

Highlight Review

Task Specific Ionic Liquids for Cellulose Technology

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Abstract

Design of ionic liquids for dissolution, depolymerization, and energy conversion of cellulose and their derivatives is described. Importance of physicochemical properties such as polarity and hydrogen-bonding ability of the ionic liquids is described, and some practical approaches to prepare novel ionic liquids as solvents for cellulose technology are reviewed with latest results.

◆ Introduction

The energy crisis is a major concern. There have been many discussions of substitute materials to replace petroleum and other decreasing natural fuel resources. These natural resources derive from plants, namely, sugar derivatives have been synthesized by plants with the aid of solar energy. Biomass can then be converted into hydrocarbon fuel under the ground. However, we cannot wait for plants to be turned spontaneously but slowly into hydrocarbons. An excellent strategy for providing a new energy source is the immediate use of the biomass. It is, however, ridiculous to convert edible crops or vegetables into energy materials. We do not want to go into details, but energy should be extracted from *inedible* biomass, such as cereal straws, corn bagasse, cotton, and even used papers. Cellulose is the major component of such biomass, and it can be depolymerized into glucose. Furthermore, energy can be taken from glucose with the aid of enzymes. For efficient energy conversion, it is necessary to dissolve and depolymerize cellulose under mild reaction conditions. Accordingly, it is essential to design solvents for cellulose and to propose a system with minimum energy.

Cellulose is stabilized by intra- and inter-molecular hydrogen bonds so as to form tough bundles. Multiple hydrogen-bonding between cellulose molecules results in the formation of highly ordered crystalline regions; furthermore, these are mixed or covered by lignin. It is almost impossible to solubilize cellulose with water and common organic solvents. Some mixed systems composed of organic solvents, water, and salts have been proposed. In spite of the utility of these mixed solvent systems for cellulose, there remain some drawbacks such as volatility, generation of poisonous gas or waste, and difficulty of solvent recovery with small energy. It is not so difficult to combine the above requirements for a classical solvent system for cellulose, i.e., charge and organic compounds, and hydrogen-bonding ability. Organic salts typically fit this combination. In particular, organic salts with very low melting point should be good starting materials for the design of solvents for cellulose. In this review, we discuss the use of ionic liquids in cellulose processing.

◆ Ionic Liquids

Ionic liquids (ILs) are organic salts designed to melt below 100 °C, or preferably near room temperature. Compared to molecular liquids, ILs have various advantages that include extremely low volatility, low flammability and high thermal stability. The most fascinating nature of ILs are their structural diversity. The physicochemical properties of ILs, including viscosity,¹ polarity,² and other properties³ vary according to their ionic structures. As a result, their physicochemical properties can be tuned by exploiting the diversity of component organic cations and organic or inorganic anions. ILs have consequently been described as designer solvents. Appropriate ILs might therefore act as eco-friendly polar solvents for cellulose.

Because of these promising features, ILs should have diverse applications, and they have been extensively studied.⁴ ILs have been studied as solvents in chemistry, especially for catalytic reactions. Numerous papers and several reviews on these ILs as reaction media have been published.⁵⁻⁷ There is also an increasing number of studies on bio-catalytic reactions.^{8,9} Solubilization of enzymes, and enzymatic reactions in ILs,¹⁰⁻¹² aqueous ILs,¹³ or hydrated ILs¹⁴ have been demonstrated in recent years with the aim of preparing a suitable matrix for enzymes. However, there has been little study of ILs to dissolve enzymes. There are a few discussions concerning hydrophobicity, the hydrated state, and hydrogen-bonding. It is not simple to discuss enzyme solubility in ILs in terms of a few physicochemical parameters. However, the Kamlet-Taft parameters of ILs are helpful in considering the solubilizing ability of many materials, including proteins.

Since the polarity of ILs and their compatibility with other compounds vary widely with the ionic structure, ILs immiscible with other molecular solvents should be prepared. Numerous papers have been published on the phase-separation behavior of systems such as IL/water,¹⁵ IL/alcohol,¹⁶ IL/K₂PO₄/water,¹⁷ and IL/supercritical CO₂.¹⁸ These systems have been investigated as alternatives to traditional organic solvents for liquid/liquid phase separation. Many papers found that IL-based biphasic systems were effective in biphasic separation systems. Seddon and co-workers recently reported a mixture of two immiscible ILs.¹⁹ Fukumoto and Ohno recently reported novel hydrophobic ILs with unusual lower critical solution temperature (LCST)-type phase behavior.²⁰ These findings suggest that ILs should be not only alternatives to volatile organic solvents but also novel solvents for processing. Moreover, there is a dramatic increase in the study of solubilization of nearly insoluble compounds, including cellulose, which is impossible with conventional molecular liquids.

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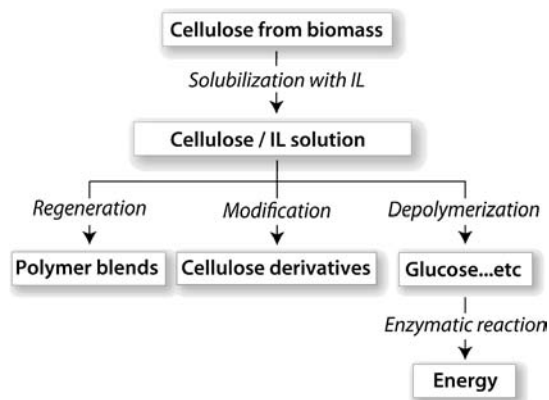


Figure 1. Contribution of ILs for cellulose-based materials and energy conversion.

In the present review, we consider bio-energy conversion. For this purpose, the following steps are particularly important as shown in Figure 1, namely such as dissolution of biomass, especially cellulose; depolymerization of cellulose to glucose or oligosaccharides; and energy conversion of these saccharides to generate electrical energy.

◆ Cellulose Dissolution with Ionic Liquids

The challenge of dissolving cellulose has been considered since the 1930s. In 1934, Graenacher reported that cellulose dissolved in a mixture of 1-ethylpyridinium chloride and nitrogen-containing base when heated at the melting point (T_m) above 120 °C.²¹ Moreover, T_m was lowered to 77 °C by mixing 1-ethylpyridinium chloride with 50% DMF or DMSO.²² These solvent systems were not typical examples of IL-based solvents because of their relatively high T_m and the volatility of the co-solvents. Rogers et al. first demonstrated that some ILs could solubilize cellulose, in 2002.²³ They studied a series of 1-butyl-3-methylimidazolium ([C₄mim]) salts as solvents for cellulose. In that study, 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) solubilized cellulose best under conventional heating. For instance, with [C₄mim]Cl, clear solutions containing 3 and 10 wt % pulp cellulose (DP ≈ 1000) could be obtained by simple mixing at 70 and 100 °C, respectively.

Rogers et al. also investigated the solubilizing mechanism of cellulose in ILs using NMR spectroscopy.²⁴ The ¹³C NMR spectra of cellulose in [C₄mim]Cl containing 15 wt % DMSO-*d*₆ indicated that cellulose was disordered in the ILs/DMSO mixed solution. Moreover, to examine the interactions between IL and cellulose at the molecular level, Moyna et al. took NMR relaxation measurements.²⁵ They determined the NMR longitudinal (T_1) and transverse (T_2) relaxation times of [C₄mim]Cl, both for the cation (¹³C), and the anion (^{35/37}Cl). These relaxation times were analyzed as a function of the concentrations of cellobiose, glucose, and glucose pentaacetate. Variations in relaxation times generally yield information about the molecular dynamics of the compound under investigation. Investigation of the relaxation times as a function of increasing cellobiose concentration revealed that the interaction between [C₄mim] cation and the sugar unit is negligible. However, that with chloride anion was very strong. This difference is due to hydrogen-bond-

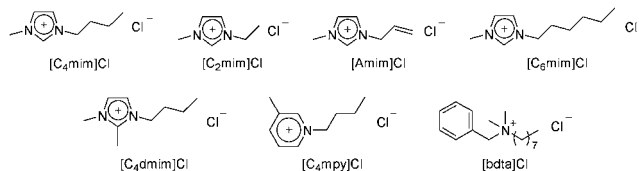


Figure 2. Chloride salts used for cellulose dissolution.

ing of chloride anion to the OH groups of the sugar unit. Whereas glucose interacted strongly with the anion, the glucose pentaacetate had almost no effect on the relaxation rate of ³⁵Cl. The dissolving of cellobiose or glucose in [C₄mim]Cl involves the formation of hydrogen bonds between the Cl anions of ILs and the hydroxy groups of sugar, in stoichiometric ratio. Youngs, Hardacre, et al. investigated the interaction between D-glucose (model compound) and [C₄mim]Cl by means of a molecular dynamics simulation. They also reported that the cations could interact only weakly with the sugar.²⁶

These previous studies stated that the most dominant interaction was between a chloride anion and the hydroxy group of cellulose. Chloride anion were reported to show strong hydrogen-bonding basicity according to chromatographic analysis. Indeed, [C₄mim] combined with a series of other anions has weaker hydrogen-bonding basicity. Accordingly, Br, [SCN], [PF₆], and [BF₄] anions are inappropriate for dissolving cellulose.

As shown in Figure 2, 1-butyl-3-methylimidazolium chloride, and also a series of chloride salts, composed of a series of cations, have been proposed as solvents for cellulose. For example, Rogers et al. reported that the chloride salts combined with longer-chain substituted imidazolium cations such as 1-hexyl-3-methylimidazolium cation ([C₆mim]Cl) could dissolve cellulose, whereas this IL was less efficient at this task.²³ For example, at 100 °C, [C₆mim]Cl dissolves 5 wt % of cellulose, whereas cellulose could be soluble up to 10 wt % in [C₄mim]Cl. Allyl-substituted imidazolium chloride salts ([Amim]Cl) have also been used to dissolve cellulose.²⁷ Because of very low glass-transition temperature of imidazolium salt after introduction of the allyl group, these chloride salts can be used in liquid form without heating. Moreover, Heinze et al. reported the dissolving of cellulose in pyridinium salt and ammonium salt; the solubility of cellulose was found to have a relation with the cationic structure of ILs. Moreover, these ILs have been reported to dissolve a series of cellulose. Heinze et al. reported that [C₄mim]Cl could be used as solvents for microcrystalline cellulose (DP ≈ 290), spruce sulfate pulp (DP ≈ 600), cotton linters (DP ≈ 1200), and microbial cellulose (bacterial cellulose) (DP ≈ 6500).²⁸

Recent efforts have been concentrated on lignocellulose. As shown in Figure 3, lignocellulose consists of three main fractions: cellulose, hemicellulose and lignin. Several previous reports have found that certain ILs can dissolve cellulose, hemicellulose, and lignin.²⁹ Since certain ILs can dissolve these component materials of lignocellulose, ILs have been proposed as solvents for lignocellulose. Rogers et al. recently reported that some ILs could be used to dissolve lignocelluloses from wood.³⁰ A mixture of [C₄mim]Cl/DMSO (84:16 wt %) dissolves pine, eucalyptus, and oak wood shavings after heating at 100 °C for several hours. Argyropoulos et al. also reported that several ILs dissolved the lignocelluloses from wood chip, saw dust, and thermomechanical pulp (TMP).³¹ In particular, when 1-benzyl-3-

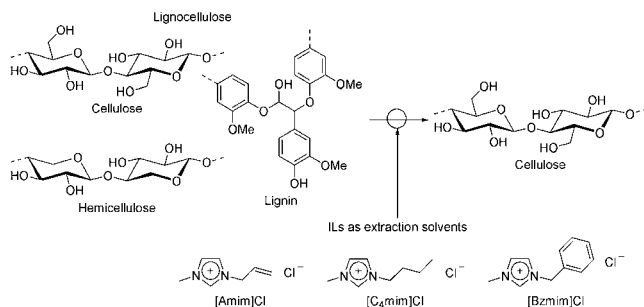


Figure 3. Application of ILs as solvents for lignocellulose.

methylimidazolium chloride ([Bzmim]Cl), which is designed to improve interaction with lignin by introducing the benzene ring, was used as a solvent, clear and amber solution of TMP was reportedly obtained. These results clearly show that suitable design of the ionic structure makes it possible to dissolve lignocellulose efficiently.

◆ Application of Chloride Salts for Cellulose Processing

Cellulose has long been processed in solvents that are non-standard and accordingly there are limited applications. Dissolved cellulose can easily be recovered in amorphous form by injecting the IL solution into water or alcohols. Any molecular liquid can be used if it has sufficient compatibility with the IL. By this means, cellulose can be prepared as films, powder, gels, and even capsules. Cellulose nanofiber, recently published as super-strong materials,³² in which the molecular alignment is regulated at molecular level, may also be prepared from IL solution via gradual crystallization by slow addition of poor molecular liquids.

Because of the great ability of ILs to dissolve cellulose as well as many other organic and inorganic materials including bio and synthetic polymers, novel cellulose-based composite materials can be prepared which are unattainable through the use of conventional molecular liquids. In view of the excellent solubilizing ability of chloride salts, some chloride salts have been applied as solvents for cellulose processing. Rogers et al. prepared various cellulose blended or composite materials.^{33,34} Zhang et al. prepared wool keratin/cellulose composite fiber or membrane using chloride based ILs, [C₄mim]Cl.³⁵ Since chloride containing ILs can dissolve wool keratin, Zhang et al. demonstrated the preparation of wool keratin/cellulose films and fibers. Recently, the same group proposed novel cellulose composite materials containing multi-walled carbon nanotubes.³⁶ Kawanami et al. recently prepared titania nanowire composites on natural cellulose fibers using ILs containing chloride.³⁷

Zhang et al. reported that the homogeneous acetylation of cellulose was carried out in [Amim]Cl without catalysts.³⁸ Barthel and Heinze have also carried out acetylation or carbonylation of cellulose in [C₄mim]Cl under mild conditions.³⁹

◆ Application of ILs as Solvents for Biomass Processing

To produce glucose from cellulose, hydrolysis has usually been used, with acids or enzymes. Acid hydrolysis is widely

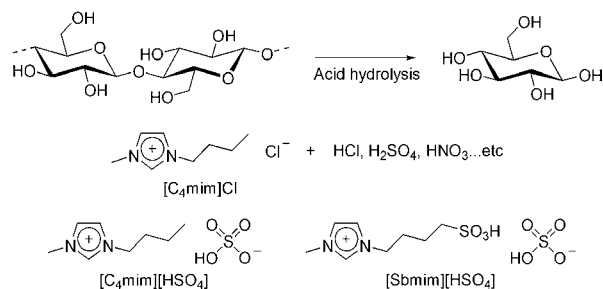


Figure 4. Hydrolysis of cellulose with IL based systems.

used for saccharification of cellulose. Since multiple intra- and inter hydrogen bonds between cellulose molecules help to form highly ordered crystalline regions protected from acid, hydrolysis generally requires excess acid.

Chloride-type ILs disorder the crystalline region of cellulose. As a result, acidic saccharification in ILs is a very efficient process (Figure 4) compared to conventional processing in aqueous media. Recently, Li et al. reported the hydrolytic reaction of cellulose and lignocellulose in ILs using acid catalyst.^{40,41} In the literature, hydrolysis of corn stalk in [C₄mim]Cl in the presence of catalytic amounts of HCl at 100 °C for 30 min provided 66% of reducing sugar. The cellulose homogeneously dissolved in IL readily promoted acid attack. Moreover, certain acidic ILs, such as [C₄mim][HSO₄] and [Sbmim][HSO₄], have been proposed as both solvents and catalysts. Hydrolytic reaction of cellulose in [C₄mim][HSO₄] and [Sbmim][HSO₄] yielded 23% and 15% reducing sugars within 5 and 2 min, respectively. Furthermore, a mixture of [C₄mim]Cl with these acidic ILs has been reported to effectively hydrolyze cellulose (70%, 35–45 min).

Although acid treatment is an effective technique for saccharification of cellulose, it produces several potential inhibitors. In contrast, enzymatic hydrolysis of both cellulose and lignocellulose proceeds under mild conditions, and is consequently an active research field with the aim of industrialization. To hydrolyze cellulose efficiently by enzymes, pretreatment is required to soften its tough assembled structure. Since some ILs dissolve cellulose and lignocellulose, ILs have also been examined as a pretreatment fluid for enzymatic reaction in an aqueous phase. Recently, Schall et al. demonstrated enzymatic hydrolysis of regenerated cellulose from [C₄mim]Cl solution.⁴² The rate of cellulose-catalyzed saccharification of microcrystalline cellulose after regeneration from [C₄mim]Cl solution was more than 50 times faster than that of untreated cellulose. Also, cellulose was reported to be regenerated as an amorphous mixture after dissolution, and the regenerated cellulose was efficiently converted to glucose by enzymatic hydrolysis in an aqueous phase.

These authors also reported that regenerated cellulose was obtained from wood chip by ILs, and was efficiently depolymerized to glucose by enzymatic hydrolysis.^{43,44} Rogers et al. have challenged the saccharification of cellulose using cellulase in [C₄mim]Cl.⁴⁵ However, [C₄mim]Cl induced significant denaturation of cellulase, even in aqueous mixtures due to high concentration of Cl⁻ anions. These results suggest that depolymerization of cellulose is not easy in ILs. Advances in methodology, especially to solubilize enzymes into polar ILs, design of new ILs for enzymes should be considered.

◆ Disadvantages of Chloride Salts

Previous studies all indicated that chloride salts are potential solvents for cellulose. However, most chloride salts have inherent disadvantages, such as high T_m and extremely high viscosity. Both make the processing of cellulose expensive and inefficient. These drawbacks cause critical problems when chloride salts are applied in the production of bio-fuels from cellulosic biomass. For efficient processing of cellulosic biomass, no extra energy (for example, heating) should be necessary to reduce the energy cost.

To bring down the high T_m of the salts, advanced molecular design is required.^{46,47} Some imidazolium halide salts bearing longer alkyl chains ($-C_nH_{2n+1}$, $n = 5-10$) are known to form super-cooled states, but they have inherent high viscosity. To overcome this high viscosity, relatively low melting and low viscosity halide salts are candidates.^{48,49} We have already reported relatively low viscosity halide salts composed of allylimidazolium cation.⁵⁰ Although the viscosity of allylimidazolium halide is remarkably low from the viewpoint of the strong electrostatic interaction forces of chloride anions, these ILs are still more viscous than general ILs.

◆ Design of Ionic Liquids to Dissolve Cellulose under Mild Conditions

To exploit cellulose successfully, we need a new class of polar ILs to replace current chloride salts. Low melting and low-viscosity ILs with sufficient polarity are necessary for further efficient processing of cellulose. However, chloride anion plays a key role as a strong proton acceptor in interaction between hydroxy groups of cellulose. In other words, we can design novel ILs as solvents for cellulose when we find anions working as strong hydrogen-bonding acceptors. Physicochemical properties, especially the hydrogen-bonding basicity of ILs, become important for this purpose. The design of a new class of ILs as potential solvents for cellulose under mild conditions depends centrally on the selection of component anions.

To design ILs as solvents for cellulose it is important to know their polarity, especially their hydrogen-bonding characteristics. The hydrogen-bonding characteristics of ILs have been empirically estimated using a variety of solvatochromic probes as shown in Figure 5. The Kamlet–Taft parameters specify three distinct solvent polarities: hydrogen-bonding acidity (α), hydrogen-bonding basicity (β), and dipolarity/polarizability (π^*).^{51–54} These parameters have been determined by visible spectroscopy for individual or pairs of dyes.

Some ILs containing carboxylate anions (Figure 6) were reported to show strong hydrogen-bonding basicity. In 1996,

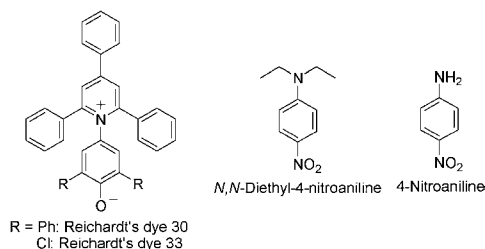


Figure 5. Probe dyes for Kamlet–Taft parameter measurements.

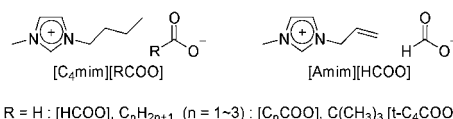


Figure 6. Chemical structure of carboxylate salts.

Table 1. Kamlet–Taft parameters of [C₄mim] salts

Anions	Kamlet–Taft parameters		
	α	β	π^*
[HCOO]	0.56	1.01	1.03
[C ₁ COO]	0.55	1.09	0.99
[C ₂ COO]	0.57	1.10	0.96
[C ₃ COO]	0.56	1.10	0.94
[<i>t</i> -C ₄ COO]	0.54	1.19	0.91
Cl	0.47	0.87	1.10

Bonhôte et al. reported that 1-ethyl-3-methylimidazolium acetate had strong hydrogen-bonding basicity.⁵⁵ Moreover, this salt had relatively low viscosity of 162 cP at 25 °C. Some carboxylic acid anions, such as lactic acid⁵⁶ and amino acid,⁵⁷ are reported effective in preparing polar room temperature ILs. Since there are wide varieties of carboxylic acid derivatives and many of them are commercially available, some ILs composed of carboxylate anions are good candidates as solvents for cellulose.^{58,59}

Table 1 shows Kamlet–Taft parameters of carboxylic acid-derived ILs. In general, the β value (hydrogen-bonding basicity) is governed by the nature of the corresponding anions. A series of carboxylate based ILs were obtained as low viscosity liquids at room temperature. These ILs were found to be effective in dissolving the same amount of cellulose at lower temperature by comparing chloride salts. For example, formate ([HCOO]) anion forms IL with low viscosity that dissolves cellulose under mild conditions.⁶⁰ As mentioned, hydrogen-bonding basicity is necessary to dissolve cellulose, in order to weaken the inter- and intramolecular hydrogen bonds of the cellulose chains. Spectroscopic study revealed that [C₄mim][RCOO] had stronger hydrogen-bonding basicity than chloride salts as shown in Table 1. Solubilization of cellulose was improved with these carboxylates. For example, to dissolve 10 wt % cellulose, [C₄mim]Cl should be heated to 85 °C, whereas [C₄mim][HCOO] dissolved it at 35 °C. Since [*t*-C₄COO] salt exhibited higher hydrogen-bond basicity than any other carboxylate salt, the [*t*-C₄COO] salt was expected to dissolve cellulose readily. Contrary to our expectations, the solubilization temperature of cellulose in [*t*-C₄COO] was higher than that for other ILs evaluated here. The alkyl side chain of carboxylate anions has an effect on the solubilization of cellulose. The solubilization temperature of cellulose increased with larger alkyl side chains of the imidazolium cation. The solubilization temperature of cellulose tends to decrease with decreasing viscosity. Cellulose powder dispersed easily in lower viscosity ILs relative to more viscous ones. The viscosity of ILs appears to be a further important factor in dissolving cellulose under mild conditions. It has been generally known that ILs composed of imidazolium salts with short alkyl side chain tend to be low viscosity ILs.

Moreover, allylimidazolium based salts have reported to be low viscosity ILs. Then, to lower the viscosity, novel formate salts were prepared with both 1-ethyl-3-methylimidazolium

([C₂mim]) cation and 1-allyl-3-methylimidazolium ([Amim]) cation. Since [Amim][HCOO] has low viscosity, 66 cP at 25 °C and strong hydrogen-bonding capability especially hydrogen-bond basicity, cellulose dissolved in high concentrations in this [Amim][HCOO] under mild conditions.

In spite of their strong hydrogen-bonding basicity and potential to solubilize cellulose, carboxylate salts displayed relatively poor thermal stability. Furthermore, a series of carboxylate-type ILs is prepared by three-step reactions, namely, following quaternization of imidazole with alkyl halide, the halide counter anion of the imidazolium cation was first converted to hydroxide, then coupled with the carboxylic acids providing desired anions. To overcome the drawbacks stated above, a new class of easily preparable ILs having sufficient polarity to dissolve cellulose should be proposed.

◆ Alkylphosphate Type ILs

A series of carboxylate based ILs has been described above, as candidates to dissolve cellulose. Moreover, these ILs are effective in dissolving cellulose at lower temperatures than chloride salts. However, [R₁R₂mim][R₃COO] had relatively poor thermal stability. Also, [R₁R₂mim][R₃COO]-type ILs needed three-step reactions for synthesis. These drawbacks motivated the development of further polar and thermally stable ILs.

As an easy one-pot procedure for preparation of ILs, reaction of tertiary amines with alkyl esters of organic acids forms quaternized salts having anions derived from acid esters. Owing to reactivity of alkyl esters, we mostly use methyl esters (R' should be CH₃ in Figure 7). 1-Ethyl-3-methylimidazolium ([C₂mim]) salts with a series of anions, namely methanesulfonate ([MeSO₃]), methylsulfate ([MeOSO₃]), and dimethylphosphate ([MeO)₂PO₂]), were synthesized and evaluated as solvents for cellulose.⁶¹ The polarity and hydrogen-bonding characteristics of these room temperature ILs were estimated using their Kamlet-Taft parameters. Among these ILs, [C₂mim]-[(MeO)₂PO₂] exhibited stronger hydrogen-bonding basicity ($\beta = 1.00$) than [MeOSO₃] ($\beta = 0.61$) or [C₂mim][MeSO₃] ($\beta = 0.70$). As expected from the hydrogen-bonding basicity, only [C₂mim][(MeO)₂PO₂] was confirmed to dissolve cellulose at elevated temperatures.

To improve the physicochemical properties and cellulose solubility, further investigation was undertaken in order to design better anions. As discussed in a previous section, the alkyl chain attached to the anion strongly affects solvent properties of the ILs. Many anions have been examined, including alkyl phosphonate and alkyl phosphite (Figure 7). [C₂mim][(MeO)(H)PO₂]⁶² was readily prepared by the reaction of 1-ethylimidazole with the corresponding dimethyl phosphite, and [C₂mim]-[(MeO)(Me)PO₂] by the reaction of 1-ethylimidazole with the corresponding dimethyl phosphonate. These ILs were found to be room temperature ILs.

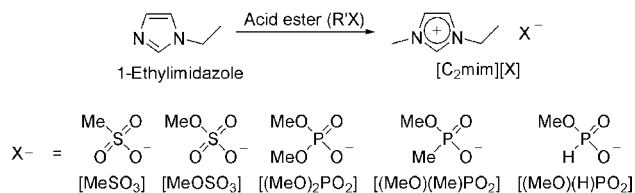


Figure 7. Synthetic procedure for a series of ILs.

These ILs have almost identical π^* values and α values. On the other hand, the ILs prepared here had high β value, exceeding 1.0, especially [C₂mim][(MeO)(Me)PO₂] for which β was 1.07. The thermal stability of phosphate derivative ILs prepared here is generally better than that for previously reported polar ILs. A [C₂mim][(MeO)(R)PO₂] series was thermally stable up to 260–290 °C. The viscosity of [C₂mim][(MeO)(R)PO₂] at 25 °C is in the range 100–500 cP, which is much lower than that for chloride salts.

These ILs are able to dissolve cellulose owing to their strong hydrogen-bonding basicity. The temperature needed to solubilize the same concentration of cellulose powder depends strongly on the anion structure of the ILs. A 2.0 wt % cellulose powder was found to dissolve completely in these ILs at room temperature (25 °C) within 3 h, and 4.0 wt % cellulose powder dissolved within 5 h. These ILs also act as solvents for a series of cellulose samples, namely high polymer cellulose; naturally obtained cellulose including cotton and wood biomass. Solubility tests of a variety of samples will be reported elsewhere.

◆ Conclusion and Future Aspects

ILs are now analyzed widely for use in a variety of applications. There have been two major waves of study of ILs as new solvents for organic chemistry and non-flammable electrolyte solutions for energy devices, and application of ILs to bio-related science is set to become the third wave. On the other hand, energy generation (or conversion) from biomass is now a big issue. It is not easy to use molecular liquids to gain energy, and increasing attention is paid to ILs. Most biochemists still believe that natural biomaterials should be treated only in an aqueous phase. ILs having unusual properties such as high polarity should be the next generation of liquids to dissolve insoluble materials including biomaterials in ordinary molecular solvents. There is increasing study of enzymatic reactions in ILs. Development of IL design and enzyme treatment should open the next generation of bioscience. Efficient and closed systems for bio-energy conversion could be developed with the aid of ILs.

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