Fukaya et al. [23], Copyright (2006) American Chemical Society)



Scheme 2.5 Structure and atom number of [C2mim][OAc] and cellobiose (Reproduced from Zhang et al. [25] with permission from the PCCP Owner Societies)

hydroxyl group of cellobiose, especially via the most acidic proton in the C-2 position (Fig. 2.3).

Liu and co-workers carried out molecular dynamics simulations to clarify the interaction of cellulose and ILs [26]. They suggested that the interaction energy between a series of (1–4) linked β-D-glucose oligomers and [C2mim][OAc] was stronger than that with water or methanol. The estimated energy for hydrogen bonding between the hydroxide group on glucose unit and water or ethanol was estimated to be around 5 kcal mol^{-1}, whereas that in [C2mim][OAc] was estimated to be 14 kcal mol^{-1}. Furthermore, some of these cations interacted with these polysaccharides through hydrophobic interactions. Xu and co-workers reported that the cellulose solubility of [C4mim][OAc] was certainly improved by addition of lithium salts [27]. They have suggested that lithium cation interacts with an oxygen atom of C3-hydroxyl group of cellulose, and it causes cleavage of the O(6)H-O(3) inter-molecular hydrogen bonding. This result means that cations also make a certain contribution to dissolve cellulose depending on their structure.

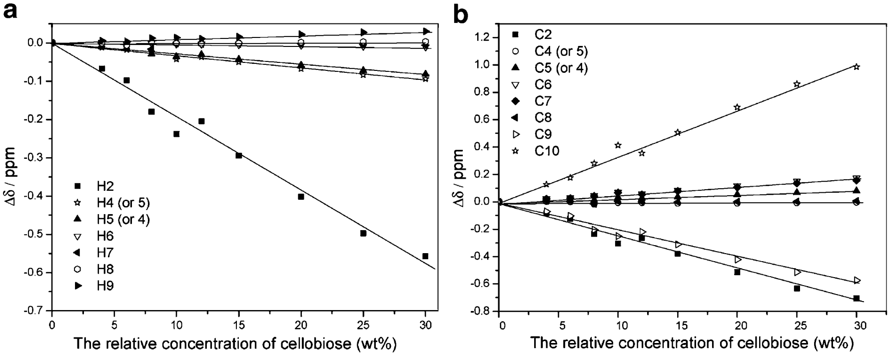


Fig. 2.3 Chemical shift of proton (**a**) and carbon (**b**) in [C2mim][OAc] as the function of concentration of cellobiose in $DMSO\text{-}d_6$ ($\Delta\delta = \delta - \delta_{neat}$) (Reproduced from Zhang et al. [25] with permission from the PCCP Owner Societies)

2.4 Phosphonate Type Salts for Cellulose Dissolution Without Heating

As described above, carboxylate salts have a good ability to dissolve cellulose and the dissolution mechanism has been analyzed. However these carboxylate type ILs also have a drawback in terms of thermal stability. These ILs still require heat to dissolve certain amounts of cellulose. To overcome these problems, methylphosphonate salts were proposed as stable CDILs. Fukaya and co-workers have synthesized 1-ethyl-3-methylimidazolium methylphosphonate ([C2mim][$(CH_3)(H)PO_2$]; IL5 in Scheme 2.6), and found that this IL5 had a good stability and dissolved cellulose without heating [28].

This IL5 has very low glass transition temperature (−86 °C), low viscosity (107 cP at 25 °C), and high Kamlet-Taft β value (1.00). The physicochemical properties of IL5 allow dissolution of 6 wt% cellulose within 1 h at 30 °C (Fig. 2.4), and allow it to dissolve 4 wt% cellulose without heating (at 25 °C) within 5 h.

Considering the above mentioned results, the structure of CDILs and cellulose solubility data are summarized in Table 2.5.

2.5 Functional Ionic Liquids for Cellulose Dissolution

Recently, a novel type of CDIL has been developed that has high added-value as well as cellulose dissolving ability. Ito and co-workers reported that some amino acid type ILs dissolved cellulose [19]. Especially, *N*,*N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium alanine dissolved cellulose well at 100 °C. These amino acid-based ILs are halogen-free and polar ILs [34, 35]. Since amino acids are biomolecules, cheap products, and environmentally-friendly materials.

Scheme 2.6 Structure of phosphonate type salts [28]

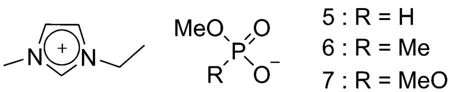
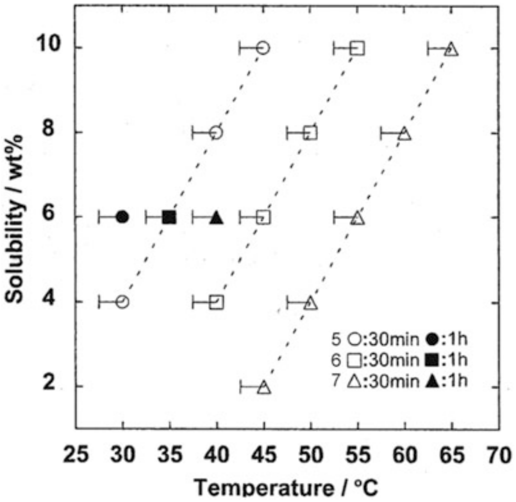


Fig. 2.4 Cellulose solubility (wt%) in phosphonate type salts (ILs**5**, **6**, and **7**) as a function of temperature [28]

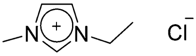
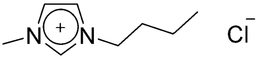
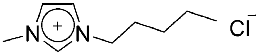
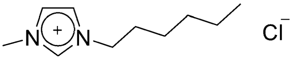
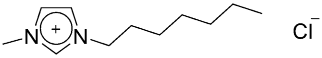
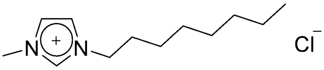
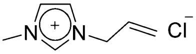
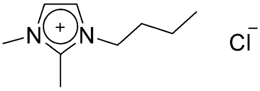
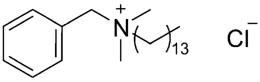
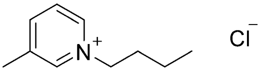


ILs composed of amino acids are expected to generate more interest as potential solvents in the near future [36–38]. More recently, they reported that the alanine containing salt dissolved 23 wt% cellulose at room temperature with the aid of DMSO [39]. Mixtures of ILs and molecular liquids are gaining attention of IL researchers as new liquids containing the advantages of both IL and molecular liquids. The properties of these mixtures are of course a function of the mixing ratio. In other words, it is not difficult to control the fluid properties by adjusting the mixing ratio when adequate IL and molecular liquids are chosen.

For most processes, highly pure ILs are needed to maintain the efficiency of the cellulose dissolution due to keep their unique properties. ILs have a characteristic properties about vapor pressure, namely ILs are non- or very low-volatile liquids. In other words, it is quite difficult to purify ILs by distillation. Polar and distillable ILs are expected to improve some processes. One of solutions is the use of ILs prepared by the neutralization [40]. King and co-workers reported the distillable acid–base conjugate ILs which has cellulose dissolving ability [41]. They found that the neutralized salt of 1,1,3,3-tetramethylguanidine (TMG) with propionic acid ([TMGH][CO_2Et]) has been shown to be technically distillable, and it dissolved 5 wt% cellulose within 10 min at 100 °C. This dissolution capability and distillable property are dependent upon the relative basicity of the competing base, and the equilibrium is temperature dependent.

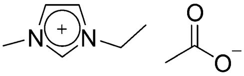
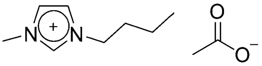
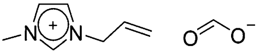
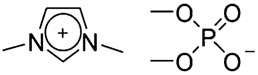
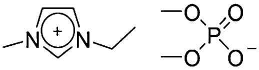
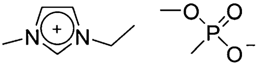
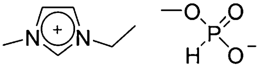
Phosphonate type salts require low energy cost to dissolve cellulose, and they would be potential solvents for cellulose technology. However, most CDILs have a

Table 2.5 IL structure and cellulose solubility

Ionic liquids	Raw material	Solubility (wt%)	Condition	Refs.
 [C2mim]Cl	Cellulose	15.8	85 °C	[29]
	Avicell	10–14	100 °C, 1 h	[7]
	Avicell	5	90 °C	[30]
	Cellulose, DP = 268	12	90 °C, 12 h	[31]
 [C4mim]Cl	Pulp cellulose, DP = 1,000	10	100 °C	[6]
		3	70 °C	[6]
	Avicel, DP = 286	18	83 °C, 12 h	[8]
	Avicel	20	100 °C, 1 h	[7]
	Cellulose	1.8	80–90 °C, 20 min	[32]
	Cellulose	13.6	85 °C	[29]
 [C5mim]Cl	Avicel	1.5	100 °C	[33]
	Avicel	1	100 °C, 1 h	[7]
 [C6mim]Cl	Pulp cellulose	5	100 °C	[6]
	Avicel	7	100 °C	[33]
	Avicel	5	50 °C	[30]
 [C7mim]Cl	Pulp cellulose	Slightly soluble	100 °C	[6]
	Avicel	5	100 °C	[33]
		5	100 °C, 1 h	[7]
 [C8mim]Cl	Avicel	4.5	100 °C	[33]
		4	100 °C, 1 h	[7]
		Slightly soluble	100 °C	[30]
 [Amim]Cl	Cellulose, DP = 250	10	100 °C	[23]
	Avicel	5	90 °C	[30]
	Cellulose pulp	14.5	80 °C	[10]
 [C4dmim]Cl	Cellulose, DP = 286	9	90 °C	[31]
	Cellulose, DP = 593	6	90 °C	[31]
	Cellulose, DP = 1,198	4	90 °C	[31]
 [BzDTA]Cl	Cellulose, DP = 286	5	62 °C	[8]
	Cellulose, DP = 593	2	62 °C	[8]
 [3MBPy]Cl	Cellulose, DP = 286	39	105 °C, 12 h	[8]
	Avicel	5	105 °C	[30]

(continued)

Table 2.5 (continued)

Ionic liquids	Raw material	Solubility (wt%)	Condition	Refs.
	Cellulose	13.5	85 °C	[29]
	Avicel	8	100 °C, 1 h	[7]
[C2mim][OAc]	Avicel	5	90 °C	[30]
	Celulose, DP = 569	13.2		[29]
[C4mim][OAc]	Avicel	12	100 °C, 1 h	[7]
	Cellulose, DP = 250	21.5	85 °C	[23]
[Amim][HCOO]	Cellulose, DP = 250	10	60 °C	[23]
 [C1mim][$(MeO)_2PO_2$]	Avicel	10	100 °C, 1 h	[7]
 [C2mim][$(MeO)_2PO_2$]	MCC	10	65 °C	[28]
 [C2mim][$(MeO)(Me)PO_2$]	Avicel	10	100 °C, 1 h	[7]
 [C2mim][$(MeO)(H)PO_2$]	MCC	6	30 °C, 1 h	[28]

critical drawback for biomass treatment process, especially for an energy conversion system. Addition of a small amount of water to the ILs certainly decreases the cellulose dissolving ability. These ILs cannot dissolve cellulose in the presence of a certain amount of water. Mazza and co-workers reported that the influence of water on the precipitation of cellulose in ILs [42]. Addition of a small amount of water was reported to greatly decrease the cellulose dissolving ability of CDILs. Gericke and co-workers analyzed cellulose precipitation from CDILs by addition of several anti-solvents including water [43]. According to the paper, once dissolved cellulose was easily precipitated from CDILs by the addition of 20 wt% water. This precipitation was found in all ILs used in the study, namely [C4mim]Cl, [Amim]Cl, and [C2mim][OAc]. Hauru and co-worker also reported the cellulose precipitation from CDILs [44]. The cellulose solutions became turbid by the addition of 2–3 equivalents of water, which is equivalent to 20–25 wt% water content. ILs easily absorb water from air [45], and especially CDILs have a high water absorption rate because they are very polar. Generally polar materials are hydrophilic. Troshenkova and co-workers reported on the water absorbability of a CDIL, [C2mim][OAc] [46]. This IL adsorbed up to 27 wt% of water from air at 25 °C. [C2mim][OAc] was hydrated by the water exothermically (11 kJ mol^{-1}), such values being

Table 2.6 Correlation between water content of TBPH and cellulose solubility (wt%) at 25 °C

Water content (wt%)	Cellulose (wt%)[a]	Dissolution time (min)
60	0.5	>2 weeks
50	15	5
	20	–[b]
40	1	1
	15	3
	20	5
	25	–[c]
30	15	5
	20	–[b]
20	5	7
	10	–[b]
10	0.5	Not dissolved

Reproduced from Abe et al. [47] with permission from The Royal Society of Chemistry

[a] Final concentration

[b] Most of the cellulose were dissolved within 30 min, but complete dissolution was not confirmed even after 1 h

[c] Difficult to stir

comparable to the thermal effect of chemical reactions. This means that CDILs should be sufficiently dried before cellulose treatment, and this might require a considerable amount of energy.

Quite recently, a novel IL derivative was reported as a cellulose solvent which dissolves cellulose without heating even in the presence of water. Abe and co-workers reported that tetra-*n*-butylphosphonium hydroxide (TBPH) containing 30–50 wt% water dissolved cellulose (15–20 wt% at final concentration) without heating at 25 °C (Table 2.6) [47]. Since this solution contained water, we do not need to dry the cellulose materials before dissolution process. TBPH/water mixture is expected as a potential solvent for cellulose regardless of water content.

2.6 Ionic Liquids for Lignocellulose Dissolution

ILs are being investigated as a solvent for not only pure cellulose but also other cellulosic biomass. Cellulosic biomass, such as wood, is composed of several hardly soluble polymers and many other materials. Other polysaccharides are also an attractive target to be extracted from biomass. In 2007, Fort and co-workers reported wood biomass treatment by ILs, and they clarified that a mixture of [C4mim]Cl and DMSO partially dissolved wood biomass at 100 °C (Fig. 2.5) [48]. The dissolving degree was achieved to about 70 % (wt/wt at added biomass). They analyzed the extracted materials and clarified that they were a mixture of polysaccharides and lignin. Shortly after this, Kilpeläinen and co-workers reported on wood dissolution by [C4mim]Cl and [Amim]Cl [49]. They treated soft- and hard-wood such as Norway spruce sawdust and southern pine thermomechanical pulp at temperatures between 80 and 130 °C for 8 and 13 h, respectively, and

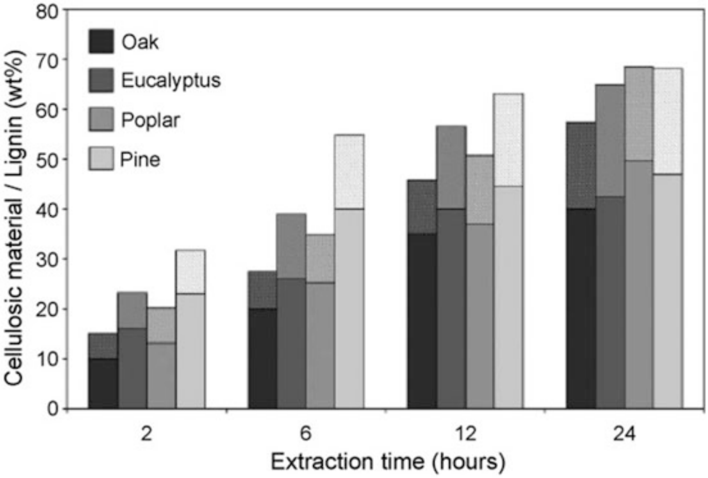


Fig. 2.5 Cellulosic material (*solid bars*) and lignin material (*dashed bars*) extraction profiles in [C4mim]Cl/DMSO-d_6 at 100 °C for the different wood (Reproduced from Fort et al. [48] with permission from The Royal Society of Chemistry)

observed that the biomass samples were partially dissolved. When the dissolution of the same lignocellulosic samples was soaked in 1-benzyl-3-methylimidazolium chloride ([Bnmim]Cl), transparent amber solutions were obtained. Wang and co-workers used a room temperature IL, [Amim]Cl to extract cellulose-rich material from several wood chips such as pine, poplar, Chinese parasol, and catalpa [50]. They showed that pine was one of the most suitable wood species for cellulose extraction with ILs, and its cellulose extraction degree reached to 62 %.

Miyafuji and co-worker observed the state of woodchips from softwood, *Cryptomeria japonica*, during the ILs treatment using light microscope [51]. Figure 2.6 shows micrographs of latewood, earlywood, and the latewood/earlywood boundary after treatment with [C2mim]Cl at 120 °C. The cell walls in latewood became disordered after 0.5 h treatment. In addition, some destruction or flaking was observed in the cell walls after 4 h treatment. By contrast, no significant change was observed in earlywood even after 4 h treatment. They suggested that latewood swells easier than earlywood because of the difference in the density.

Although ILs could dissolve only a part of wood biomass in an early stage, the complete dissolution of wood was achieved by Sun and co-workers in 2009 with carboxylate salts under heating [52]. After that the following separation methods were also investigated. Kilpeläinen and co-workers also reported the complete dissolution of lignocellulose materials [49]. That process helps to break some of interchain chemical bonds such as lignin-carbohydrate bond, and the lignocellulose material was used after mechanical pulping. Sun and co-workers clarified that [C2mim][OAc] completely dissolved softwood (southern yellow pine) and hardwood (red oak) after 46 and 25 h heating at 110 °C for pine and oak, respectively. In addition, they suggested that carbohydrate-free lignin and cellulose-rich materials

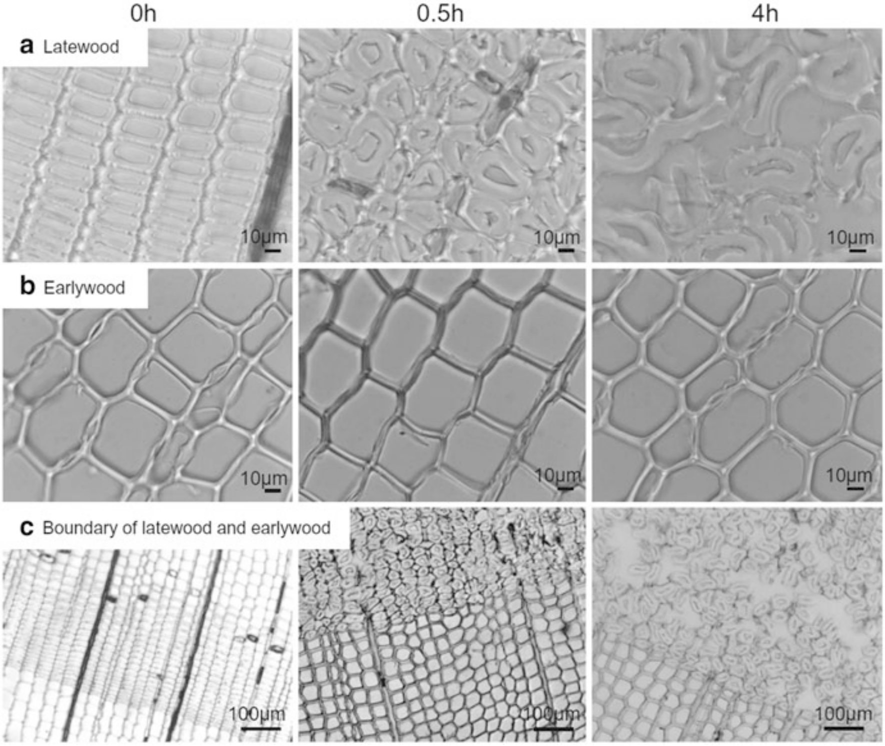
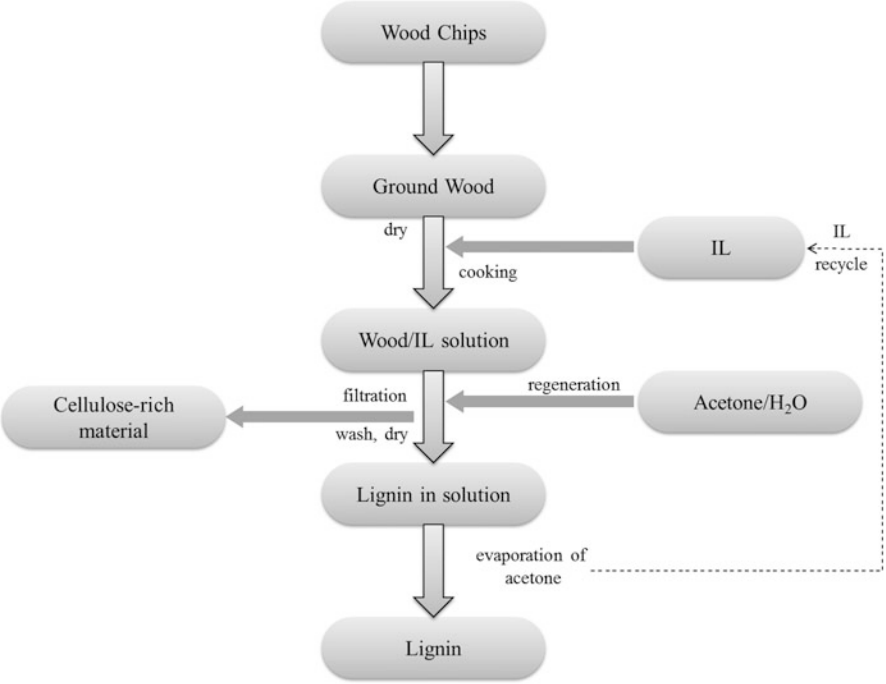


Fig. 2.6 Light microscopic images of wood ((**a**) latewood, (**b**) earlywood, (**c**) boundary of latewood and earlywood) treated with [C2mim]Cl at 120 °C [51] (With kind permission from Springer Science+Business Media)

were obtained by adequate precipitating process by the addition of acetone and water. On this basis, they developed the biomass treatment process as shown in Scheme 2.7.

Regarding lignin regeneration, Casas and co-workers also studied and reported some interesting results [53]. They collected regenerated lignin from *Pinus radiata* and *Eucalyptus globulus* woods dissolved in imidazolium-type ILs. Lignin was successfully regenerated by precipitation with methanol from wood solutions in [Amim]Cl, [C4mim]Cl, or [C2mim]Cl. Against this, lignin was not regenerated from acetate-type ILs. In addition, contents of different functional groups in the regenerated lignin were found to depend on the species of IL employed as well as wood species dissolved.

In the next section, direct lignin extraction from wood is mentioned. Sun and co-workers investigated the effect of particle size of the added biomass [52]. For [C4mim]Cl, the particle size was observed to have a significant influence on the extraction of lignin. The IL dissolved 52.6 % of the finely milled biomass (<0.125 mm), but only 26.0 % of coarser biomass (0.25–0.50 mm). It is easy to comprehend that smaller particles have larger gross surface area and lignin is easier to be solubilized. On the other hand, for [C2mim][OAc], the particle size of biomass did



Scheme 2.7 Suggested wood biomass treatment process using IL (Reproduced from Sun et al. [52] with permission from The Royal Society of Chemistry)

not affect the results significantly. The [C2mim][OAc] dissolved more than 90 % of the added wood even from the particles as large as 0.5–1.0 mm. Sun et al. also evaluated the effects of some pretreatments, i.e., microwave or ultrasound irradiation (Table 2.7) [52]. These pretreatments accelerated the lignocellulose dissolution. With 60 × 3 s microwave pulses, the time for complete dissolution (t_{cd}) was reduced to shorter than half of that without pretreatment. As seen in Table 2.7, ultrasound pretreatment also accelerated the dissolution. In spite that these pretreatments are effective, it should not be ignored that these steps also consume energy.

In 2011, Sun et al. reported that complete dissolution of lignocellulose was carried out with shorter mixing time at temperature above the glass transition temperature of lignin [54]. Complete dissolution of 0.5 g bagasse in 10 g of [C2mim][OAc] requires more than 15 h heating at 110 °C, by contrast, it dissolves completely in the IL within 5–15 min heating at 175–195 °C. In addition, processing bagasse in the IL at 185 °C for 10 min gave higher yields of both recovered lignin and carbohydrate than the previous methods using lower temperatures and longer times (e.g., 110 °C, 16 h). There was an associated problem with the thermal stability of [C2mim][OAc], because about 15 % of the IL degraded after processing at the higher temperature.

Miyafuji and co-workers reported that cellulose dissolving ILs work as not only a solvent for plant biomass but also a reaction medium. They found that [C2mim]Cl

Table 2.7 Effect of pretreatment on the time required to achieve complete dissolution (t_{cd}) of 0.50 g of southern yellow pine sawdust (particle size 0.125–0.250 mm) in 10 g of [C2mim][OAc] at 110 °C [52]

Pretreatment method	Pretreatment condition	t_{cd} (h)
None	None	46
Microwave	30 × 3 s pulses	45
Microwave	60 × 3 s pulses	21
Microwave	100 × 3 s pulses	16
Ultrasound irradiation	1 h at 40 °C	23

dissolved wood and that the solubilized polymers such as cellulose were depolymerized to low molecular weight compounds just by mixing [55]. Japanese beech wood flours (0.09 g) were added to 3 g of [C2mim]Cl, and the mixture was heated to 90–120 °C under gentle stirring. After that, the molecular weight distribution of the solubilized compounds in [C2mim]Cl was studied by gel permeation chromatography. As a result, the molecular weight of the solubilized compounds was found to decrease as the treatment time was extended, and such depolymerization was more enhanced at higher temperature. They suggested that [C2mim]Cl penetrated into wood and liquefied polysaccharides such as cellulose at the initial stage of the reaction, and the crystal structure was gradually broken down.

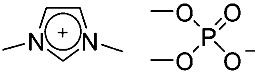
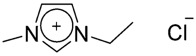
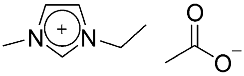
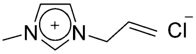
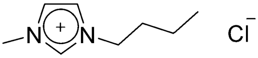
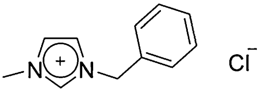
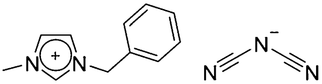
The cellulosic biomass dissolving ability of several CDILs is summarized in Table 2.8.

2.7 Selective Extraction from Plant Biomass

In the previous section, the dissolution of plant biomass was mentioned. Those studies dissolve cellulose, hemicellulose, lignin, and some other materials altogether. On the other hand, some researchers are interested in isolating target or useful materials selectively from plant biomass. In the case of dissolution and collection process of cellulose, some separation processes of lignin and other polysaccharides are required. When one can design ILs suitable to extract only lignin selectively, the ILs should become a promising solvent in the pulping method of plant biomass.

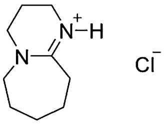
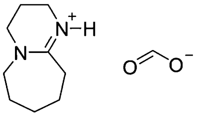
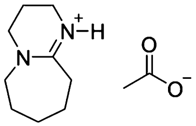
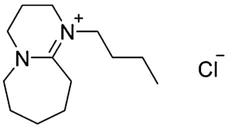
Pu and co-workers reported about lignin dissolution using several ILs in 2007 [57], and Lee and co-workers reported on a similar process in 2009 [58]. Pu and co-workers investigated several imidazolium type ILs have a good ability to dissolve softwood kraft pulp lignin. In their study, 344 g/L lignin was dissolved in methylsulfate type ILs, and it was suggested that the selection of anions for ILs is important to dissolve lignin. In the case of [C4mim] salts, the order of lignin solubility was the function of anion species as follows: $MeOSO_3^- > Br^- > Cl^- > BF_4^-$. Lee and co-workers also investigated the lignin dissolving ability of imidazolium salts having several anions. According to their study, CDILs such as [C2mim][OAc] have good ability to dissolve lignin, and less polar ILs which have non-coordinating anions such as BF_4^- dissolve a small amount of Kraft lignin.

Table 2.8 Cellulosic biomass treatment ability of several CDILs

Ionic liquid	Biomass	Dissolution	Condition	Refs.
 [C1mim][(MeO)$_2$PO$_2$]	Spruce chips	5 wt%, partial	90 °C	[30]
 [C2mim]Cl	Spruce chips	5 wt%, partial	90 °C	[30]
	Spruce chips	5 wt%, Complete	90 °C	[30]
[C2mim][OAc]	Southern yellow pine, chips	92.6%[a]	110 °C, 16 h	[52]
	Southern yellow pine, chips	Complete	110 °C, 46 h	[52]
	Norway spruce saw dust	8 wt%	80 °C, 8 h	[49]
[Amim]Cl	Norway spruce TMP	7 wt%	130 °C, 8 h	[49]
	Pine	67%[a]	120 °C	[50]
	Poplar	30%[a]	120 °C	[50]
	Catalpa	23%[a]	120 °C	[50]
	Spruce chips	5 wt%, Complete	90 °C	[30]
	Pine	67%[a]	100 °C, 24 h, with DMSO-d_6	[48]
[C4mim]Cl	Poplar	68%[a]	100 °C, 24 h, with DMSO-d_6	[48]
	Oak	56%[a]	100 °C, 24 h, with DMSO-d_6	[48]
	Eucalyptus	64%[a]	100 °C, 24 h, with DMSO-d_6	[48]
	Wood chips	Partially soluble	130 °C, 15 h	[49]
	Norway spruce TMP	7 wt%	130 °C, 8 h	[49]
	Spruce chips	5 wt%, partial	90 °C	[30]
	Southern yellow pine, chips	26%[a]	110 °C, 16 h	[52]
 [Bnmim]Cl	Southern pine TMP	2 wt%	130 °C, 8 h	[49]
 [Bnmim][DCA]	Aspen wood chips or powder	Dissolved	150 °C, 24 h	[49]

(continued)

Table 2.8 (continued)

Ionic liquid	Biomass	Dissolution	Condition	Refs.
 [HDBU]Cl	Aspen wood chips or powder	Partially dissolved	100 °C, 24 h	[56]
 [HDBU][HCOO]	Aspen wood chips or powder	Partially dissolved	100 °C, 48 h	[56]
 [HDBU][OAc]	Aspen wood chips or powder	Partially dissolved	100 °C, 48 h	[56]
 [C4DBU]Cl	Aspen wood chips or powder	Partially dissolved	100 °C, 48 h	[56]

Other values in wt% mean the amount of biomass against the ILs used as solvents

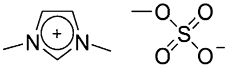
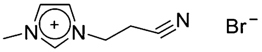
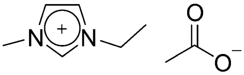
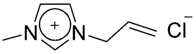
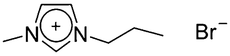
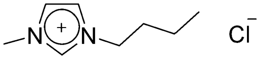
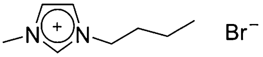
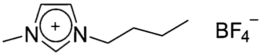
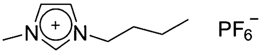
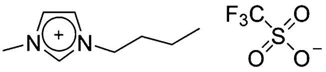
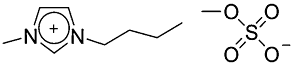
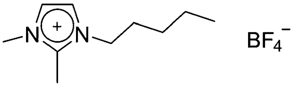
[a] The value was wt/wt of added biomass. The biomass was added to become 5 wt% against ILs

Based on the effectiveness of sodium xylenesulfonate as an agent for hydrotropic pulping of lignocellulose, Tan and co-workers studied the use of IL mixtures containing 1-ethyl-3-methylimidazolium alkylbenzenesulfonates ([C2mim][ABS]) to selectively dissolve lignin from sugarcane bagasse at atmospheric pressure and elevated temperature [59]. An extraction yield of up to 93 % was achieved. Compared with conventional lignin extraction methods, this system has several advantages such as no emission of toxic gases. But, a certain amount of carbohydrate losses (about 55 %) was caused during the biomass treatment.

Pinkert and co-workers reported that a class of food-additive derived ILs have a great ability to dissolve lignin without dissolving or degrading cellulose [60]. They suggested that 1-ethyl-3-methylimidazolium acesulfamate ([C2mim][Ace]) extracted 0.38 mass fraction of lignin of the added biomass in gentle extraction step (100 °C, 2 h), and the presence of a co-solvent (DMSO) increased the extraction degree to 0.56 mass fraction. Since this IL dissolves lignin, but not wood cellulose, it should become a promising solvent for pulping methods of lignocellulose materials.

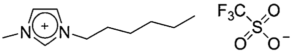
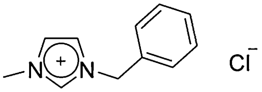
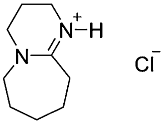
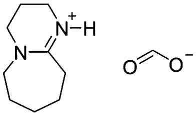
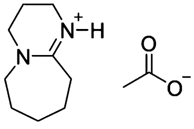
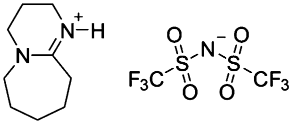
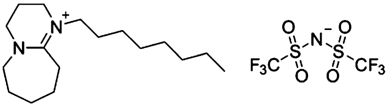
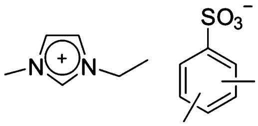
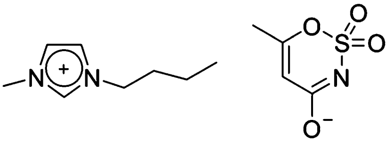
Table 2.9 shows the lignin dissolving ability of several ILs.

Table 2.9 Lignin dissolving ability of several ILs

Ionic liquid	Lignin	Dissolution	Condition	Refs.
 [C1mim][MeOSO$_3$]	Softwood kraft pulp lignin	344 g/L	50 °C	[57]
	Kraft lignin	>500 g/kg	90 °C, 24 h	[58]
 [Cyanomim]Br	Alkali, low sulfonate content lignin	9.5 wt%	80–90 °C, 20 min	[32]
 [C2mim][OAc]	Kraft lignin	300 g/kg	90 °C, 24 h	[58]
	Triticale straw	52.7 % of acid insoluble lignin	150 °C, 90 min	[61]
 [Amim]Cl	Kraft lignin	>300 g/kg	90 °C, 24 h	[58]
 [C3mim]Br	Alkali, low sulfonate content lignin	6.2 wt%	80–90 °C, 20 min	[32]
 [C4mim]Cl	Softwood kraft pulp lignin	13.9 g/L	75 °C	[57]
	Alkali, low sulfonate content lignin	8.8 wt%	80–90 °C, 20 min	[32]
 [C4mim]Br	Softwood kraft pulp lignin	17.5 g/L	75 °C	[57]
 [C4mim][BF$_4$]	Kraft lignin	40 g/kg	90 °C, 24 h	[58]
 [C4mim][PF$_6$]	Kraft lignin	1 g/kg	90 °C, 24 h	[58]
 [C4mim][OTf]	Kraft lignin	>500 g/kg	90 °C, 24 h	[58]
 [C4mim][MeOSO$_3$]	Softwood kraft pulp lignin	312 g/L	50 °C	[57]
 [C4dmim][BF$_4$]	Softwood kraft pulp lignin	14.5 g/L	70–100 °C	[57]

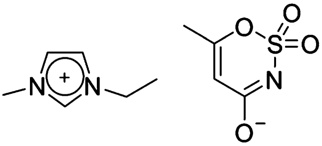
(continued)

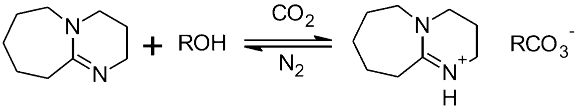
Table 2.9 (continued)

Ionic liquid	Lignin	Dissolution	Condition	Refs.
 [C6mim][OTf]	Softwood kraft pulp lignin	275 g/L	50 °C	[57]
 [Bnmim]Cl	Kraft lignin	>100 g/kg	90 °C, 24 h	[58]
 [HDBU]Cl	Sulfur free lignin	Dissolved	150 °C, 24 h	[56]
 [HDBU][HCOO]	Sulfur free lignin	Dissolved	100 °C, 24 h	[56]
 [HDBU][OAc]	Sulfur free lignin	Dissolved	100 °C, 24 h	[56]
 [HDBU][NTf_2]	Sulfur free lignin	Dissolved	100 °C, 24 h	[56]
 [C8DBU][NTf_2]	Sulfur free lignin	Dissolved	100 °C, 48 h	[56]
 [C2mim][ABS]	Sugarcane bagasse	97 % of lignin Extracted ~23 g/kg	190 °C, 90 min	[59]
	Pinus radiate wood flour	38 wt% of added lignin (>5.7 g/kg)	100 °C, 2 h	[60]
	Pinus radiate wood flour	51 wt% of added lignin (>7.7 g/kg)	100 °C, 16 h	[60]

(continued)

Table 2.9 (continued)

Ionic liquid	Lignin	Dissolution	Condition	Refs.
[C4mim][Ace]	Eucalyptus nitens	38 wt% of added lignin (>6.1 g/kg)	100 °C, 2 h	[60]
 [C2mim][Ace]	Pinus radiate wood flour	43 wt% of added lignin (>6.5 g/kg)	100 °C, 2 h	[60]



Scheme 2.8 Reaction scheme of the switchable ionic liquid (Reprinted from Anugwom et al. [62], Copyright (2012), with permission from Elsevier)

Selective extraction of not only lignin but also other components from biomass is important to construct an effective biomass conversion process. Anugwom and co-workers constructed the selective extraction process for hemicellulose from spruce, a typical plant biomass, using switchable ILs [62]. A switchable IL (Scheme 2.8) was investigated as dissolution/fractionation solvents for plant biomass. After the treatment for 5 days without stirring, the amount of hemicellulose in the undissolved fraction was reduced by 38 wt% as compared with that before treatment. They stated that the recovered hemicelluloses were very important in many industrial fields, because the spruce hemicellulose was mainly galactoglucomannans, which could be used as bioactive polymers, hydrocolloids, or papermaking chemicals [63].

ILs are useful to extract not only the main components of biomass such as polysaccharides and lignin but also some valuable materials. For example, a pharmaceutical ingredient, shikimic acid, was extracted from *Ginkgo biloba* with [C4mim]Cl [64]. Shikimic acid is the starting material for the synthesis of oseltamivir phosphate (Tamiflu®), which is used as an antiviral agent for the H5N1 strain of influenza [65]. As seen in Fig. 2.7, using [C4mim]Cl at 150 °C, the extraction yield of shikimic acid reached to 2.3 wt%, which was 2.5 times higher than that extracted with methanol at 80 °C. Usuki and co-workers also established the isolation process using an anion-exchange resin. They clarified that CDILs are useful and important to collect valuable materials from plant biomass.

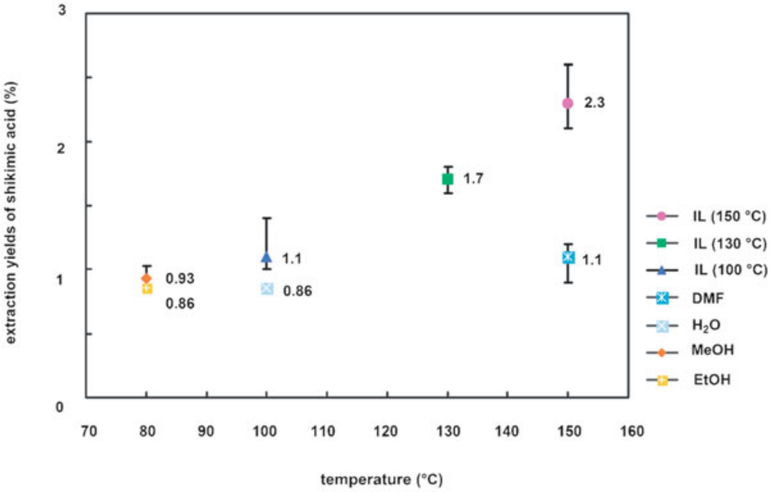


Fig. 2.7 Extraction degree of shikimic acid using [C4mim]Cl (100, 130, or 150 °C), DMF (150 °C), deionized H_2O (100 °C), methanol (80 °C), or ethanol (80 °C) (Reproduced from Usuki et al. [64] with permission from The Royal Society of Chemistry)

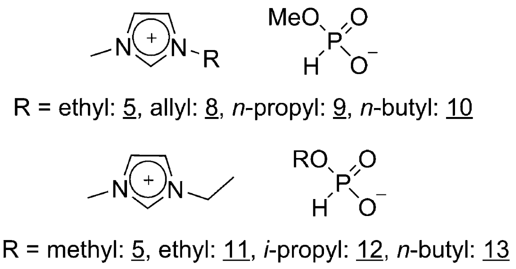
2.8 Energy Saving Dissolution of Plant Biomass

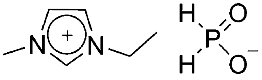
As described in the above two sections, ILs are promising solvents to treat plant biomass. The most important thing is the treatment capability of plant biomass under mild conditions. CDILs dissolve polysaccharides and a part of lignin at about 100 °C without any pressurization; this means that the energy-cost to treat biomass was reduced compared to other existing biomass treatment processes under heating above 150 °C and pressurization. It is very important for any industrial fields because energy-cost is directly linked to the price of the final product. The consumption of energy becomes of particular importance for the energy-producing industry, because the use of excess amount of energy to get comparable or less energy is meaningless. Although ILs can treat plant biomass under mild condition compared to some other methods such as kraft-pulping method, heating and long mixing time are still needed to dissolve plant biomass in ILs, too. These requirements should further be improved to reduce energy consumption.

Some researcher use ILs for just pretreatment of plant biomass and not for dissolution of cellulose. Li and co-workers reported that enzymatic hydrolysis was significantly improved by the use of CDIL, 1-ethyl-3-methylimidazolium diethyl phosphate ([C2mim][DEP]) [66]. They investigated the effect of temperature and time of the IL treatment on the hydrolysis efficiency. The pretreatment temperature was changed from 25 to 150 °C for 1 h stirring, and the hydrolysis efficiency of the pretreated wheat straw was significantly improved when the temperature was changed from 70 to 100 °C. On the other hand, the difference of the pretreatment time slightly affects the hydrolysis degree, and they reached the conclusion that only 30 min treatment was enough to accelerate the following hydrolysis. The yield of reducing sugars from wheat straw reached 54.8 % when the wheat straw was pretreated with [C2mim][DEP] at 130 °C for only 30 min. It remained only 20 % when the straw was enzymatically hydrolyzed in water for 12 h. In addition, the hydrolysis products did not show a negative effect on *S. cerevisiae* fermentation. Tan and co-workers reported the IL pretreatment of palm frond after extracting the palm oil for improving conversion of cellulose into reducing sugar through subsequent enzymatic hydrolysis [67]. During the pretreatment, lignin was partly decomposed and was dissolved in [C4mim]Cl and remained in the solution after regeneration process of cellulose. In addition, hemicellulose was autohydrolyzed during the pretreatment. Apart from crystallinity of cellulose, cellulose digestibility should also be influenced by other factors such as DP, surface area of cellulose, as well as state of cellulose protected by lignin and hemicellulose complexes. Uju and co-workers also studied the effect of pretreatment with ILs for plant biomass [68]. They used [C4mpy]Cl as a pretreatment IL for bagasse or *Eucalyptus*. The pretreatment of the biomass resulted in up to eightfold increase in the enzymatic saccharification compared with the untreated biomass. At short time pretreatment, [C4mpy]Cl showed higher potential to increase the initial degree of cellulose conversion than that in [C2mim][OAc]. They suggested that the significant acceleration of enzymatic saccharification was possibly caused by the reducing of DP of cellulose by the [C4mpy]Cl pretreatment. Bahcegul and co-workers studied the correlation between the particle size of plant biomass in detail and the pretreatment efficiency with ILs for subsequent enzymatic saccharification [69]. They used cotton stalks with four different particle size pretreated in [C2mim][OAc] or [C2mim]Cl. For [C2mim]Cl, the highest glucose yield (49 %) was obtained when the biomass had the smallest particle size, while cotton stalks with larger particle size gave lower glucose yield (33 %). On the contrary, for [C2mim][OAc], the lowest glucose yield (57 %) was obtained when the cotton stalks with the smallest particle size was examined, while cotton stalks with larger particle size gave higher glucose yield (71 %). Simply considering the overall surface area of the biomass particles, smaller particles gave higher glucose yield. Other unknown factor(s) should exist to affect the enzymatic saccharification. They suggested that the most suitable particle size of lignocellulosic biomass prior to pretreatment may change depending on the IL species.

For pretreatment of lignocellulosic biomass, it is not necessary to completely dissolve cellulose but heating is still a necessary step. On the other hand, some researchers are trying to dissolve plant biomass without heating. Abe et al. found that phosphinate-type ILs dissolved plant biomass and extracted polysaccharides from plant biomass without heating [70]. Since some phosphonate type ILs as seen in Scheme 2.9 have a good ability to dissolve cellulose at ambient temperature [28], we have prepared several phosphonate type ILs and evaluated their biomass treatment ability. As a result, polysaccharide extraction degree was found to be closely related to the viscosity. This means that the IL with low viscosity had good

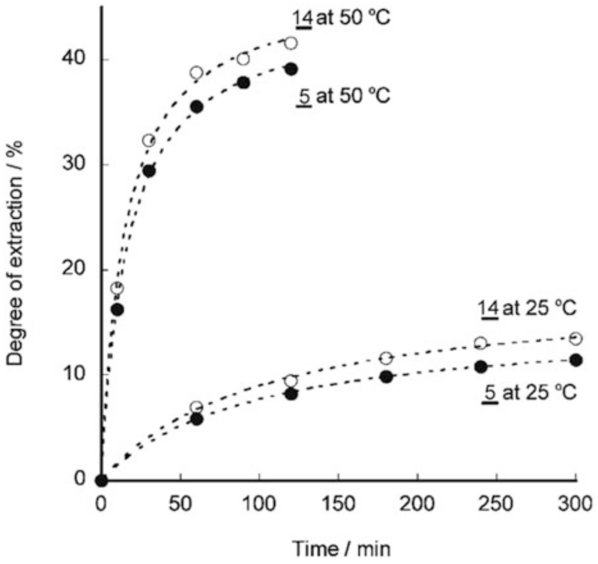
Scheme 2.9 Structure of alkylphosphonate type salts [70]





Scheme 2.10 Structure of 1-ethyl-3-methylimidazolium phosphinate (IL**14**) (Reproduced from Abe et al. [70] with permission from The Royal Society of Chemistry)

Fig. 2.8 Extraction degree of polysaccharides from bran using phophinate salt (IL**14**) or methylphosphonate salt (IL**5**) [70]



capacity to dissolve plant biomass within a short period of mixing time under mild condition when ILs have sufficiently high polarity. We accordingly designed a low viscosity and highly polar IL; 1-ethyl-3-methylimidazolium phosphinate (Scheme 2.10). With this IL, it became easy to extract polysaccharides rapidly from plant biomass under mild conditions (Fig. 2.8). Since this IL did not require any heating to extract polysaccharides from biomass, the energy-cost was reduced and this IL should be a promising solvent for plant biomass treatment. In addition, this IL is stable and recyclable. Thus, a closed system for biomass treatment as seen in Fig. 2.9 can be proposed.

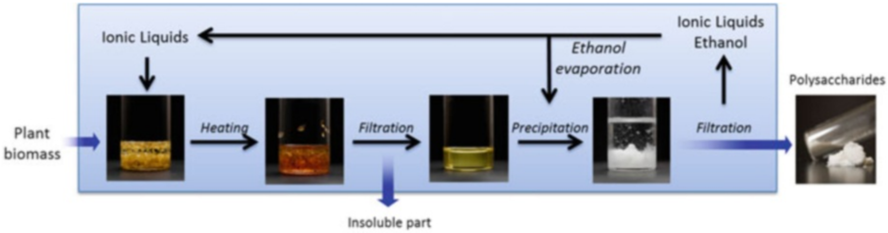


Fig. 2.9 Closed and energy-saving system (scheme) to extract polysaccharides from plant biomass [70]

Table 2.10 Correlation between water content of TBPH and extraction degree of polysaccharides after 1 h stirring at 25 °C

Water content of TBPH solution (wt%)	Polysaccharides extraction degree (%)
70	4.9
60	28
50	36
40	37
30	24

The extraction degree was calculated from the weight of the added poplar powder (5 wt% against the TBPH solution)

There are a few reports about the effect of water addition on the solubility of cellulose. Padmanabhan and co-workers reported about the influence of water on the lignocellulose solubility [71]. Prior to solubility measurements, 3–5 wt% water was added to cellulose dissolving ILs, namely chloride, acetate and phosphate-based ILs. After that, powder of *Miscanthus*, a lignocellulosic material, was added to the ILs, and stirred the mixture at over 100 °C. However, no cellulose was extracted. This result strongly suggested that water considerably suppressed the dissolution of lignocellulose in wet ILs. They concluded that ILs should be dried well in advance to extract cellulose from biomass. Since plant biomasses also contain a certain amount of water, the biomasses have to be dried before treatment with ILs. On the other hand, as mentioned above, TBPH has a great ability to dissolve cellulose without heating even in the presence of water [47]. So, we next tried to use this novel solvent to treat wood biomass. As expected, polysaccharides such as cellulose were extracted from wood powder without heating (Table 2.10). Poplar powder was used as a wood sample, and the powder was added to reach 5 wt% against TBPH solution. In the presence of 70 wt% water, TBPH could extract polysaccharides only 4.9 % of the weight of the added poplar. On the other hand, TBPH containing 40–50 wt% water successfully extracted cellulose and other polysaccharides for 36–37 % of the weight of the added popular. These results indicate that the extraction of cellulose from powder of wood such as poplar could be carried out even in the presence of considerable amounts of water.

For the development of sustainable human societies, we have to develop new energy conversion methods based on renewable energy sources instead of fossil fuels. ILs, which dissolve renewable cellulosic biomass with low energy cost, should serve as the foundation for future development of sustainable world, especially for the development of bioenergy production.

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References

1. Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev. 1999;99:2071–83.
2. Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog Energy Comb Sci. 2012;38:449–67.
3. Zugenmaier P. Conformation and packing of various crystalline cellulose fibers. Prog Polym Sci. 2001;26:1341–417.
4. Bochek AM. Effect of hydrogen bonding on cellulose solubility in aqueous and nonaqueous solvents. Russ J Appl Chem. 2003;76:1711–19.
5. Graenacher C. Cellulose solution. US Patent, No. 1943176.
6. Swatloski RP, Spear SK, Holbrey JD, Rogers RD. Dissolution of cellose with ionic liquids. J Am Chem Soc. 2002;124:4974–5.
7. Vitz J, Erdmenger T, Haensch C, Schubert US. Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chem. 2009;11:417–24.
8. Heinze T, Schwikal K, Barthel S. Ionic liquids as reaction medium in cellulose functionalization. Macromol Biosci. 2005;5:520–5.
9. Mizumo T, Marwanta E, Matsumi N, Ohno H. Allylimidazolium halides as novel room temperature ionic liquids. Chem Lett. 2004;33:1360–1.
10. Zhang H, Wu J, Zhang J, He J. 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: a new and powerful nonderivatizing solvent for cellulose. Macromolecules. 2005;38:8272–7.
11. Remsing RC, Swatloski RP, Rogers RD, Moyna G. Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a C-13 and Cl-35/37 NMR relaxation study on model systems. Chem Commun. 2006;2006:1271–3.
12. Youngs TGA, Hardacre C, Holbrey JD. Glucose solvation by the ionic liquid 1,3-dimethylimidazolium chloride: a simulation study. J Phys Chem B. 2007;111:13765–74.
13. Gross AS, Bell AT, Chu J-W. Thermodynamics of cellulose solvation in water and the ionic liquid 1-butyl-3-methylimidazolim chloride. J Phys Chem B. 2011;115:13433–40.
14. Hansen CM. 50 years with solubility parameters – past and future. Prog Org Coat. 2004;51:77–84.
15. Klamt A. Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. J Phys Chem. 1995;99:2224–35.
16. Kamlet MJ, Taft RW. The solvatochromic comparison method. I. The beta.-scale of solvent hydrogen-bond acceptor (HBA) basicities. J Am Chem Soc. 1976;98:377–83.
17. Crowhurst L, Mawdsley PR, Perez-Arlandis JM, Salter PA, Welton T. Solvent-solute interactions in ionic liquids. Phys Chem Chem Phys. 2003;5:2790–4.
18. Brandt A, Gräsvik J, Hallett JP, Welton T. Deconstruction of lignocellulosic biomass with ionic liquids. Green Chem. 2013;15:550–83.
19. Ohira K, Abe Y, Kawatsura M, Suzuki K, Mizuno M, Amano Y, Itoh T. Design of cellulose dissolving ionic liquids inspired by nature. ChemSusChem. 2012;5:388.

20. Ohno H, Fukaya Y. Task specific ionic liquids for cellulose technology. Chem Lett. 2009;38:2–7.
21. Hermanutz F, Gähr F, Uerdingen E, Meister F, Kosan B. New developments in dissolving and processing of cellulose in ionic liquids. Macromol Symp. 2008;262:23–7.
22. Swatloski RP, Rogers RD, Holbrey JD. Dissolution and processing of cellulose using ionic liquids. 2003, WO 029329.
23. Fukaya Y, Sugimoto A, Ohno H. Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formats. Biomacromolecules. 2006;7:3295–7.
24. Remsing RC, Hernandez G, Swatloski RP, Massefski WW, Rogers RD, Moyna G. Solvation of carbohydrates in N, N′-dialkylimidazolium ionic liquids: a multinuclear NMR spectroscopy study. J Phys Chem B. 2008;112:11071–8.
25. Zhang J, Zhang H, Wu J, Zhang J, He J, Xiang J. NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids. Phys Chem Chem Phys. 2010;12:1941–7.
26. Liu H, Sale KL, Holmes BM, Simmons BA, Singh S. Understanding the interactions of cellulose with ionic liquids: a molecular dynamics study. J Phys Chem B. 2010;114:4293–301.
27. Xu A, Wang J, Wang H. Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. Green Chem. 2010;12:268–75.
28. Fukaya Y, Hayashi K, Wada M, Ohno H. Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. Green Chem. 2008;10:44–6.
29. Kosan B, Michels C, Meister F. Dissolution and forming of cellulose with ionic liquids. Cellulose. 2008;15:59–66.
30. Zavrel M, Bross D, Funke M, Buchs J, Spiess AC. High-throughput screening for ionic liquids dissolving (ligno-)cellulose. Bioresour Technol. 2009;100:2580–7.
31. Barthel S, Heinze T. Acylation and carbanilation of cellulose in ionic liquids. Green Chem. 2006;8:301–6.
32. Lateef H, Grimes S, Kewcharoenwong P, Feinberg B. Separation and recovery of cellulose and lignin using ionic liquids: a process for recovery from paper-based waste. J Chem Technol Biotechnol. 2009;84:1818–27.
33. Erdmenger T, Haensch C, Hoogenboom R, Shubert US. Homogeneous tritylation of cellulose in 1-butyl-3-methylimidazolium chloride. Macromol Biosci. 2007;7:440–5.
34. Fukumoto K, Yoshizawa M, Ohno H. Room temperature ionic liquids from 20 natural amino acids. J Am Chem Soc. 2005;127:2398–9.
35. Kagimoto J, Noguchi K, Murata K, Fukumoto K, Nakamura N, Ohno H. Polar and low viscosity ionic liquid mixtures from amino acids. Chem Lett. 2008;37:1026–7.
36. Ohno H, Fukumoto K. Amino acid ionic liquids. Acc Chem Res. 2007;40:1122–9.
37. Fukumoto K, Ohno H. LCST-type phase changes of a mixture of water and ionic liquids derived from amino acids. Angew Chem Int Ed. 2007;46:1852–5.
38. Kagimoto J, Taguchi S, Fukumoto K, Ohno H. Hydrophobic and low-density amino acid ionic liquids. J Mol Liq. 2010;153:133–8.
39. Ohira K, Yoshida K, Hayase S, Itoh T. Amino acid ionic liquid as an efficient cosolvent of dimethyl sulfoxide to realize cellulose dissolution at room temperature. Chem Lett. 2012;41:987–9.
40. Hirao M, Sugimoto H, Ohno H. Preparation of novel room-temperature molten salts by neutralization of amines. J Electrochem Soc. 2000;147:4168–72.
41. King AWT, Asikkala J, Mutikainen I, Jarvi P, Kilpelainen I. Distillable acid-base conjugate ionic liquids for cellulose dissolution and processing. Angew Chem Int Ed. 2011;50:6301–5.
42. Mazza M, Catana DA, Garcia CV, Cecutti C. Influence of water on the dissolution of cellulose in selected ionic liquids. Cellulose. 2009;16:207–15.
43. Gericke M, Liebert T, Seoud AE, Heinze T. Tailored media for homogeneous cellulose chemistry: ionic liquid/co-solvent mixtures. Macromol Mater Eng. 2011;296:483–93.

44. Hauru LKJ, Hummel M, King AWT, Kilpeläinen I, Sixta H. Role of solvent parameters in the regeneration of cellulose from ionic liquid solutions. Biomacromolecules. 2012;13:2896–905.
45. Cammarata L, Kazarian SG, Salter PA, Welton T. Molecular states of water in room temperature ionic liquids. Phys Chem Chem Phys. 2001;3:5192–200.
46. Troshenkova SV, Sashina ES, Novoselov NP, Arndt K-F, Jankowsky S. Structure of ionic liquids on the basis of imidazole and their mixtures with water. Russ J Gen Chem. 2010;80:106–11.
47. Abe M, Fukaya Y, Ohno H. Fast and facile dissolution of cellulose with tetrabutylphosphonium hydroxide containing 40 wt% water. Chem Commun. 2012;48:1808–10.
48. Fort DA, Remsing RC, Swatloski RP, Moyna P, Moyna G, Rogers RD. Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. Green Chem. 2007;9:63–9.
49. Kilpeläinen I, Xie H, King A, Granstrom M, Heikkinen S, Argyropoulos DS. Dissolution of wood in ionic liquids. J Agric Food Chem. 2007;55:9142–8.
50. Wang X, Li H, Cao Y, Tang Q. Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). Bioresour Technol. 2011;102:7959–65.
51. Miyafuji H, Suzuki N. Observation by light microscope of sugi (Cryptomeria japonica) treated with the ionic liquid 1-ethyl-3-methylimidazolium chloride. J Wood Sci. 2011;57:459–61.
52. Sun N, Rahman M, Qin Y, Maxim ML, Rodriguez H, Rogers RD. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. Green Chem. 2009;11:646–55.
53. Casas A, Oliet M, Alonso MV, Rodriguez F. Dissolution of Pinus radiata and Eucalyptus globulus woods in ionic liquids under microwave radiation: lignin regeneration and characterization. Sep Purif Technol. 2012;97:115–22.
54. Li W, Sun N, Stoner B, Jiang X, Lu X, Rogers RD. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin. Green Chem. 2011;13:2038–47.
55. Miyafuji H, Miyata K, Saka S, Ueda F, Mori M. Reaction behavior of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride. J Wood Sci. 2009;55:215–19.
56. D'Andola G, Szarvas L, Massonne K, Stegmann V. (BASF), Ionic liquids for solubilizing polymers. 2008, WO 043837.
57. Pu Y, Jiang N, Ragauskas AJ. Ionic liquid as a green solvent for lignin. J Wood Chem Technol. 2007;27:23–33.
58. Lee SH, Doherty TV, Linhardt JS. Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. Biotechnol Bioeng. 2009;102:1368–76.
59. Tan SSY, MacFarlane DR, Upfal J, Edye LA, Doherty WOS, Patti AF, Pringle JM, Scott JL. Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. Green Chem. 2009;11:339–45.
60. Pinkert A, Goeke DF, Marsh KN, Pang S. Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids. Green Chem. 2011;13:3124–36.
61. Fu D, Mazza G, Tamaki Y. Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues. J Agric Food Chem. 2010;58:2915–22.
62. Anugwom I, Mäki-Arvela P, Virtanen P, Willför S, Sjöholm R, Mikkola J-P. Selective extraction of hemicelluloses from spruce using switchable ionic liquids. Carbohydr Polym. 2012;87:2005–11.
63. Xu C, Leppänen A-S, Eklund P, Holmlund P, Sjöholm R, Sundberg K, Willför S. Acetylation and characterization of spruce (Picea abies) galactoglucomannans. Carbohydr Res. 2010;345:810–16.
64. Usuki T, Yasuda N, Yoshizawa-Fujita M, Rikukawa M. Extraction and isolation of shikimic acid from Ginkgo biloba leaves utilizing an ionic liquid that dissolves cellulose. Chem Commun. 2011;47:10560–2.

65. Farina V, Brown JD. Tamiflu: the supply problem. Angew Chem Int Ed. 2006;45:7330–4.
66. Li Q, He Y-C, Xian M, Jun G, Xu X, Yang J-M, Li L-Z. Improving enzymatic hydrolysis of wheat straw using ionic liquid 1-ethyl-3-methyl imidazolium diethyl phosphate pretreatment. Bioresour Technol. 2009;100:3570–5.
67. Tan HT, Lee KT. Understanding the impact of ionic liquid pretreatment on biomass and enzymatic hydrolysis. Chem Eng J. 2012;183:448–58.
68. Uju N, Shoda Y, Nakamoto A, Goto M, Tokuhara W, Noritake Y, Katahira S, Ishida N, Nakashima K, Ogino C, Kamiya N. Short time ionic liquids pretreatment on lignocellulosic biomass to enhance enzymatic saccharification. Bioresour Technol. 2012;103:446–52.
69. Bahcegul E, Apaydin S, Haykir NI, Tatli E, Bakir U. Different ionic liquids favor different lignocellulosic biomass particle sizes during pretreatment to function efficiently. Green Chem. 2012;14:1896–903.
70. Abe M, Fukaya Y, Ohno H. Extraction of polysaccharides from bran with phosphonate or phosphinate-derived ionic liquids under short mixing time and low temperature. Green Chem. 2010;12:1274–80.
71. Padmanabhan S, Kim M, Blanch HW, Prausnitz JM. Solubility and rate of dissolution for Miscanthus in hydrophilic ionic liquids. Fluid Phase Equilib. 2011;309:89–96.