

Quaternary Ammonium Salts and their Low-Melting Eutectics for the Conversion of Cellulose and Cellulose-Derived Sugars

by

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To my family

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LIST OF ABBREVIATIONS

DoE	Department of Energy
GHG	greenhouse gas
APR	Aqueous Phase Reforming
ILs	Ionic Liquids
DSC	Differential Scanning Calorimetry
[bmim]Cl	1-butyl-3-methyl-imidazolium chloride
[emim]Cl	1-ethyl-3-methylimidazolium chloride
HMF	5-hydroxymethylfurfural
QAS	Quaternary Ammonium Salts
ChCl	Choline Chloride
ChCl-OA	Choline Chloride-Oxalic Acid
ChCl-CA	Choline Chloride-Citric Acid
ChCl-BA	Choline Chloride-Benzoic Acid
ChCl-Ph	Choline Chloride-Phenol
Q8881Cl	Methyltrioctylammonium chloride
DP	Degree of Polymerization
DMF	2,5-Dimethylfuran
TON	Turnover Numbers
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
FID	Flame Ionization Detector

TGA Thermogravimetric Analyzer

DP Degree of Polymerization

BCA 2,2'-bichinoninate

LFER Linear Free Energy Relationships

ABSTRACT

Quaternary Ammonium Salts and their Low-Melting Eutectics for the Conversion of Cellulose and Cellulose-Derived Sugars

by

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The use of Ionic Liquids (ILs) as solvents presents a promising route for the conversion of cellulosic biomass feedstock to value-added products, like 5-hydroxymethylfurfural (HMF), levulinic acid and 2,5-dimethylfuran. These products form the basis for the production of renewably-sourced fuels and chemicals, with HMF and levulinic acid being platform chemicals from which polymers like polyethers and polyesters can be made. 2,5-dimethylfuran, a hydrogenation product of HMF, has been shown to be a superior alternative to fuels like ethanol. 1,3-dialkylimidazolium Ionic Liquids (ILs) in particular, have become a popular and thoroughly-studied reaction media for this purpose. Many reactions have been demonstrated to proceed in these ILs including the dissolution and hydrolysis of cellulose, and the dehydration of glucose. While these ILs have proven to be quite capable of processing large macromolecules like cellulose, their widespread adoption has been limited due to their toxicity and prohibitive costs.

There is a clear need for less expensive, and more environmentally benign alternatives. In this work, the challenges in designing low-cost solvents for biomass conversion are highlighted. In particular, Quaternary Ammonium Salts (QAS) and

their eutectics are explored as possible alternatives to conventional ILs. These materials have been chosen since they can either be renewably sourced, or are already being produced in large quantities for alternate uses.

Solvent properties such as hydrogen-bond formation ability and acidity have been studied for both imidazolium-based and QAS-based ILs to examine their effects on reactivity. Using probe reactions like the isomerization and dehydration of sugars, and the hydrolysis of disaccharides and cellulose, relationships between chemical properties and reactivity are discussed. Reaction networks and mechanisms are analyzed, and differences between the different classes of ILs are highlighted.

In the dehydration of fructose, it was found that in imidazolium ILs like [bmim]Cl, HMF is the primary reaction product, with high yields of HMF, about 98 % after 4 h. It was found that in the eutectics, it was possible to tune selectivities of the products from HMF to levulinic acid, based on the acidity of the partner molecules. In acidic eutectics like ChCl-OA, yields of HMF, levulinic and formic acids are about 20 %, with larger amounts of levulinic and formic acids expected at longer times for reactions carried out at 100 °C. Other eutectics with lower acidity showed higher selectivities towards HMF with yields higher than 78 %.

The role of hydrogen bonding in these solvents was also studied, and it was found that the eutectics had low hydrogen bonding ability. This inhibited isomerization reactions of glucose to fructose, and caused low product yields in the catalytic dehydration of glucose, less than 10 %. However, in low melting single species quaternary ammonium salts like Q8881Cl, no inhibition of the isomerization reaction was observed, which was attributed to higher hydrogen bond acceptor strength of the solvent. Higher yields, about 50 % of HMF were also observed.

In studying the depolymerization of cellulose, it was found that even though the eutectics lacked the ability to solvate cellulose, due to the low hydrogen bond acceptor strength, it was still possible to perform hydrolysis of the polysaccharide, and dehy-

drate the resulting monosaccharides to HMF or levulinic acid, based on the choice of the solvent. However, the kinetics of this reaction were slow, with the reaction not complete even after 45 h at 100 °C in ChCl-OA. However, the correlations of product selectivity with acidity observed in the dehydration of simple sugars were observed here as well. The depolymerization of cellulose was studied by tracking the degree of polymerization of cellulose as the reaction progressed. It was found that in a solvent like [bmim]Cl, the rate of depolymerization is higher than that in a eutectic like ChCl-OA. This was attributed to the ability of [bmim]Cl to break the crystallinity of cellulose during the solvation process. This results in greater access to the glycosidic bonds to the catalyst. In the eutectics, since solvation does not occur, depolymerization occurs sequentially, resulting in large cellulose fragments in solution. This difference in depolymerization mechanism is responsible for the slow hydrolysis and subsequent dehydration in the eutectics.

This work has culminated in new and valuable insights into rationally selecting ILs to perform targeted chemistries. It represents a significant step towards the development of economical and environmentally-friendly conversion methods for biomass to fuels and chemicals.

CHAPTER I

Introduction

Fossil petroleum has traditionally been the primary source of both transportation fuels as well as a raw material for the chemical industry. Over the past couple of decades, concerns have been raised over carbon dioxide releases associated with the use of fossil fuels, and the resulting implications, especially with regards to the adverse climate effects being observed. In addition, access to petroleum supplies at predictable prices has also been historically a concern. These issues have spurred a desire to develop renewable and sustainable energy sources and processes. While biomass is considered a carbon-neutral renewable resource that results in a decrease of greenhouse gas (GHG) emissions, this labeling has been contentious. Annual basis carbon has been suggested as a better tool for such assessments than the conventionally used life cycle analyses, since the former accounts for the excess carbon intensity that arises from the land use required for growing the biomass [1]. Nevertheless, biomass has attracted considerable research and development efforts to employ it as a feedstock for fuels and chemicals.

While the global energy consumption growth trends predict that oil, gas and coal will still dominate in the future, as Figure 1.1 shows, renewables and biofuels occupy an increasingly significant part of the pie. In fact, biofuels, primarily ethanol, occupies 3% of the U.S. transportation fuel on an energy basis [2]. Current first and

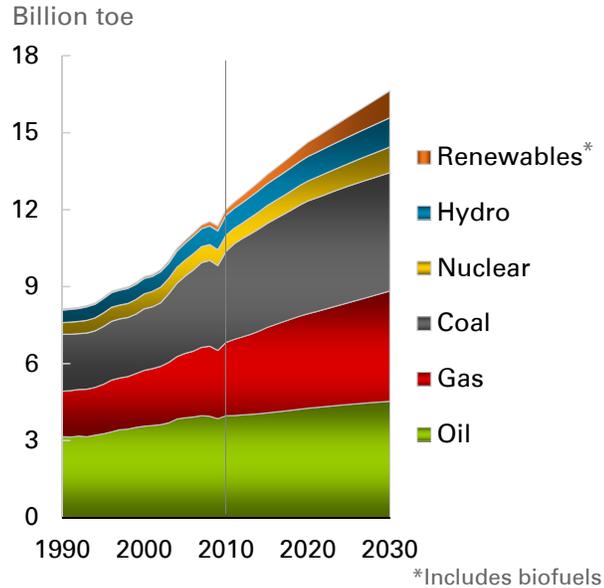


Figure 1.1: Energy consumption (in tonnes of oil equivalent) broken down by energy source. Values after 2010 are projected values. Figure from [3]

second generation biofuels have their own disadvantages. So, in efforts to develop better methods of production, it behooves us to be cognizant of the conventional technologies and their drawbacks.

1.1 The Need for Alternate Biomass Conversion Strategies

Conventional thermochemical conversion methods are primarily gasification and pyrolysis. Gasification of biomass is a very mature technology, and occurs under conditions characterized by slow heating rates, high temperatures (> 800 °C) and long vapor residence times. These conditions result in high syngas yields and low liquid yields. Syngas, being a mixture of CO and H₂, can then be converted in to liquid fuels using the Fischer-Tropsch Process. These gasification processes have formed the basis for many large scale gasifiers. Gasification processes, however, are not without technical hurdles. The formation and build-up of condensible organic compounds called tars is a major problem as this can cause corrosion and blockages in equipment. The prevention of tar formation has been the topic of research for a long

time now [4, 5]. Catalytic processes have been developed on two concepts: primary and secondary catalytic systems. Primary catalysts, directly mixed with biomass prior to gasification, are aimed at reducing tar formation in the bed. Primary catalysts have ranged from dolomite, alkali metal [5], Ni and Pt-based catalysts, to Pt/Ni [6] and other combinations. Secondary catalysts, used downstream of the gasifier, are primarily used for gas clean up. They are generally cracking and reforming catalysts based on precious metals, Ni [7] or La-Ni-Fe perovskites [8].

Pyrolysis on the other hand refers to the decomposition of biomass at moderate temperatures (≈ 500 °C) using very high heating rates, short vapor residence times and generally in the absence of oxygen. These conditions result in high liquid yield and low gas yields [9]. The liquid product, known as bio-oil, is highly viscous, chemically unstable, highly oxygenated, and has a low heating value. It has to be deoxygenated and upgraded (historically by hydrotreating and catalytic vapor cracking) to transportation fuel. However, these processes have been found to be expensive which results in the products not being competitive with petroleum-based fuels.

Biochemical processes for the conversion of cellulosic biomass to fuels have been another approach for biomass conversion. Processes have primarily relied on enzymatic hydrolysis of the cellulosic feedstock followed by fermentation to produce ethanol as a fuel. The processes have high theoretical yields and operate at low temperatures (<100 °C) and atmospheric pressures. These processes have been used on corn-based feedstock on large scales for the good part of a decade now, with strong political and policy support. However, the choice of corn-derived ethanol and soy-derived biodiesel as a potential biofuel is questionable. Ethanol has lower energy densities than gasoline (23 MJ/L vs. 35 MJ/L), which results in lower energy content of the resulting fuel blends. Additionally, ethanol is completely miscible with water which further lowers the energy content in fuels, and results in inefficiencies in existing fuel systems. The production of corn-derived ethanol is highly water-intensive

compared to fossil fuels production, and also uses resources needed for food production, which can be alleviated to a certain extent with the use of cellulosic feedstock. However, these processes rely on energy-intensive processes for the separation of the fuels [10].

Second generation processes have focused on the production of butanol. A better alternative to ethanol, butanol has an energy density (29.2 MJ/L) closer to gasoline. Various strains of *Clostridium* have been used for the fermentation processes [11]. Its similarity to ethanol production makes retrofitting production facilities an attractive option. Major producers like BP and DuPont have announced partnerships to produce butanol as a biofuel [12]. However, butanol faces similarly expensive distillation-based separation processes as ethanol. Current processes have low butanol yields, and breakthroughs in metabolic engineering need to occur in order to increase the butanol yield of fermentation processes.

While butanol is a promising alternative, ethanol remains the dominant biofuel being produced currently. In addition, all these conventional processes are economically viable only on very large scales. Since biomass has very low energy densities, the cost of transporting this feedstock to these large scale production sites is very high [13]. Additionally, the transitioning of chemicals production from petroleum feedstock to a renewable one is more challenging than for fuels production.

To address these challenges, the U.S Department of Energy (DoE) has identified alternate conversion routes which result in renewably-sourced platform chemicals for the production of commodity chemicals while employing similar routes for the production of alternate fuels [14]. These conversion routes will be discussed in further detail in Section 1.2. New techniques and processes are being developed to take action on the DoE mandate. Liquid phase conversion of biomass attempts to achieve this by making use of the inherent functionality present in biomass. Aqueous Phase Reforming (APR), for example, uses water as a solvent to convert sugars into sugar

alcohols and other chemicals. These processes take place around 180 – 300 °C and 10 – 50 atm pressures [15]. In APR, the sugars are first dehydrated into furfurals before further conversion into fuels and chemicals. The dehydration of fructose with the help of mineral acids like HCl has been carried out in water and water-organic phases at 180 °C, with high sugar conversion (>60 %) and 5-hydroxymethylfurfural (HMF) selectivity (>50 %) [16]. The conversion of feedstocks like cellulose has also been attempted in hot compressed water, primarily using metal chloride catalysts at temperatures of 180 °C. These processes have been found to be selective towards levulinic acid, but with low yields, 20 – 30 % [17]. Processes have also been developed for the production of 2,5-Dimethylfuran (DMF), a potential biofuel from fructose [18]. While this approach has many benefits like the use of water as solvents, and possible inexpensive separations, the process is limited to feedstock containing simple sugars. Raw biomass feedstock which primarily contains macromolecules like cellulose needs to undergo extensive pretreatment before reaction.

It is clear that while the options for biomass conversion are plenty and varied in their approaches, there is still a need for a more efficient and economical process. The aforementioned adverse climate effects have also dictated the development of processes that are environmentally friendly. ILs as solvents have the potential to mitigate a lot of the drawbacks previously discussed in the biomass conversion processes. Macromolecules like cellulose and hemicellulose can be processed at mild temperatures and pressures, and processes can be theoretically designed around ILs to have low separation costs and varied product spectrum. Thus, an in-depth study of ILs, their advantages and drawbacks is required in order to provide insights into the direction of future technological developments.

1.2 A Brief Introduction to Ionic Liquids and their Applications in Biomass Conversion

ILs as solvents form one of the emerging technologies that promote the development of processes by using the principles of green chemistry. One of the goals of green chemistry is to redesign chemical processes so as to eliminate losses of solvents, especially in the form of volatile organics [19]. ILs are salts that melt below 100 °C. Being molten salts, they have negligible vapor pressure, and hence can be used to attain this goal. First reported in 1914 with work on ethylammonium nitrate, room temperature molten salts or ionic liquids gained prominence in the latter half of the 20th century with the use of chloraluminum eutectics for electrochemistry [20]. ILs based on imidazolium, pyridinium and other quaternary ammonium cations have been the most common in literature. Their structures are shown in Figure 1.2. New ILs can be formed by changing the substituents on the cation, and the anion it is paired with. It has been estimated that over 10^{18} ILs can be prepared by varying the substitutions within just the imidazolium and pyridinium systems [21]. By changing the cation and anion, it is also possible to change the physical and chemical properties of the IL. This tunability also makes ILs attractive as solvents for chemical reactions since they can be designed to have desired physical and chemical properties. This was exemplified by the synthesis of moisture and air stable ILs based on an imidazolium cation and tetrafluoroborate and hexafluorophosphate anions [22], further fueling growth in the field.

Since then, ILs have been used as solvents for a wide variety of reactions. Using ILs as a solvent for the Diels-Alder reaction has become quite popular. These reactions have been found to proceed with higher reaction rates and selectivities to endo products in the case of cycloadditions compared to organic solvents [23, 24]. Another class of reactions that have made use of ILs as solvents are isomerization reactions.



Figure 1.2: The general structures of commonly-used ILs with (a) an imidazolium cation and (b) a pyridinium cation. These cations are generally paired with a wide variety of anions depicted here as X.

The isomerization and hydrogenation of alkenes has been reported in imidazolium-based ILs [25]. The isomerization of pent-1-ene to pent-2-ene was reported with Rh catalysts. It was observed that the cis/trans selectivity depended on the anion. It was opined that this was a unique observation in the IL where the cationic catalyst was in close proximity to the anion, unlike in conventional solvents where solvent separation would be present [23].

Other reaction classes of importance include Lewis Acid catalysis and hydrogenation reactions in ILs. Since Lewis Acid based ILs were primarily responsible for the growth of the ionic liquid research area, there has been a substantial amount of work in using Lewis Acids. Gordon, in his review paper, points out that the field has generally transitioned into using neutral ILs as opposed to acidic ones. However, acidic ILs based on metal chlorides have been used to perform esterification reactions. In addition, Lewis Acid catalysts have also been used to catalyze Friedel-Crafts alkylations, Diels-Alder reactions [26] and hydroformylation reactions [27, 28].

Hydrogenation reactions have been attempted by designing biphasic processes. Transition metal complexes have been used as catalysts. However, designing these complexes have proven to be expensive. Nevertheless, these catalysts have been used in imidazolium-based systems to perform hydrogenation of aromatic compounds

[25]. Most hydrogenation reactions have involved homogeneous catalysts, at high pressures (430 atm) [23]. Ru pre-catalysts immobilized in ILs have also been used in the hydrogenation of aromatic ketones in biphasic processes at 700 psi [29]. In general, most hydrogenation reactions in ILs have been noted to take place at much higher pressures than in organic solvents due to the low solubility of hydrogen gas in ILs.

The specific reaction classes discussed in this section are important because, as will be seen in proceeding sections, they are reaction classes that are being targeted for biomass conversion. These examples set a precedent for the ability of ILs to act as solvents for these reaction classes, and help in designing processes for biomass conversion.

1.2.1 Identified Schemes for Biomass Conversion Process

As described earlier, the U.S DoE have identified building blocks for the transformation of the chemical industry from a petrochemical basis to a renewable basis [14]. These building block chemicals can then be converted to high-value chemicals and other materials. Examples of these building block intermediates include succinic acid, levulinic acid, glycerol, etc. A two step synthesis pathway, one from renewable feedstock to these building blocks, and another from the building blocks to the value-added products have been highlighted.

In this work, cellulosic biomass, which consists primarily of cellulose, has been targeted as the renewable feedstock of choice. Cellulose is a polysaccharide composed of glucose monosaccharides bound by a glycosidic bond. These monosaccharides act as the secondary or intermediate platforms. Hence the cleavage of these glycosidic bonds is of particular importance in the biomass conversion process. When feedstocks other than cellulosic biomass are targeted, for e.g., starches and sugarcane, other intermediates platforms like fructose, lactose, and sucrose might also be formed. While

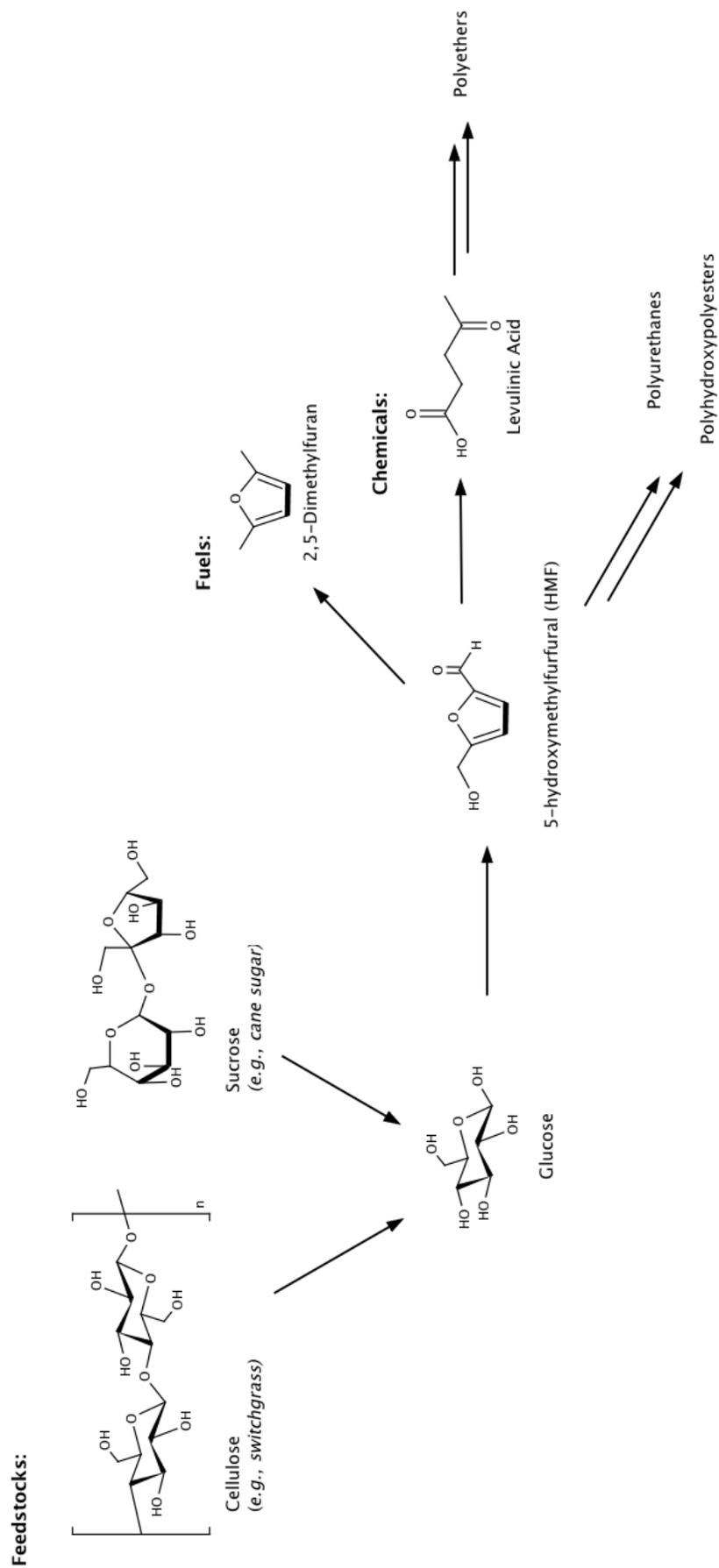


Figure 1.3: Scheme for the conversion of biomass to value-added products

building blocks of varied sizes and carbon numbers can be formed from these intermediate platforms, in this study, C-6 and C-5 building blocks are targeted since this allows the retention and utilization of additional functional groups. Particularly in our study, HMF, a C-6 building block, and levulinic acid, a C-5 building block are desired. HMF, which can be formed from the sugars via a dehydration reaction, is an intermediate to the production of renewably-sourced polyurethanes and polyhydroxypolyesters. Levulinic acid can act as an intermediate for polyether production. A representation of the scheme described from cellulosic biomass has been shown in Figure 1.3.

1.2.2 Choice and Application to Biomass Conversion

Since imidazolium-based ILs had already been a popular choice of solvent for chemical reactions, it is unsurprisingly a very popular solvent for the conversion of biomass. However, as mentioned earlier, an inordinate number of ILs can be formed based on the imidazolium cation alone. A vast number of studies highlighting the effects of different cationic substituents and anions are available. It is important to understand the choice of the solvents and the properties that dictate this choice. This knowledge will particularly be useful for designing new solvents for biomass conversion.

By definition, ILs have melting points less than 100 °C. The melting point defines the lowest operability limit for any reaction in the solvent. Among imidazolium-based cations with a butyl and methyl group substituent, it was found that increased anion size caused a decrease in melting point [30], for example, the IL with a chloride anion had a melting point of 41 °C, the one with the hexafluorophosphate anion has a melting point of 11 °C and that with Tf₂N was -2 °C. While the melting point of an IL sets the floor for the operability, the decomposition temperature sets the ceiling, and provides insight about the thermal stability of the ILs. The thermal

stability of ILs has been studied by various researchers, mostly with the use of Differential Scanning Calorimetry (DSC). A few ILs that don't decompose up to 400 °C have been reported [31]. These ILs have bigger anions like bis(triflyl)amide. More detailed studies of the effect of substitutions on the imidazolium ring and the anion are available. For example, it has also been reported that the thermal stability of these solvents can be increased by increasing the substitution on the imidazolium ring, and hence removing the ring hydrogens [32]. The same study also reports that the thermal stability of the anions are: $\text{PF}_6^- > \text{BF}_4^- > \text{I}^-$, Br, Cl. Long term stability studies have shown that these imidazolium ILs decompose at lower temperatures, slightly above 200 °C especially in the presence of air [33]. In some cases, especially in ILs with chloride anions, the onset of decomposition was much lower, around 150 °C [34].

In addition to the benefits of ILs as solvent as highlighted above, the most attractive reason for using ILs for biomass conversion is macromolecules like cellulose and even raw biomass has been found to be soluble in these solvents, primarily dialkylimidazolium-based [35, 36]. Since eventually, the goal of this work is to be able to process cellulosic biomass, an understanding of this property is important. The implications from the solubility and thermal stability studies have resulted in imidazolium-based cations paired with Cl^- being the most studied of the ILs for biomass conversion. Other ILs used to study the conversion of biomass have been detailed elsewhere in literature, but have mostly been imidazolium-based, with varying cationic substitution, and anions like halides, BF_4^- , HSO_4^- , etc. [37]. In addition to just dissolving cellulose, several reactions in the scheme proposed by the U.S DoE, and shown in Figure 1.3 have been carried out in imidazolium-based ILs. The hydrolysis of cellulose into the monosaccharides has been demonstrated by many researchers. Most studies have used an acid, for e.g., sulfuric acid, to catalyze this [38]. From the monosaccharide glucose, it has been shown that HMF can be made using a Lewis

Acid like chromium chloride [39]. A few studies have demonstrated the conversion of HMF into fuels like DMF. Most of them have used biphasic mixtures of IL and an organic solvent [40]. These studies will be discussed in more detail in following chapters. Of importance is that the reaction scheme detailed in Figure 1.3 has been demonstrated in imidazolium-based ILs.

However, the manufacture of imidazolium-based ILs requires complex syntheses, and hence are expensive. More importantly, these ILs are also toxic - with category 5 dermal toxicity and category 3 oral toxicity according to the GHS classification [41]. They are also not easily degradable and are toxic to aquatic life, so disposal of these substances is difficult. Further discussion on this subject can be found in Section 3.2. Hence, there is a need for the development of new classes of ILs that retain the advantages of the imidazolium ILs while improving on the cost and toxicity parameters. In this study, quaternary ammonium salts and salt mixtures are explored as possible alternatives. These substances have the potential to be renewably sourced and inexpensive, and most importantly retain some of the benefits of the imidazolium ILs. As laid out in Section 1.3, the insights gained by the study of the imidazolium ILs and solute-solvent systems in general can be used in the rational design of new solvents.

1.3 Plan of Study and Thesis Layout

The plan of study implemented to achieve the goal of developing new solvents for biomass conversion targeted two aspects: the chemistry being attempted, and the solvent system under study. The conversion route in this study follows the one described earlier in Section 1.2. In implementing this conversion route, a reduction problem approach is undertaken. The simplest problem is first tackled, and then additional complexity is introduced, once the simpler problem is thoroughly studied and understood. In the instance of biomass conversion, for example, the options for

feedstock are primarily cellulose, and in some cases, sucrose. Both these feedstocks can be hydrolyzed to simple sugars, like glucose. Thus, glucose is a good starting point for this study. In this work, the dehydration of glucose to HMF is first studied. After this, additional complexity is added to the feedstock side, with the study of both sucrose and cellulose feedstock. The conversion of HMF into value-added fuels and chemicals is also discussed as part of this thesis.

In order to test potential new solvents, it was essential to develop an experimental protocol and analytical capability. In addition it was also essential to establish a benchmark to compare the new solvents to. Therefore, reactions were first carried out in a well-studied solvent. In this work, the solvent chosen was 1-butyl-3-methylimidazolium chloride ([bmim]Cl). The catalytic dehydration of glucose was first attempted. This study has been detailed in Chapter II. The effect of two different Lewis Acid catalysts, viz., chromium chloride hexahydrate and iron (III) chloride has been studied. It was found that HMF yield was significantly higher when chromium chloride hexahydrate was used as the catalyst. Therefore, in order to fully understand the reaction pathways involved, a detailed study of the effect of different variables like catalyst loading, temperature and time, on the reaction was carried out. A phenomenological model for the reaction network was then developed and kinetic parameters were estimated to predict HMF yields. This work establishes the activity of [bmim]Cl against which the activity of other solvents can be compared.

Chapter III describes how salt pairs based on QAS that form deep eutectics were rationally chosen. Their solvent characteristics were studied, and the reduction approach described earlier was again employed to study the effect of these solvents on biomass conversion. One notable result from Chapter II is that the route from glucose to HMF goes through fructose via an isomerization aided by a Lewis Acid. This means that studying the non-catalyzed dehydration of fructose to HMF will be a true indicator of solvent activity. Hence, in Chapter III, this reaction was first studied in

detail. Reaction pathways in this conversion were investigated and are compared to the imidazolium-based IL studied in Chapter II. This allows the construction of a correlation between the solvent properties and activity. Additional complexity was introduced by studying the catalytic dehydration of glucose, followed by that of sucrose and cellulose. In each case, it was observed that correlations between solvent property and behavior were present. It was seen that by varying the solvent pairs (and hence controlling solvent properties like acidity), it was possible to either selectively stop the reaction and make HMF, or proceed to make other value-added chemicals like levulinic acid. In studying the conversion of sucrose in these solvents, insight on their ability to facilitate the hydrolysis reaction was also gained. This work has also provided additional insights into the effect the number of solvent species in solution have in coordinating with the catalyst, and thence the coordination and subsequent isomerization of glucose species. This forms the basis for work in Chapter IV.

Chapter IV explores the hypothesis that in QAS-based eutectics, the solvent pairs coordinate among themselves, and hence cannot coordinate with the Lewis Acid. This results in blockage of pathways that isomerize glucose, and leads to increased humins production. This hypothesis is tested by employing a low-melting, single species, QAS, in this case, Methyltrioctylammonium chloride (Q8881Cl), as a solvent. The production of HMF from the non-catalytic dehydration of fructose and the catalytic dehydration of glucose are compared to gain additional insight into the effect of solvent species. The conversion of sucrose in Q8881Cl is also studied, and it further supports the proposed hypothesis.

Having studied the activity of the different classes of solvents for the conversion of different sugars, Chapter V adds further complexity by introducing biomacromolecules in the form of cellulose - a more challenging problem. The H-bonding ability of the solvents are characterized. This property is used as an indicator to predict the ability of imidazolium and quaternary ammonium salt-based ILs to dissolve cellu-

lose. The ability of the solvents to perform hydrolysis and subsequent dehydration of cellulose is then studied. The Degree of Polymerization (DP) of cellulose is also measured as a function of time in different ILs, and insight about the mechanism of depolymerization is gained.

Finally, in Chapter VI, the challenges in moving from the platform chemical HMF to value-added chemicals are explored. Particularly, preliminary experiments to produce DMF via catalytic hydrogenation are described. Various alternative approaches studied in literature to make DMF are also discussed. In addition to the production of levulinic acid that was discussed in earlier chapters, other possible pathways from HMF to chemicals like tetrahydrofuran are also discussed.

The overarching motive of this research was to develop a relationship between fundamental solvent properties, and reaction rates, and product selectivity, that will be instrumental in providing insight into tailoring solvents for targeted products. Using this, inexpensive, less-toxic alternatives to the more common, but expensive and toxic imidazolium-based ILs for the conversion of biomass were developed. A few probe reactions were explored to demonstrate the differences between the different classes of ILs. Developing property-performance relationships will help design reaction-specific solvents. It is hoped that this will be a fundamental, yet important step in developing low-footprint technologies to move towards renewably-sourced fuels and chemicals production.

CHAPTER II

Imidazolium-based ILs for the Dehydration of Glucose

2.1 Introduction

1,3-dialkylimidazolium-based ILs have become the most studied of the ILs for the conversion of biomass feedstock. Of the different biomass feedstocks, cellulosic and the derivative sugars are of particular interest since they form the majority of the available feedstocks [42]. The conversion routes from cellulose to platform chemicals like HMF and levulinic acid have been detailed in Section 1.2.1. One of the most important reactions in the conversion scheme is the dehydration of glucose to HMF, which represents a monosaccharide which can be derived from feedstocks like cellulose and sucrose among others.

The dehydration of glucose to HMF was first successfully carried out in a 1,3-dialkylimidazolium IL, 1-ethyl-3-methylimidazolium chloride using chromium chloride as a Lewis acid catalyst [39] with yields up to 70 %. The authors have also demonstrated better catalytic activity with CrCl_2 than with CrCl_3 . In the same study, the authors have also proposed a mechanism for the reaction where glucose first isomerizes to fructose before undergoing a dehydration to HMF. Since then a variety of transition metal chlorides, like AlCl_3 , FeCl_4 , CuCl_2 , VCl_4 , RuCl_4 , etc.,

have been used as catalysts for the reaction, but none of them have been found to be as successful as chromium-based ones, with yields less than 10 % [39, 43, 44]. A combination of in-situ X-ray Absorption spectroscopy and Density Functional Theory calculations have shown that the Cr species in the catalyst, chromium (II) chloride in this case, dimerizes, binds with the glucose, thus enabling the isomerization [45]. This supports the earlier work on the efficacy of Cr(II) species in the conversion. However, results from other studies where the dehydration of glucose was carried out in N,N-dimethylacetamide and lithium chloride have shown minimal difference between the different oxidation states of chromium [46]. In fact, studies using microwave energy to hasten the reaction have shown high yields using chromium (III) chloride [47]. Other than chromium, lanthanide-based catalysts have been shown to be fairly effective for this reaction as well [48].

In this study, the catalytic dehydration of glucose is studied using [bmim]Cl as the solvent of choice. This solvent was chosen since it is the most widely studied IL among the 1,3-dialkylimidazolium ILs. FeCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were chosen as Lewis Acid catalysts, and the difference in activity between them was highlighted. A thorough parametric study was undertaken where the effect of varying time, temperatures and catalyst loading were studied. The objective of this study was to develop a deeper understanding of the reaction network involved while also developing a phenomenological model that can correctly describe and predict HMF yields. The development of such a model will be beneficial for the development of processes involving these solvents, and the need for such detailed kinetic studies has been noted in literature for addressing process engineering concerns [37]. Since this reaction has been studied in great detail in literature, it allows for the development of experimental and analytical methodologies, while also providing additional insight into the reaction pathways involved. As detailed in Chapter I, one of the goals of this study is to develop economical and less toxic solvents for biomass conversion. The activity of the solvents that

will be studied later in this thesis will compared to the results in this study. Hence, this serves as a benchmark of activity for the use of ILs for biomass conversion.

2.2 Experimental Methods

2.2.1 Materials

All the chemicals used in this study - [bmim]Cl, chromium(III)chloride hexahydrate and D-(+)-Glucose were purchased from Sigma Aldrich. Moisture-sensitive chemicals were stored in a desiccator at room temperature and used without any pretreatment.

2.2.2 Methods

2 g of the IL was first weighed and placed in clean, dry 10 ml glass vials that contained a teflon-coated magnetic stir bar. The vials were then placed in a well-stirred oil bath. The oil bath was placed on a hot plate. The temperature of the oil bath was controlled with a thermocouple placed inside the oil bath. Using this configuration, it was possible to run 3-4 reactions simultaneously.

The temperature of the oil bath was then set to the reaction temperature (between 80-120°C). The reaction temperatures were always above the melting point of the IL. Once the IL had melted and the vials had all attained a steady temperature, the desired amount of catalyst was weighed and added to each of the reactor vials. Stirring was continued with heating till the catalyst dissolved in the solvent and a homogeneous solution was obtained.

Desired amounts of the reactant, D-(+)-Glucose (generally 0.55 mmol), were weighed and added to the reaction vials. Heating and stirring were continued until the desired reaction time elapsed. The reactors were then quenched to stop the reaction. Various methods were attempted to analyze the reaction mixture, includ-

ing the use of UV-Vis and silylation reactions followed by gas chromatography, the details of which can be found in Appendix A. The most efficient, repeatable and effective analysis was found to be possible with an HPLC. For HPLC analysis, the reaction mixture was first diluted with DI water. The samples were then filtered with a 0.22 μm cellulose acetate filter and transferred to a vial for analysis.

HPLC analysis was performed using a Phenomenex ROA ion exclusion column maintained at 60 °C. 0.005 N H_2SO_4 was used as a mobile phase and a flow rate of 0.5 ml/min was maintained through the column. A differential refractive index detector was used to quantify the amount of glucose, fructose, HMF, levulinic acid and formic acid in reaction samples. The retention times of these compounds are listed in Table 2.1:

Compound	Retention Time (min)
Glucose	11.89
Fructose	13.21
Formic Acid	17.52
Levulinic Acid	20.69
HMF	39.79

Table 2.1: Retention times for compounds analyzed on the HPLC

2.3 Results and Discussion

2.3.1 Experimental Results

Initial experiments to screen Lewis acid catalysts for the catalytic dehydration were carried out using FeCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Figure 2.1 compares the HMF yield for the two catalysts as a function of time. As can be seen, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is a much better catalyst resulting in much higher yields of HMF. At the end of the reaction, the conversion of glucose is complete in reactions with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, while in FeCl_3 some glucose remains unconverted. Hence, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was chosen for more detailed studies.

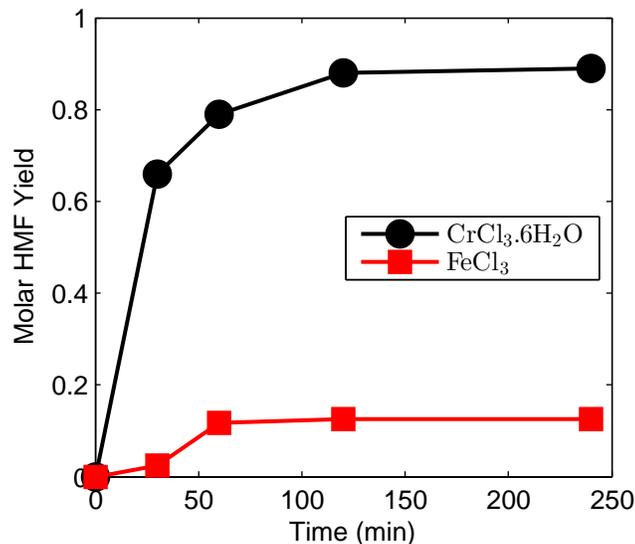


Figure 2.1: Comparison of HMF yields in the dehydration of glucose in [bmim]Cl catalyzed by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and FeCl_3 at $100\text{ }^\circ\text{C}$

In this work, catalyst concentration in the reactor, and reaction temperature were studied as a function of time. The experimental design used can be seen in Figure 2.2. With the analytical system, it is possible for us to follow the consumption of the reactant glucose, the production and subsequent consumption of the intermediate fructose and finally the production of HMF. Figure 2.3 (a) shows the concentration profiles of all the species as a function of time. In this case, the reaction was carried out at $80\text{ }^\circ\text{C}$ with a catalyst loading of 0.037 mmol . Due to the nature of the kinetics of this system, the concentration profile of fructose can only be clearly seen at lower temperatures and at low catalyst concentrations. At higher catalyst concentrations and higher temperatures, for example, 0.15 mmol and $100\text{ }^\circ\text{C}$, only glucose and HMF are present in measurable quantities, with very little fructose observed, as seen in Figure 2.3 (b). In addition to these, insoluble humins are also made. These however, are filtered out before the sample analysis.

Turnover Numbers (TON), defined as the ratio of the moles of HMF produced to the moles of catalyst used have been calculated. Figure 2.4 shows the TON averaged over all reaction times for different catalyst concentrations. It is important to note

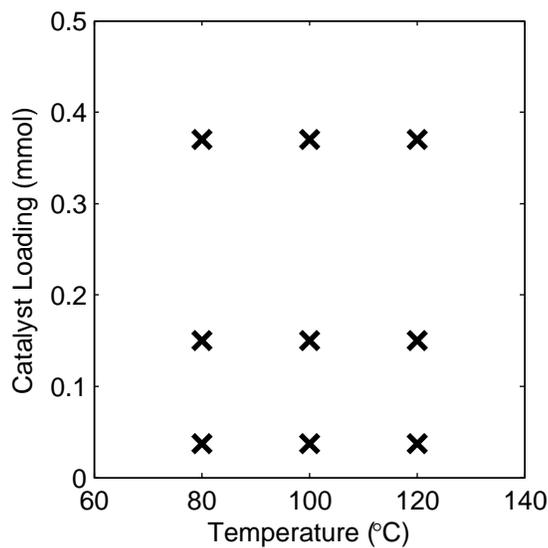


Figure 2.2: Experimental design used to study the Kinetics of Glucose Dehydration in [bmim]Cl using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst

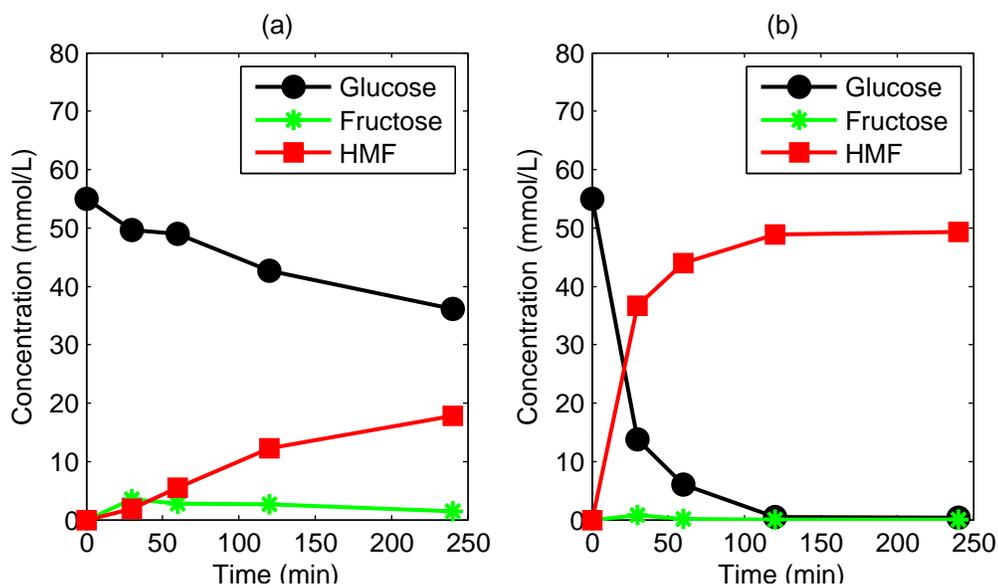


Figure 2.3: Concentration profiles observed in the Dehydration of Glucose in [bmim]Cl using a $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst at (a) 80 °C and 0.037 mmol catalyst and (b) 100 °C and 0.15 mmol catalyst

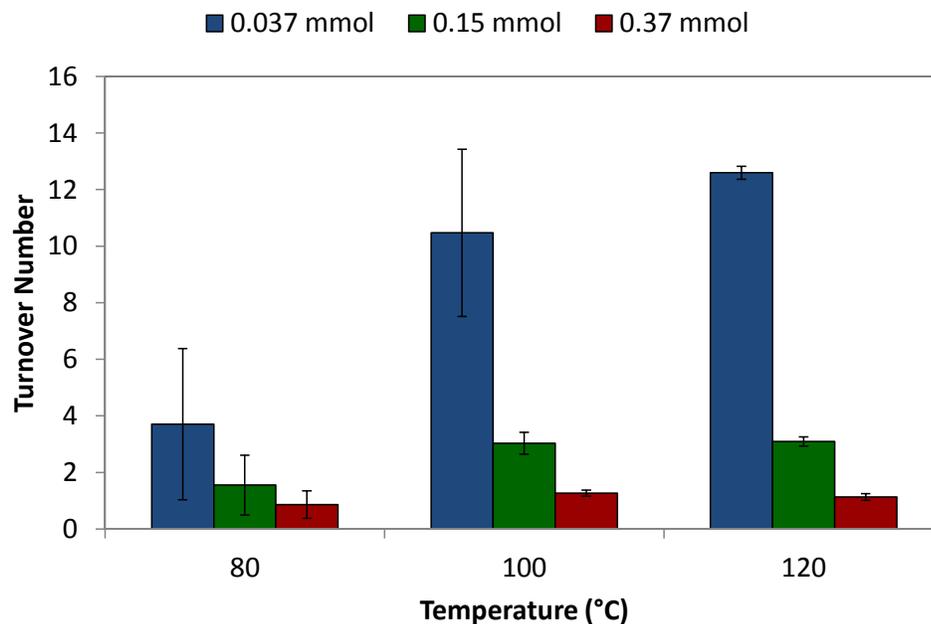


Figure 2.4: Turnover Numbers for the Dehydration of Glucose in [bmim]Cl using a $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst. For each catalyst loading and temperature, the turnover number has been averaged over all reaction times studied.

that once the ultimate yield is reached, the concentration of HMF does not change with time, especially at higher temperatures and catalyst loading, and this is reflected in the average TON calculations. In all cases, the TON is greater than unity implying that the reaction is most definitely catalytic. It is also observed that TON decreases with increasing catalyst loading. This suggests an efficient isomerization of the glucose by the catalyst, with the reaction going to completion, and the presence of excess catalyst at higher loadings.

The results can also be viewed in terms of a Molar HMF Yield, defined in Equation 2.1:

$$\text{Molar HMF Yield} = \frac{\text{mol. of HMF}}{\text{mol. of Glucose}} \quad (2.1)$$

This variable is used to study the effects of different parameters. The catalytic dehydration was carried out at three different catalyst loadings - 0.037 mmol, 0.15 mmol

and 0.37 mmol. At different temperatures, it is observed that the catalyst loading has varying effects on the molar HMF yield. For example, Figure 2.5(a) shows the results of the various catalyst loadings on reactions carried out at 80 °C. It is observed that the reaction proceeds at different rates at the different catalyst loadings tested. It is slowest at the lowest catalyst loading of 0.037 mmol, reaching a yield of 0.58 at the end of 10 h. However an increasing trend is observed, and it is reasonable to suggest that the molar HMF yield will increase with increase in time. At higher catalyst loadings of 0.15 mmol and 0.37 mmol, it is observed that in both cases, the molar HMF yield reaches the same value at the end of 10 h, and by observations at higher temperatures, it is possible to predict that the yield will plateau at this value of $\approx 0.88 - 0.90$. At a temperature of 100 °C, it can be seen clearly in Figure 2.5(b) that all three catalyst loadings ultimately result in the same Molar HMF Yield, again $\approx 0.88 - 0.90$. There is however, still a difference in the rate at which this ultimate yield is reached, with lower catalyst loadings taking longer than the higher catalyst loadings. At 120 °C however, no significant difference between the different catalyst loadings exists in the time in which ultimate molar HMF yield is reached. The value is again the same, and as in the 100 °C case, the yield does not change with time.

The effect of temperature on the kinetics were also studied. Figure 2.6 shows the effect of temperature on molar HMF yield at each of the catalyst loadings studied. It is observed that the reaction proceeds slowly at lower temperatures. At the lowest catalyst loading, the molar HMF yield does not reach its ultimate value at a reaction temperature of 80 °C even after 10 h, while at higher loadings this value is reached only after 10 h. At higher temperatures this value is reached much faster. One important result to note here is that in all these cases, HMF is a stable product, and does not decompose with time. In addition to the products shown, the only other product observed are insoluble humins which are filtered out before the samples are analyzed on the HPLC.

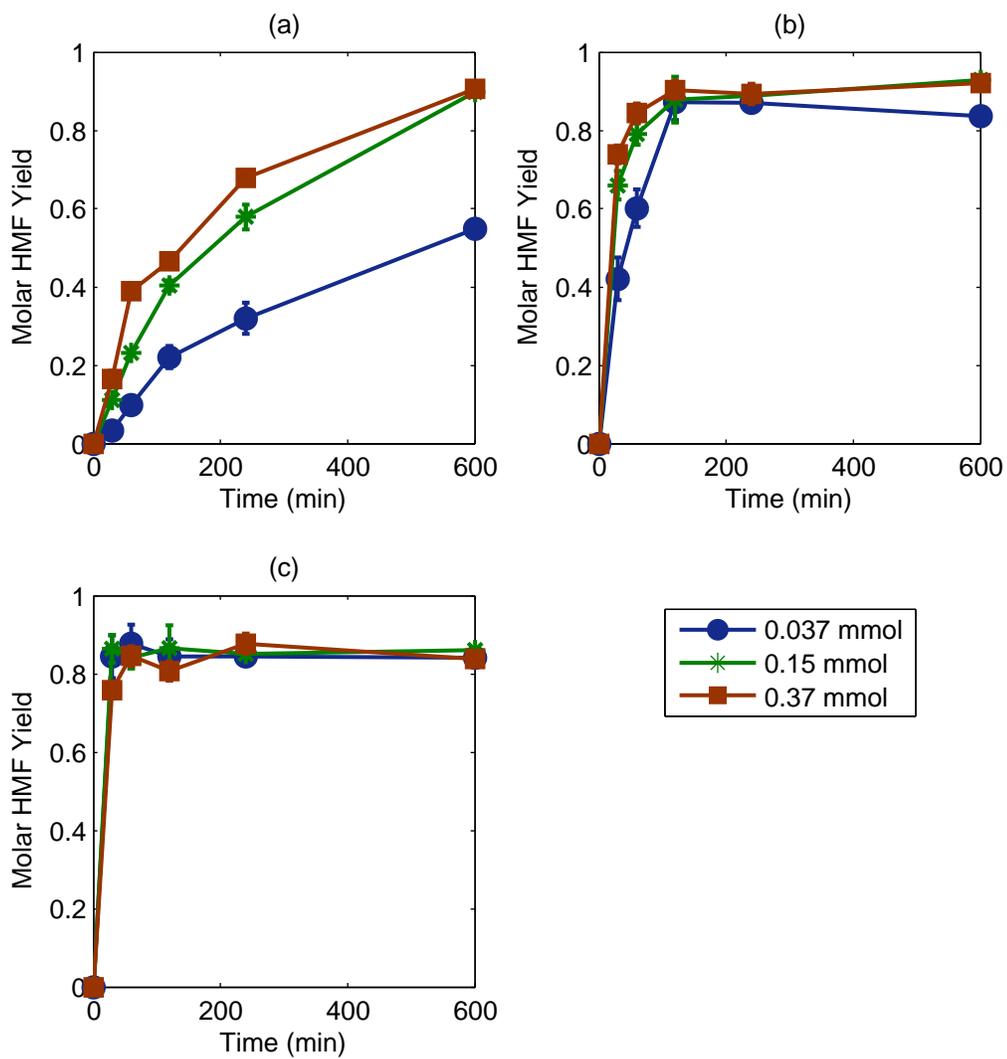


Figure 2.5: The effect of different catalyst loadings on Molar HMF Yield are seen at various temperatures, viz., (a) 80 °C, (b) 100 °C and (c) 120 °C

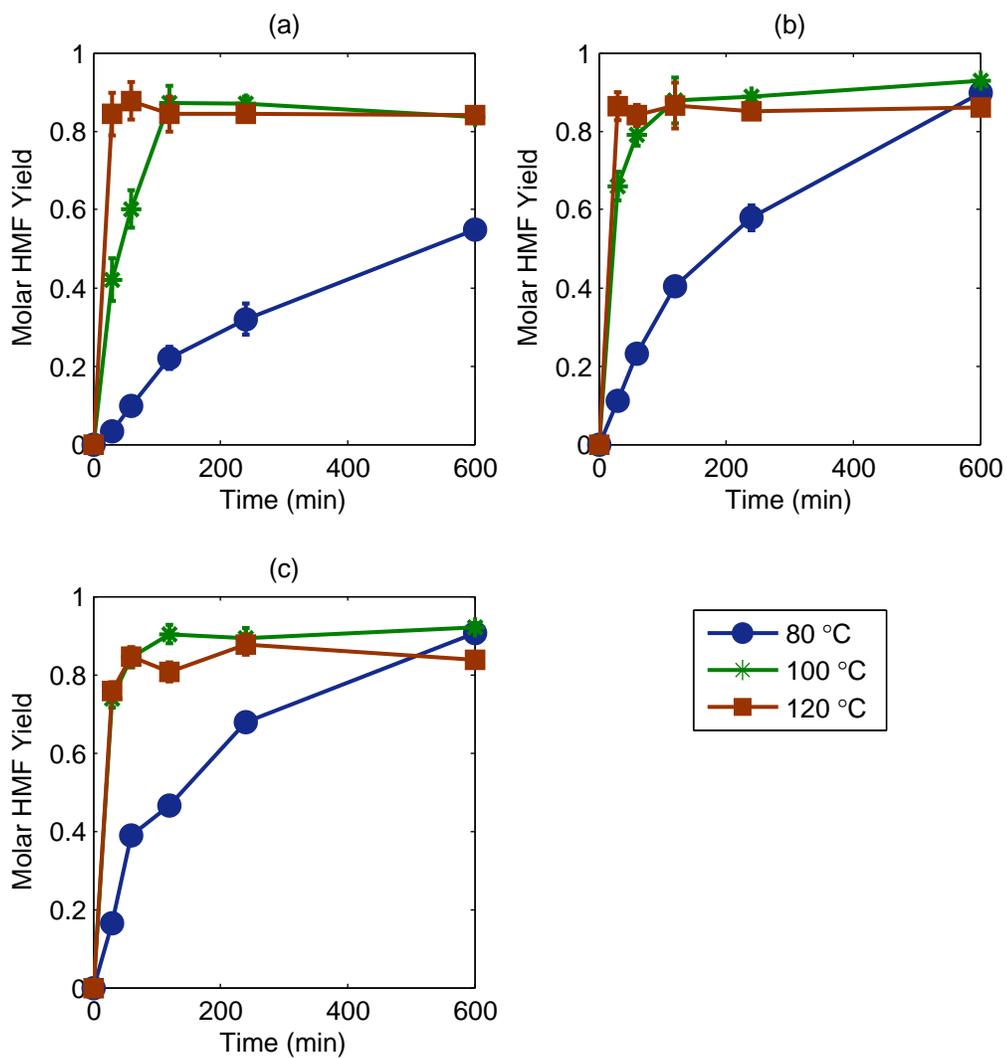


Figure 2.6: The effect of reaction temperature on Molar HMF Yield are seen at various catalyst loadings, viz., (a) 0.037 mmol, (b) 0.15 mmol and (c) 0.37 mmol

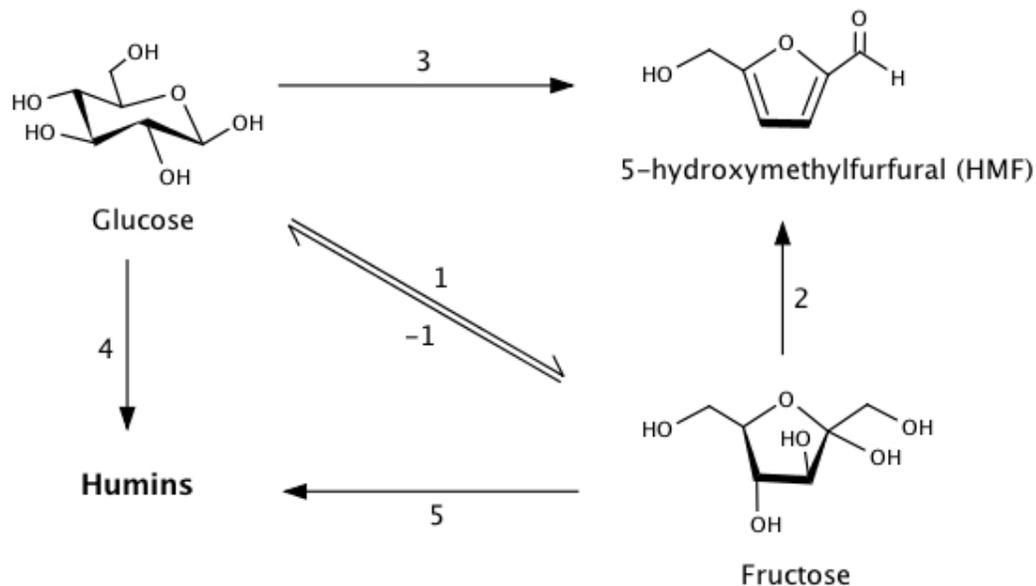


Figure 2.7: Pathways for the Catalytic Dehydration of Glucose to HMF in [bmim]Cl. Adapted from [46?].

Based on these observations, it is possible to draw a simplified schematic of the reaction pathways. Such a schematic is shown in Figure 2.7. There have been suggestions about the presence of additional pathways in the network, for e.g., decomposition products of HMF [49], however none of those products were found in our studies, and hence have not been included in the reaction pathways. However, the reaction pathways are similar to what has been proposed by various researchers [39, 46]. The reaction network shows two possible pathways for the formation of HMF - one a direct dehydration from glucose and another with glucose isomerizing to fructose followed by dehydration. Furthermore, both glucose and fructose undergo an undesirable side reaction to make humins.

2.3.2 Kinetic Modeling

The reaction network shown in Figure 2.7 was used to write mass balances for the rate of change in concentration of glucose, fructose and HMF as shown in Equa-

tions 2.2, 2.3, and 2.4 respectively.

$$\frac{dc_G}{dt} = -k_1c_G + k_{-1}c_F - k_3c_G - k_4c_G \quad (2.2)$$

$$\frac{dc_F}{dt} = k_1c_G - k_{-1}c_F - k_2c_F - k_5c_F \quad (2.3)$$

$$\frac{dc_H}{dt} = k_2c_F + k_3c_G \quad (2.4)$$

The rate constants were assumed to follow an Arrhenius form as shown in Equation 2.5

$$k_i = A_i \exp \frac{-E_i}{RT} \quad (2.5)$$

where A_i and E_i are the pre-exponential factors and activation energies.

The differential equations above were solved using a Runge-Kutta method in MATLAB[®]. The rate constants were estimated by minimizing an objective function, in this case, defined as the sum of the squared differences between the experimental and predicted concentrations. A variety of algorithms and methods were used for parameter estimation. This included Microsoft Excel with the inbuilt Solver functionality, a Nelder-Mead Simplex algorithm implemented in MATLAB[®], and a constrained nonlinear solver implementation using the `fmincon` function built into MATLAB using the Optimization Toolbox GUI. The algorithm finally implemented was a constrained nonlinear solver, using `GlobalSearch` which implements a scatter search using `fmincon` as a local solver. This was found to be the most efficient way to calculate global minima.

The results from the parameter estimation are shown in Table 2.2. Along with the pre-exponential factor and the activation energy, the rate constants for reactions carried out at 80 °C using 0.037 mmol of catalyst are shown. From these results, it can be seen that glucose predominantly isomerizes to fructose, while the reverse reaction is not favored. The formation of HMF is dominated by the pathway from fructose as opposed to the one from glucose. The reaction proceeds rapidly once

fructose is produced towards HMF. Humins production has been found to primarily occur from glucose. These observations are in line with the experimental observations in this study and those found in literature [39, 45, 46]. While the kinetic parameters for this specific reaction network could not be found, similar kinetic studies have been performed in water using sulfuric acid as a catalyst [50]. The activation energies reported in that study are similar to those predicted in the present study. For e.g., the activation energies for reactions 3 and 5 from glucose have been reported as 152 and 165 kJ/mol [50]. The activation energies reported in this study (Table 2.2) are in the same range, with a similar activation energy difference between the two paths. The different solvents, catalysts and temperature ranges used in the two studies might explain the differences between the values reported in the two studies.

Reaction, i	A_i (s^{-1})	E_{a_i} (kJ/mol)	k_i (s^{-1})
1	7.80E12	105	6.23E-3
-1	2.58E18	145	6.38E-4
2	2.37E12	100	4.09E-3
3	1.88E15	120	1.47E-3
4	2.32E12	105	4.22E-3
5	1.97E18	146	5.17E-5

Table 2.2: Results of the Rate Parameters Estimated for the Catalytic Dehydration of Glucose. The rate constants k_i shown for reactions carried out at 80 °C using 0.037 mmol of catalyst

The ability of the model to correlate the determined parameters to experimental results has been shown in the form of a parity plot in Figure 2.8. The parity plots compare the experimental and the calculated Molar HMF Yields. All the points are scattered on the principal diagonal. Some of the deviations observed have been noted to mostly arise from the large standard deviations from the sampling of experiments carried out at short times, around 30 minutes. In these cases, the dehydration kinetics compete with the dissolution kinetics of the reactant in the solvent, though the latter is typically much faster.

The effect of catalyst concentration on the determined rate parameters was also

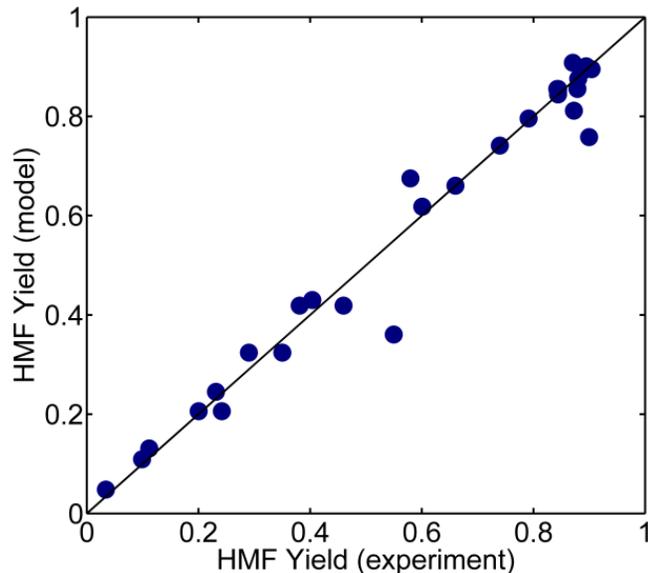


Figure 2.8: Parity plot comparing experimentally determined HMF yields to that calculated by the model in the dehydration of glucose in [bmim]Cl catalyzed by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

studied. For reactions that are not catalyzed by the Lewis Acid, it is observed that the rate constant does not change with catalyst loading. A good example of this is Reaction 3, the dehydration of fructose to HMF. Figure 2.9 compares the rate constants for Reaction 3 at 80 °C across the different catalyst loadings. As has been mentioned before, once fructose is formed, it rapidly dehydrates to form HMF, and this does not depend on the catalyst. Hence it is expected that the rate constants do not change with catalyst concentration. This further illustrates the fact that the model correctly captures the behavior of this reaction network.

One objective of the phenomenological model developed here is to be able to provide predictive capability, especially for molar HMF yield. To test this, additional experiments were carried out using parameters that were outside the space under which the model was developed. In our case, the initial glucose concentration was changed from 55 mmol/l to 550 mmol/l, a 10-fold increase. The experimental HMF yields were then overlaid on those predicted from the model using the parameters estimated in Table 2.2. The results are shown in Figure 2.10. This shows that though

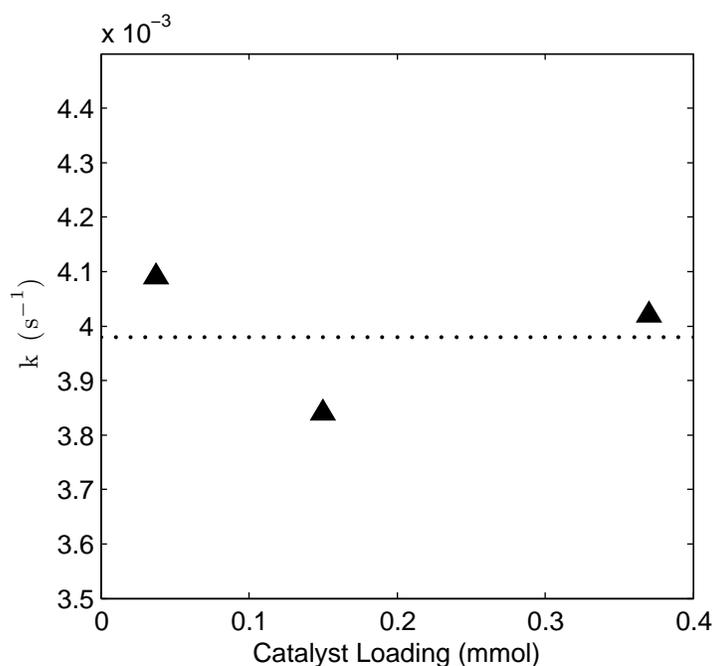


Figure 2.9: Comparison of rate constants from the model to the catalyst loading for Reaction 3. Since the step is not dependent on the catalyst, the rate constants are the same.

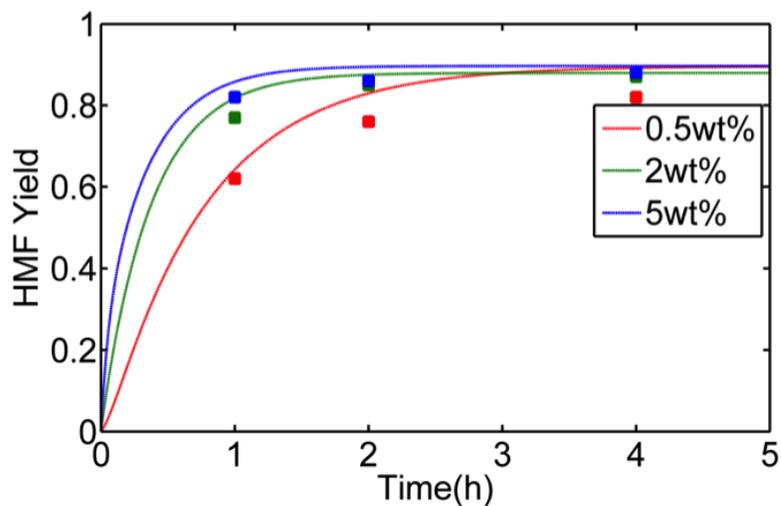


Figure 2.10: Model Predictions compared to data from experiments that were carried out using a parameter space outside the ones used for prediction. In this case, the initial glucose loading was increased 10x. Here, 0.5 wt%, 2 wt% and 5 wt% refer to catalyst loadings of 0.037 mmol, 0.15 mmol and 0.37 mmol respectively. All reactions were carried out at 100 °C.

our predictions are in the same range as the experiments, for the three different catalyst loadings tested, the model tends to overpredict HMF Yields. This can be attributed to our assumption about the kinetics of the formation of humins. The production of humins, and even their composition have not been very well understood by the scientific community. There are some reports of the kinetics of humins production. In a study of the dehydration of glucose in water using sulfuric acid as a catalyst, it has been assumed that the rate of production of humins depended both on glucose and sulfuric acid concentration with non-unity orders [50]. However, the results of this study cannot be directly used in our model since the solvent, the catalyst and the model assumptions are completely different. A better understanding, however, of the kinetics of the production of humins would be beneficial in improving the predictive capability of our model.

2.4 Conclusions

In this chapter, the dehydration of glucose was studied using [bmim]Cl as a solvent. FeCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were used as Lewis acid catalysts. The goal of this work was two-fold. The first aim was to use the well-studied solvent catalyst system consisting of [bmim]Cl and chromium-based catalysts in order to develop experimental and analytical protocols to detect the species in the reaction mixture. This was successfully carried out, as described in Section 2.2.2. This work also led to the development of additional methods of analysis that have been detailed in Appendix A. The second goal of this work was to develop a phenomenological model that can help with process development.

In experiments designed to screen the Lewis acid catalysts, it was observed that $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was a much better with higher yields of HMF seen. This was in agreement with observations made by other researchers [39]. Detailed experiments were then carried out studying the effect of time, temperature and catalyst loading. Based on

these results, reaction pathways were constructed which were once again in agreement with literature. A model was built to describe this reaction network. Rate parameters were estimated using `GlobalSearch` algorithm in MATLAB. These parameters were then used to predict HMF yields in experiments that were carried out in a parameter space outside the range that was used to build the model. While the model was successful in describing the experimental data and in predicting behavior, there was a tendency to over-predict HMF yields. This was attributed to the inability of the model to correctly capture the kinetics of humins formation. A better understanding of humins formation needs to be developed in order to improve our model.

One of the goals of this research was to develop alternate solvents to the imidazolium-based ILs for the conversion of biomass. Studying the [bmim]Cl system has resulted in the development of experimental and analytical protocols that have been used throughout this thesis. The results from this work have also been used as a benchmark for activity of the solvents studied in Chapters III, IV and V. Additionally, the insights into the reaction pathways that were developed have also been instrumental in the study of reaction pathways in these alternate solvents.

CHAPTER III

Quaternary Ammonium Salt-based Eutectics for Sugar Conversion

3.1 Introduction

Imidazolium-based ILs have attracted much of the attention for the conversion of biomass feedstock. In addition to the conversion of glucose to platform chemicals like HMF demonstrated in Chapter II, macromolecules like cellulose has been converted to HMF [47, 51, 52]. Value-added molecules from HMF like DMF, a potential biofuel have also been produced in [bmim]Cl using biphasic processes [40] as well. However, the use of imidazolium-based ILs raise concerns of environmental toxicity and prohibitively high costs of synthesis and purification. This has led to the development of ILs synthesized from renewable materials like amino-acids [53, 54] and quaternary ammonium salts.

Salt mixtures when mixed in their eutectic decrease the freezing point. Quaternary ammonium salts and metal salts have been known to form eutectics by forming a complex, decreasing the lattice energy and hence decreasing the freezing point of the system [55]. These eutectics have been in use for a long time for a variety of applications such as, for annealing steel, as a heat storage fluid [56], etc. It was discovered that quaternary ammonium salts such as choline chloride formed a eutectic

with urea, that was a liquid at room temperature [57]. Compounds that were capable of forming hydrogen bonds with chloride ions were found to form liquids with high depressions in freezing points. It was also observed that a variety of other amides exhibit similar behavior. A correlation relating the depression in freezing point to hydrogen bond strength of the functional group forming the hydrogen bonds was reported [57]. Characterization of eutectics formed between imidazole and a quaternary ammonium salt, tetrabutylammonium chloride using IR and UV measurements confirm the hydrogen bond interactions [58]. Most importantly, it was also found that a wide variety of solutes were soluble in these eutectics, opening up the possibility of their use as solvents.

These ideas were then extended to other hydrogen bond donors, metal halides and hydrated metal salts [59]. Eutectics were also formed without quaternary ammonium salts using metal salts and organic amides [60]. Perhaps more importantly for us - since the chemistry we are attempting in this study is catalyzed by acids, quaternary ammonium compounds were found to form eutectics with carboxylic acids. These eutectics also have properties that make them ideal prospects as solvents for reactions. The phase behavior of the eutectics thence formed have been characterized. For example, Figure 3.1 shows the freezing points of eutectics between a quaternary ammonium salts and a few carboxylic acids. Another property that is important to consider in choosing solvents is the solvent viscosity. It has been found that while the viscosity depends on the hydrogen bond donor type and composition, they lie in the 50 – 5000 cP range [61]. These favorable properties further support the proposed use of these eutectics as solvents.

As solvents, eutectics, especially those formed from quaternary ammonium salts, like choline chloride-metal chloride, have been used to perform Diels-Alder reactions [62]. High yields (>90 %) were reported, and it was found that the solvent acted both as a medium and as a catalyst. These eutectics have also been used to carry out the

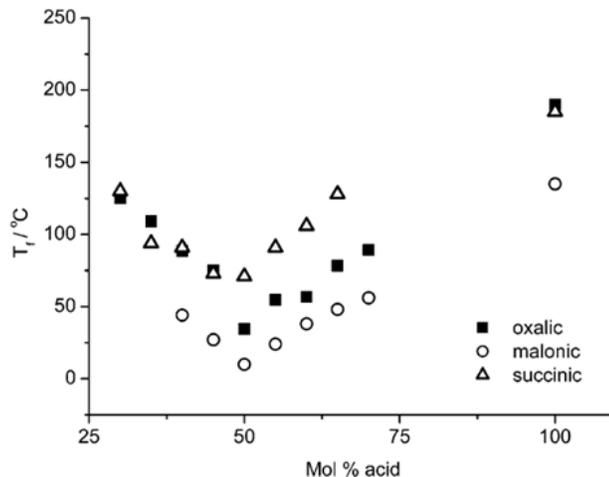


Figure 3.1: The freezing points of mixtures of ChCl and various carboxylic acids as a function of composition. The freezing point of the mixture at the eutectic composition is also shown here. Figure from [61].

Fischer indole annulation [63]. Choline chloride based eutectics have also been used as templates for the synthesis of zeolites having novel structures [64]. In addition to these reactions, some progress has been made in the area of biomass utilization using these solvents. Though not directly related to the production of value-added chemicals and fuels production that is the target of this study, a eutectic composed of choline chloride derivative and urea was used for the functionalization and acylation of cellulose [65]. In this reaction, the eutectic acts as both the solvent and a reactant.

However, very few studies have used eutectics for the conversion of biomass-based feedstock. The dehydration of fructose using choline-chloride based eutectics has been studied [66]. It was noted that high fructose conversions and high HMF selectivities could be achieved at mild temperatures (80 °C) and 1 h reaction time. The focus of that study was on the development of a biphasic system for the extraction of HMF. While activity of the solvent was described at very specific conditions, much of the pathways involved and the effect of time, temperature and the choice of the eutectic itself remains unknown.

In this study, QAS-based eutectics based on ChCl have been studied in detail for

the conversion of biomass feedstock. The conversion scheme detailed in Chapter I has been targeted. Various biomass-derived feedstocks ranging from simple sugars like fructose to disaccharides like sucrose have been studied. Reaction pathways involved in these conversions have been analyzed, and have been used to determine the effect of solvent properties like acidity on the activity of the solvent. The aim of this study was to present a rationale for the choice of eutectic solvents for biomass conversion, and to provide insights into selecting solvents to perform chemistries to produce targeted compounds. The determination of solvent property-performance relationships represents a valuable addition to the current knowledge in the field.

3.2 Choice, Synthesis, and Characterization of QAS-based Eutectics

The choice of ILs for the conversion of biomass has conventionally been rather Edisonian in nature. In choosing partners to make the QAS-based Eutectics, it was necessary to pick solvents that have favorable physical properties like low toxicity and thermal stability in the range of operation. In addition, partner compounds were also chosen based on the type of chemistry that was attempted. The QAS chosen for this study was Choline Chloride (ChCl). ChCl is a commodity chemical, that is commonly present in chicken feeds and commercially available protein shakes. Since the chemistry that is being attempted is catalyzed by an acid, ChCl was paired with two acids, viz., citric acid monohydrate and oxalic acid dihydrate, herein referred to as citric acid and oxalic acid respectively, to form eutectics, denoted as Choline Chloride-Citric Acid (ChCl-CA) and ChCl-OA. Compared to imidazolium ILs like [bmim]Cl, these compounds have lower toxicities. The Oral LD50 for ChCl is 3400 mg/kg [67], that for pure citric acid is 5400 mg/kg [68], and pure oxalic acid has an oral LD50 of 1080 mg/kg [69], compared to an oral LD50 of 50 – 300 mg/kg for [bmim]Cl [41]. The

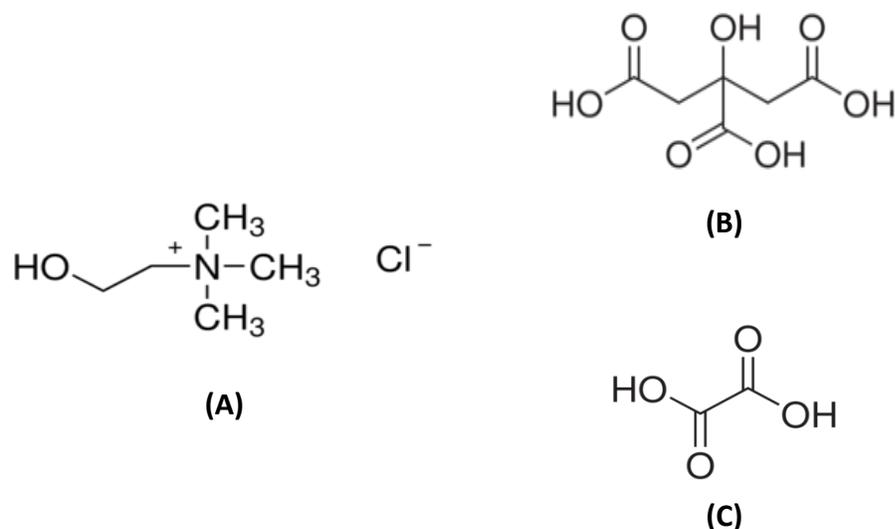


Figure 3.2: The structures of components used in the QAS-based eutectics in this study. (A) Choline Chloride (ChCl) (B) Citric Acid and (C) Oxalic Acid

Material Safety Data Sheets for the components of the eutectics also classify them as readily biodegradable while [bmim]Cl is classified as not readily biodegradable [41, 67–69]. Even on a research scale, the compounds used to make the eutectics are less expensive to procure than [bmim]Cl. For our study, Sigma Aldrich was used as a vendor, with [bmim]Cl (Product code: 94128) costing \$1.4 /g, compared to ChCl (Product code: C1879, \$0.12 /g), citric acid (Product code: C7129, \$0.22 /g) and oxalic acid (Product code: 247537, \$0.40 /g). It is expected that these savings will translate to equal if not higher savings on larger scales. The structures of ChCl, citric acid and oxalic acid are shown in Figure 3.2.

Another advantage that the QAS-based eutectics have over conventional ILs such as the imidazolium-based ones studied in Chapter II is the simplicity in synthesis. To synthesize the eutectics, equimolar quantities of the two components were thoroughly mixed using a mortar and pestle, and heated to 80 °C with constant stirring, which results in a clear liquid. The melting points of the pure components and the resulting eutectics are also presented in Table 3.1.

QAS ($T_m/^\circ\text{C}$)	Partner Acid ($T_m/^\circ\text{C}$)	Resulting Eutectic ($T_m/^\circ\text{C}$)
Choline Chloride (302)	Citric Acid (153)	ChCl-CA (69)
	Oxalic Acid (190)	ChCl-OA (34)

Table 3.1: QAS-based eutectics chosen for this study. The QAS ChCl has been paired with both the acids shown to form eutectics. The melting points (T_m) in $^\circ\text{C}$ of the corresponding compound/eutectic are shown in parentheses

In addition to the fact that acid-catalyzed chemistry is being attempted here, the choice of the two partner compounds to ChCl - citric and oxalic acids also help in evaluating the effect of varying the acidity of the resulting eutectic. The partner acids are hydrates, and water is a byproduct of the dehydration of sugars. This means that water is always present in appreciable quantities in solution. Hence, a comparison of the pK_a values of the partner acids in an aqueous medium, which is openly available in literature, is a good indicator of the acidity of the eutectics. These values, which can be seen in Table 3.2, show that the two partners clearly have different acidities.

Partner Acid	pK_{a1}	pK_{a2}	pK_{a3}
Citric Acid	3.14	4.71	6.40
Oxalic Acid	1.23	4.19	–

Table 3.2: pK_a values of citric and oxalic acids, which are the acid components of QAS-based eutectics chosen for this study

The pK_a values of ionic liquids cannot be easily measured directly. It has been shown that ILs can act as both Lewis and Brønsted bases. With the help of acid/base indicators like m-cresol purple and alizarin red S, the magnitude of these values relative to water have been understood for a few basic imidazolium ILs [70]. In the case of QAS-based eutectics however, it has been suggested that the carboxylic acid and the QAS are involved in a 1:1 complex [61]. In order to confirm this, it is imperative that the acidity of the eutectics be studied to see if the difference in acidity between the partner acids translates to a difference in acidity of the resulting eutectic. This has been done using 2,4-dinitroaniline as an acidity indicator. This indicator has been used as one of the bases for the development of the Hammett

Acidity Scale [71]. This acidity scale was first used to measure the Brønsted acidity of sulfuric and perchloric acids. It extends the pH scale by accounting for the activity and transfer coefficients in different solvents. This concept has been extended to IL solvents resulting in the development of an acidity scale for room temperature ILs [72]. While the exact values of the Hammett Acidity Factor are not important in this work, this methodology was adapted as a good way to compare the Brønsted acidity of the imidazolium IL and QAS-based eutectics in this study. The indicator was added to the solvents at known concentrations, and the extent of protonation of the indicator was measured using a UV-Vis spectrometer. While the peak for the protonated form of the indicator was at wavelengths below 270 nm, the concentration of the unprotonated form of the acid can be easily measured. It is expected that as the acidity of the solvent increases, the extent of protonation of the indicator increases, and consequently, the concentration of the unprotonated form of the indicator, along with its intensity of absorption, decreases. The results of these experiments, seen in Figure 3.3, indicate that the imidazolium IL, [bmim]Cl is the least acidic, while ChCl-OA is the most acidic. ChCl-CA is much more acidic than [bmim]Cl, but less than ChCl-OA. This difference in acidity can now be used to compare and correlate the differences in activity and reaction pathways in the solvents.

3.3 Non-catalyzed Dehydration of Fructose

In the study of the catalytic dehydration of glucose in Chapter II, it was found that the pathway from glucose to HMF proceeds through fructose. In addition, since the dehydration of fructose can proceed without the need for a catalyst, studying this reaction in different solvents will provide a true comparison of the difference in activity of the solvents alone without any interaction of the catalyst.

Reactions were carried out in stirred batch reactors. The eutectics were freshly prepared each time by physically mixing the two components using a mortar and

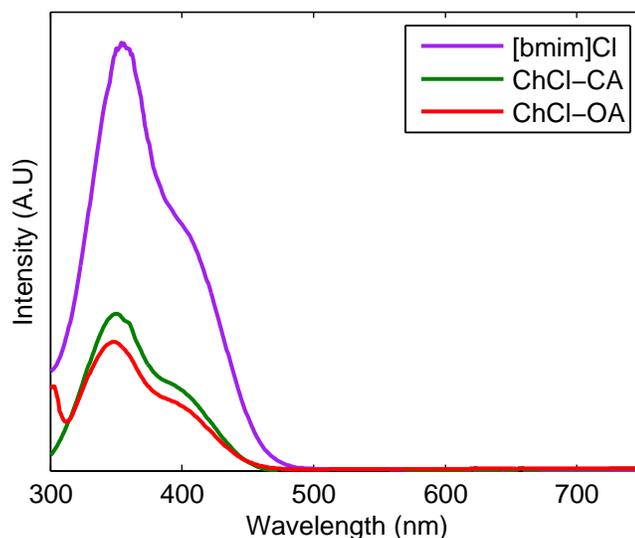


Figure 3.3: The absorbance of the unprotonated form of the acidity indicator, 2,4-dinitroaniline in different solvents. Lower absorbance intensities indicate higher acidity.

pestle before loading them in the reactor. The loading of this physical mixture in the reactor was 2 g, with an initial fructose loading of 0.55 mmol. The experimental and analytical protocols developed in Section 2.2 were then used. From the work in Chapter II involving a thorough study of parameters like catalyst loading and temperature in order to fully understand the reaction pathways involved, it was found that increased temperatures and catalyst loadings caused an increase in the rate at which these reactions proceeded, but did not affect the pathways. As will be noted later, similar behavior is seen in the eutectics as well. Therefore, carrying out these reactions at a single temperature is enough to glean much of the information needed to build reaction networks. In this case, the batch reactors were maintained at a temperature of 100 °C. All experiments were performed in triplicate, and the error bars in each case show the standard deviation from these experiments. However, in most cases, the error bars were smaller than the size of the markers used in figures.

Since the imidazolium-based ILs are being used as a benchmark for activity, the reactions performed in the eutectics are compared to those in [bmim]Cl. In Fig-

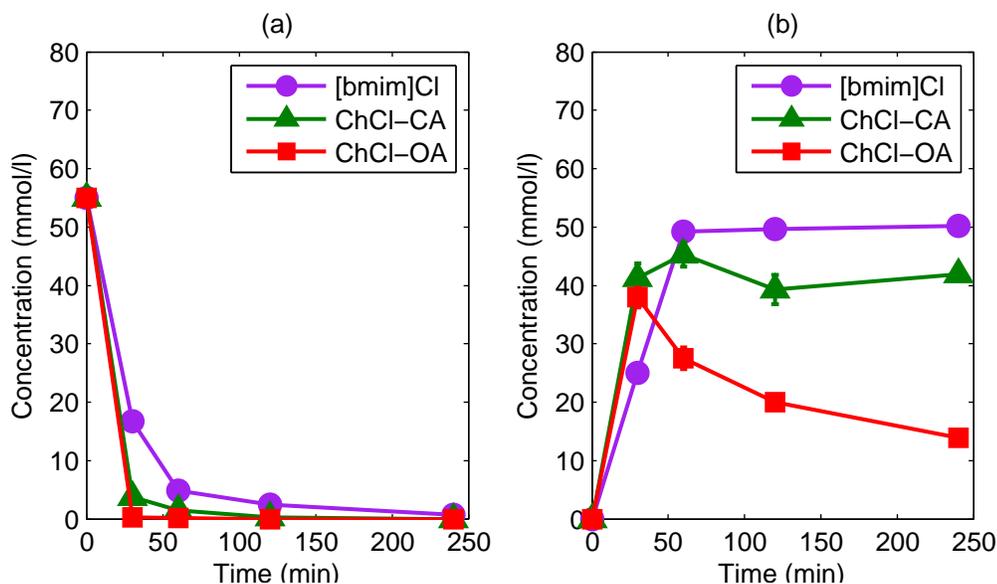


Figure 3.4: The differences in activity between [bmim]Cl, ChCl-CA and ChCl-OA is shown here for the Non-Catalyzed Dehydration of Fructose. The differences in fructose consumption is shown in (a) and the production of HMF is shown in (b). The reactions were carried out at 100 °C.

ure 3.4(a), the difference in the rate of consumption of the reactant, fructose, in the different solvents is shown. It is seen that in the most acidic solvent, ChCl-OA, fructose is consumed the fastest, while in the least acidic [bmim]Cl, it is consumed the slowest. The rate of consumption of fructose in ChCl-CA is in between the other two. Figure 3.4(b) shows the concentration profile of HMF in the different solvents. It is seen that in [bmim]Cl, the concentration of HMF plateaus at a certain maximum. This indicates that the HMF formed is a stable product. In the highly acidic ChCl-OA, there is a peak in the concentration of HMF at around 30 min before decreasing rapidly with the progress of the reaction. This points to additional pathways in ChCl-OA that are not seen in [bmim]Cl, responsible for the consumption of HMF. In ChCl-CA, the concentration of HMF is observed to drop slightly from the maximum observed at smaller timescales, and settle down at a value lower than that observed in [bmim]Cl.

Observing the full product spectrum in each of the solvents provides a good idea

about the additional pathways that exist in the eutectics. Once again, they can be compared to [bmim]Cl. Figure 3.5(a) shows the time-series data for the consumption of fructose, and the production of HMF. As was previously observed, HMF is the sole product, and is stable over time. In Figure 3.5(b), the results of the same reaction carried out in ChCl-CA is shown. In addition to HMF, minute quantities of levulinic and formic acid are seen. The appearance of these additional products correspond to the slight decrease in concentration of HMF seen in the reaction mixture at later times. This effect is more pronounced in ChCl-OA, where the concentration of HMF decreases considerably, and a corresponding increase is seen in the concentrations of levulinic and formic acids.

This indicates that in ChCl-OA, HMF is unstable, and undergoes an acid hydrolysis that results in the formation of levulinic and formic acids. The acid hydrolysis of HMF takes place in ChCl-CA too, but to a smaller extent. The extent of hydrolysis of HMF can be directly correlated to the acidity of the solvent, i.e., the greater the acidity of the solvent, the higher the extent of hydrolysis, and higher the selectivity towards levulinic acid. These results point to the versatility of the QAS-based eutectics. If the platform chemical, HMF, is the desired product of the reaction, it is possible to choose the composition of the solvent such that the selectivity towards HMF is maximized. However, if it is desired to make levulinic acid, another valuable commodity chemical, identified as one of the top 12 chemicals from biomass by the DoE [14], one can choose a solvent with high selectivity towards it.

Similar behavior was observed at other temperatures too. As was noted earlier (and in Chapter II), higher temperatures increase the rate of the reactions in the network, but do not change the pathways. Figure 3.6 shows the effect of the dehydration of fructose carried out at 80 °C and 100 °C. It is observed that at higher temperatures, the acid hydrolysis of HMF is accelerated, leading to the formation of increased amounts of levulinic and formic acids.

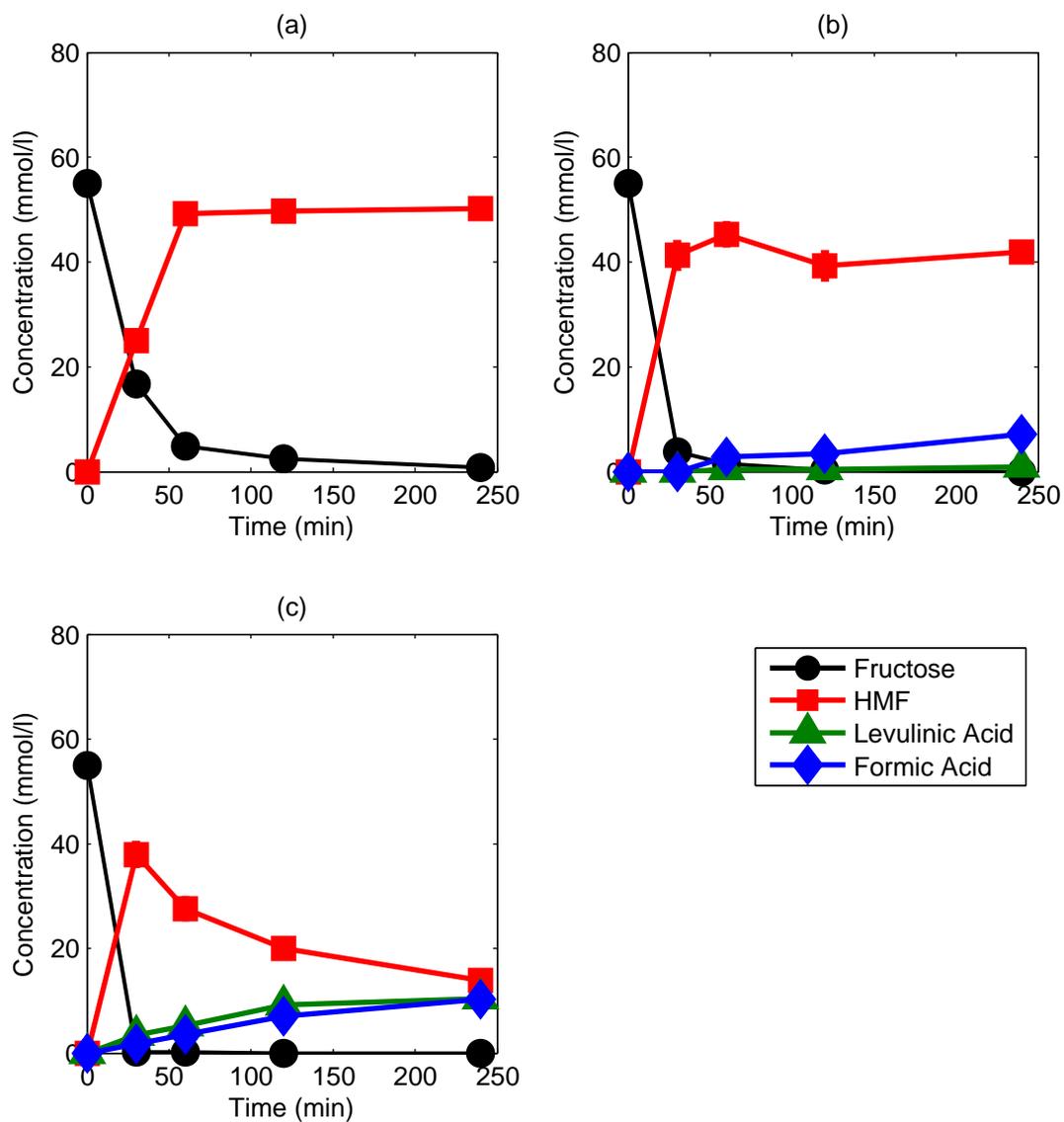


Figure 3.5: Time series data showing the reactants and products formed during the Non-Catalyzed Dehydration of Fructose in various solvents: (a) [bmim]Cl, (b) ChCl-CA and (c) ChCl-OA. All reactions were carried out at 100 °C in the absence of any catalyst.

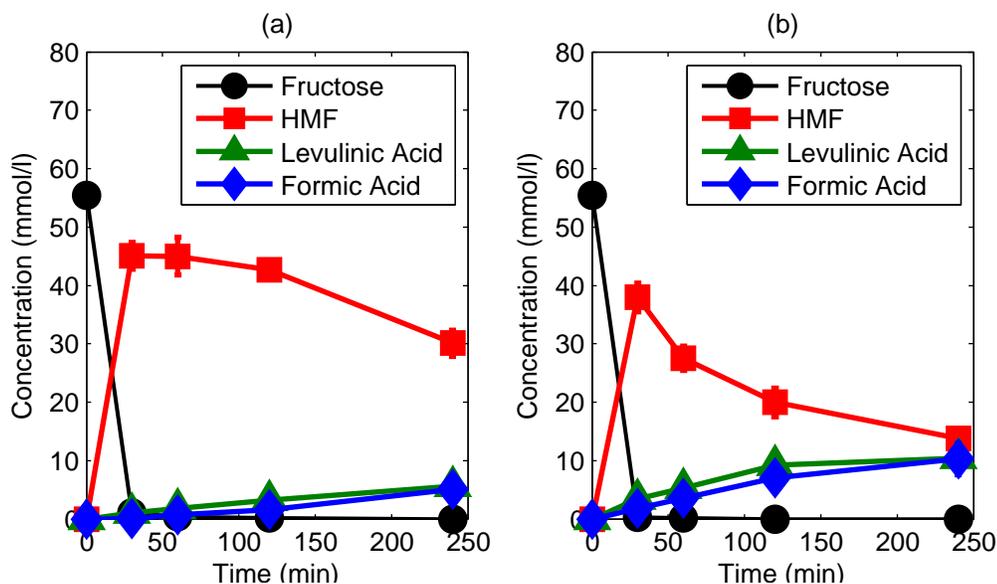


Figure 3.6: Time series data showing the reactants and products formed during the Non-Catalyzed Dehydration of Fructose at different temperatures: (a) 80 °C and (b) 100 °C in the absence of any catalyst.

In addition to the hydrolysis of HMF, it was also observed that a large amount of humins were formed in the eutectics. While humins production in [bmim]Cl has been noted, it was observed in our study that in the QAS-based eutectics, particularly ChCl-OA, they were formed in larger quantities. This can be attributed to the acidity of the solvents. The high acidity of the reaction mixture catalyzes the condensation polymerization reactions between the sugars themselves, and with HMF, which lead to the formation of humins.

To further understand the reaction pathways involved in these solvents, the stability of HMF was tested in these solvents in the absence of catalysts. It was observed that while the concentration of HMF remained constant with time in [bmim]Cl, in ChCl-OA, the HMF concentration decreased along with an increase in the formation of levulinic and formic acids and visual observation of humins. In ChCl-CA, lesser amounts of levulinic and formic acid, and the humins were observed. This means that unlike in [bmim]Cl, pathways from HMF to humins exist in the eutectics. These

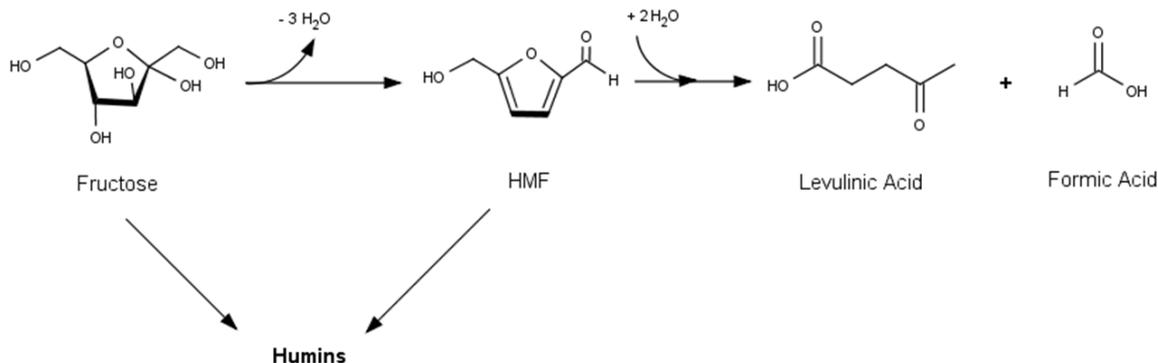


Figure 3.7: The proposed reaction pathways in the Dehydration of Fructose in ChCl-CA and ChCl-OA are shown here. In [bmim]Cl, pathways from HMF to either the humins, or levulinic and formic acids are not observed.

pathways are summarized in Figure 3.7.

3.3.1 Reduced Experimental Set with Effective Reaction Pathway Detail

The detailed experiments described in Chapter II and earlier in this chapter studied the evolution of products and the consumption of reactants. With the results of these studies, an understanding of the reaction pathways involved in the sugar conversion has been developed. These studies have also enabled the analysis and deduction of the reaction pathways involved using a much smaller experimental set. This can be done by analyzing the reaction mixture at longer timescales and looking at the product distribution. For example, Figure 3.8(a) shows the time-series data for the dehydration of fructose in [bmim]Cl. Using the concentrations at a reaction time of 4 h, the conversion of fructose and the yield of HMF have been shown in Figure 3.8(b). High yields along with the absence of any other products at longer timescales in this case imply that HMF is the only and stable product of dehydration. Since the yield is not 100 %, it can be deduced that the production of humins is not zero. Similarly, Figure 3.8(c) and Figure 3.8(d) show similar data for the dehydration of fructose in ChCl-OA. The presence of almost equimolar quantities of levulinic and formic acid

in the reaction mixture at $t = 4$ h along with low HMF yields indicates the existence of the HMF hydrolysis pathway. The increased amounts of humins account for the difference.

The effect of solvent acidity on the reaction can be seen in Figure 3.9 that shows the product yields and fructose conversion for the three solvents discussed so far. As solvent acidity increases, the yield (and hence selectivity) of HMF decreases. With this increase in acidity, the yield of levulinic and formic acids also increases, with their yield in [bmim]Cl being zero, while in ChCl-CA the yields are 1 – 2 %, and about 19 % in ChCl-OA.

3.3.2 Extension of Trend to Other QAS-based eutectics

To ensure that the acidity of the partner compounds to the QAS, and hence the acidity of the solvent was responsible for the difference in pathways observed in previous sections, two other partner compounds, benzoic acid and phenol, with vastly different pK_a s were chosen to pair with choline chloride. While phenol, having significant vapor pressure, does not have the benefits of the other eutectics, it still provides a valuable comparison. The properties of the partners, along with the melting points of the resulting eutectics, Choline Chloride-Benzoic Acid (ChCl-BA) and Choline Chloride-Phenol (ChCl-Ph), are shown in Table 3.3.

QAS ($T_m/$ °C)	Partner ($T_m/$ °C)	pK_a	Resulting Eutectic ($T_m/$ °C)
Choline Chloride (302)	Benzoic Acid (122.41)	4.19	ChCl-BA (95)
	Phenol (40.50)	9.89	ChCl-Ph (-40)

Table 3.3: Additional QAS-based eutectics chosen for this study. The partner compounds to choline chloride and their pK_a s are shown. The melting points (T_m) in °C of the pure substances and their eutectics are shown in parentheses

The non-catalyzed dehydration of fructose was carried out in these eutectics as well, and the results were compared to the other ILs. The conversion and yields in these solvents at 100 °C and 4 h are shown in Figure 3.10. It is observed that the

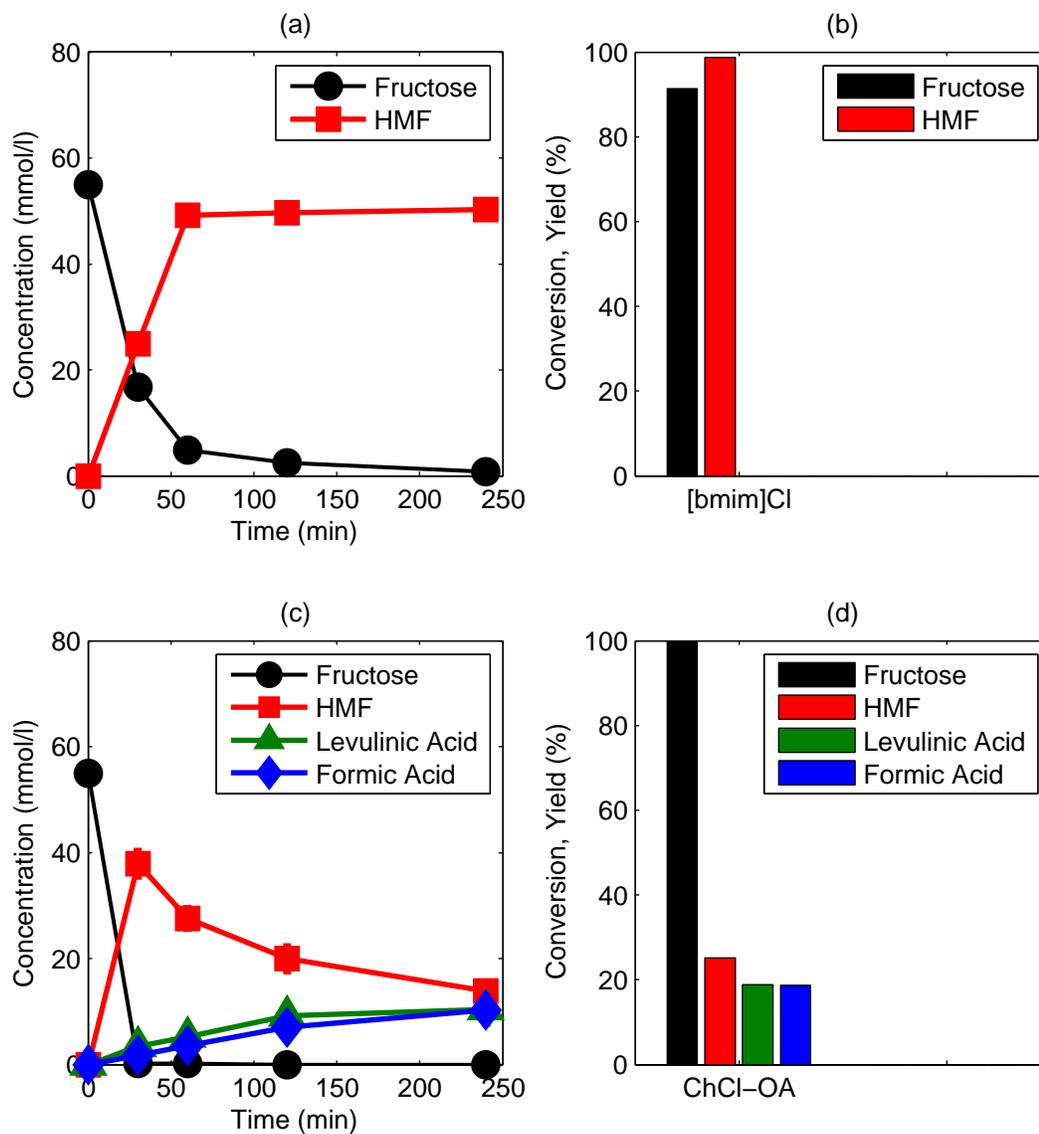


Figure 3.8: The translation of time-series data for the reactants and products of dehydration of Fructose to product yields and conversion are shown here at $T = 100\text{ }^{\circ}\text{C}$ and $t = 240\text{ min}$. The time-series data for [bmim]Cl is shown in (a), and the corresponding conversion/yield data is shown in (b). (c) and (d) show the corresponding data for ChCl-OA.

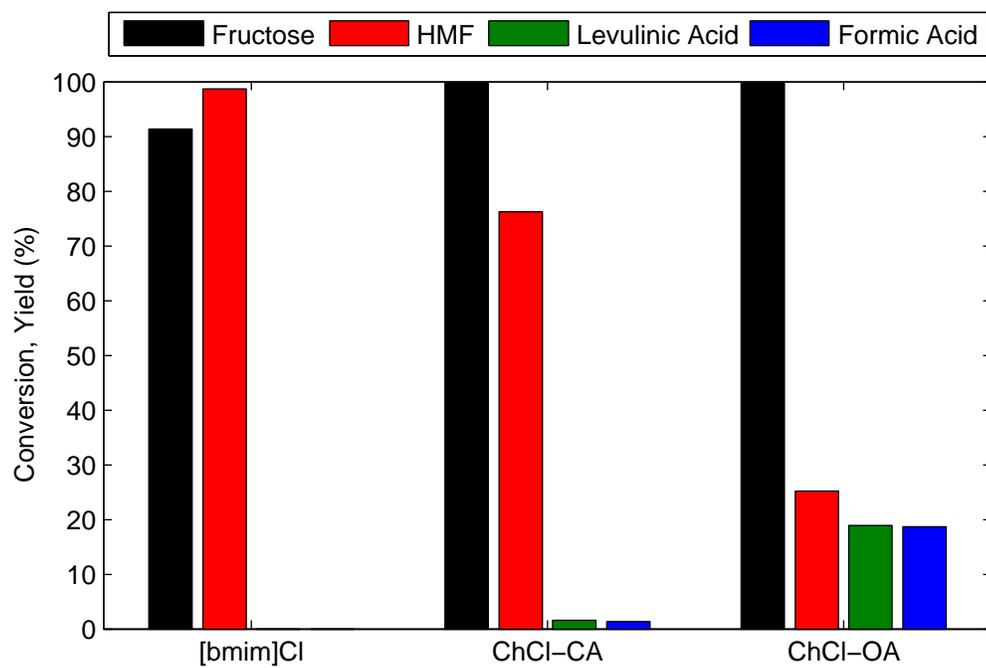


Figure 3.9: Product Yields and Fructose Conversion at $T = 100\text{ }^{\circ}\text{C}$ and $t = 240\text{ min}$ for [bmim]Cl, ChCl-CA and ChCl-OA.

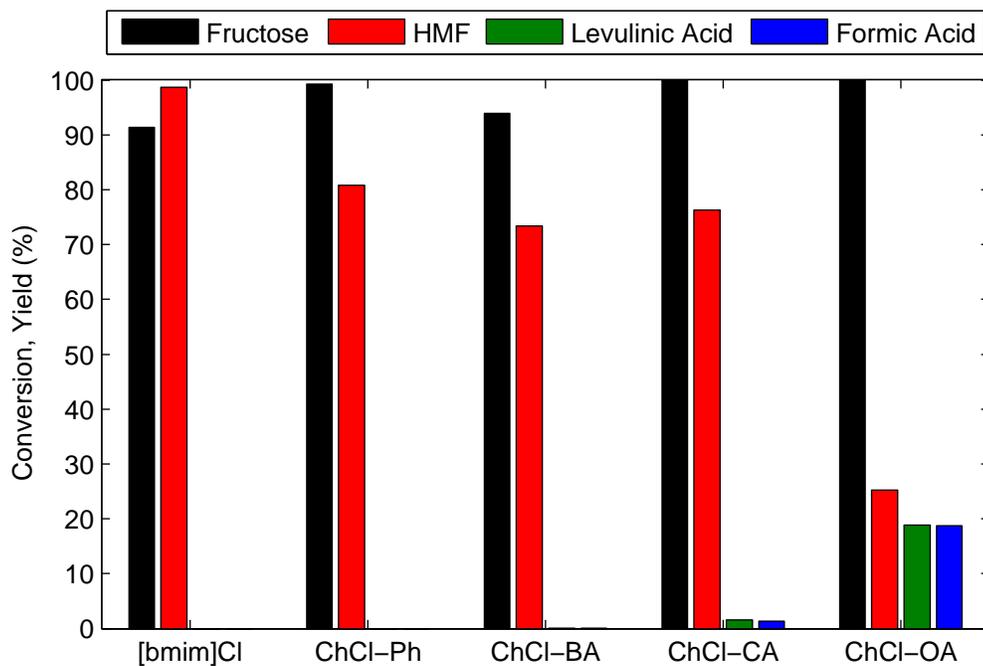


Figure 3.10: Product Yields and Fructose Conversion at $T = 100\text{ }^{\circ}\text{C}$ and $t = 240\text{ min}$ for [bmim]Cl, ChCl-Ph, ChCl-BA, ChCl-CA and ChCl-OA. The acidity of the solvents increase from left to right. It is observed that increasing acidity has implications in reaction pathways and consequently, product distribution.

effect of solvent acidity noted previously is indeed true. Solvents that are formed with partners that are less acidic have a higher yield of HMF and lower yields of levulinic and formic acid. ChCl-BA has even lower yields of levulinic and formic acids than ChCl-CA, while in ChCl-Ph, they are not formed at all. These observations confirm the hypothesis that the extent of hydrolysis of HMF is affected by acidity of the eutectic. This acidity can be controlled by the partner compound, and hence it is possible to tailor solvents to have higher selectivities towards the products of our choice.

3.4 Catalytic Dehydration of Glucose

After the non-catalyzed dehydration of fructose, the next higher level of complexity is the dehydration of glucose. From Chapter II, it is known that the pathway from Glucose to HMF and possibly further to levulinic acid and formic acid involves an isomerization to fructose. In Chapter II, a homogeneous Lewis Acid, chromium chloride hexahydrate was used to catalyze the isomerization in [bmim]Cl. In this study too, 0.15 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is used as a catalyst, with an initial reactant loading of 0.55 mmol glucose. Using a homogeneous catalyst has disadvantages in catalyst recovery. Nevertheless, it is still used in this study because of its advantages in ease of operation as well as the absence of any transport limitations. The choice of solvents is the objective of this work, and hence particular attention has not been paid to optimizing the catalyst.

The dehydration of glucose too was carried out using the methods developed in Chapter II. The reactions carried out in the QAS-based eutectics are once again compared to the ones carried out in [bmim]Cl. The results of these experiments are shown in Figure 3.11. In [bmim]Cl (Figure 3.11(a)), as previously seen, the decrease in concentration of glucose results in the increase in HMF concentration, with fructose as an intermediate, resulting in the reaction pathways described previously in Figure 2.7. In Figure 3.11(b) and Figure 3.11(c), where the results for ChCl-CA and ChCl-OA are shown respectively, the concentration of glucose is plotted on the primary y-axis, and the concentrations of the other products are plotted on the secondary y-axis. In ChCl-CA, the concentration of glucose drops off as expected, and the concentration of HMF increases. While the concentration of HMF does not fall off, and very little levulinic and formic acids are seen, the yield of HMF is very low. Minimal amounts of fructose are observed. In ChCl-OA too, HMF yield is very low (<10 %). However, HMF is consumed and the consumption is accompanied by corresponding increases in levulinic and formic acid concentrations. These results show very low concentrations

of and other products, though the conversion of glucose is high. This points to the reaction proceeding in an undesired pathway forming humins. To summarize, the behavior of HMF after it is formed in each of the eutectics is similar to what was observed in Section 3.3, but the amount of HMF formed itself is very low, about a tenth of what was seen in the dehydration of fructose.

It was seen in Chapter II that in [bmim]Cl that the dominant pathway from glucose to HMF was through an isomerization to fructose catalyzed by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. It is suggested that in the QAS-based eutectics, the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is not very active in catalyzing this isomerization reaction. The only other pathway to HMF is through the direct dehydration of glucose, which is not thermodynamically favored. This is believed to be the cause of low HMF yields. The result of this pathway being inactive is that glucose readily undergoes the undesired conversion to making large amounts of humins via condensation reactions.

It has been noted in Chapter II that the isomerization of glucose to fructose in imidazolium-based ILs is enabled by the complexing of the solvent to the catalyst first, and then to the reactant. This is enabled by hydrogen bond formation. However, in the eutectics, since the partner compounds - the quaternary ammonium salt and the acid, complex with each other to form the eutectic, utilizing the hydrogen bonding sites, and hence these sites are unavailable for the catalyst. The ability of the solvents to form hydrogen bonds were quantified by calculating the Kamlet Taft parameter, β , which describes the hydrogen bond basicity. The methods employed and their significance is detailed in Appendix B. The results are shown in Table 3.4. It is seen that compared to [bmim]Cl, the eutectics have much lower β values signifying lowered ability to form hydrogen bonds. Similar inhibition of isomerization reactions due to the absence of hydrogen bonding in a solvent has been observed in other studies, for e.g., it has been shown that hydrogen bonding between a base and an imidazolium cation can be utilized to suppress allylic isomerization reactions in allylic substitu-

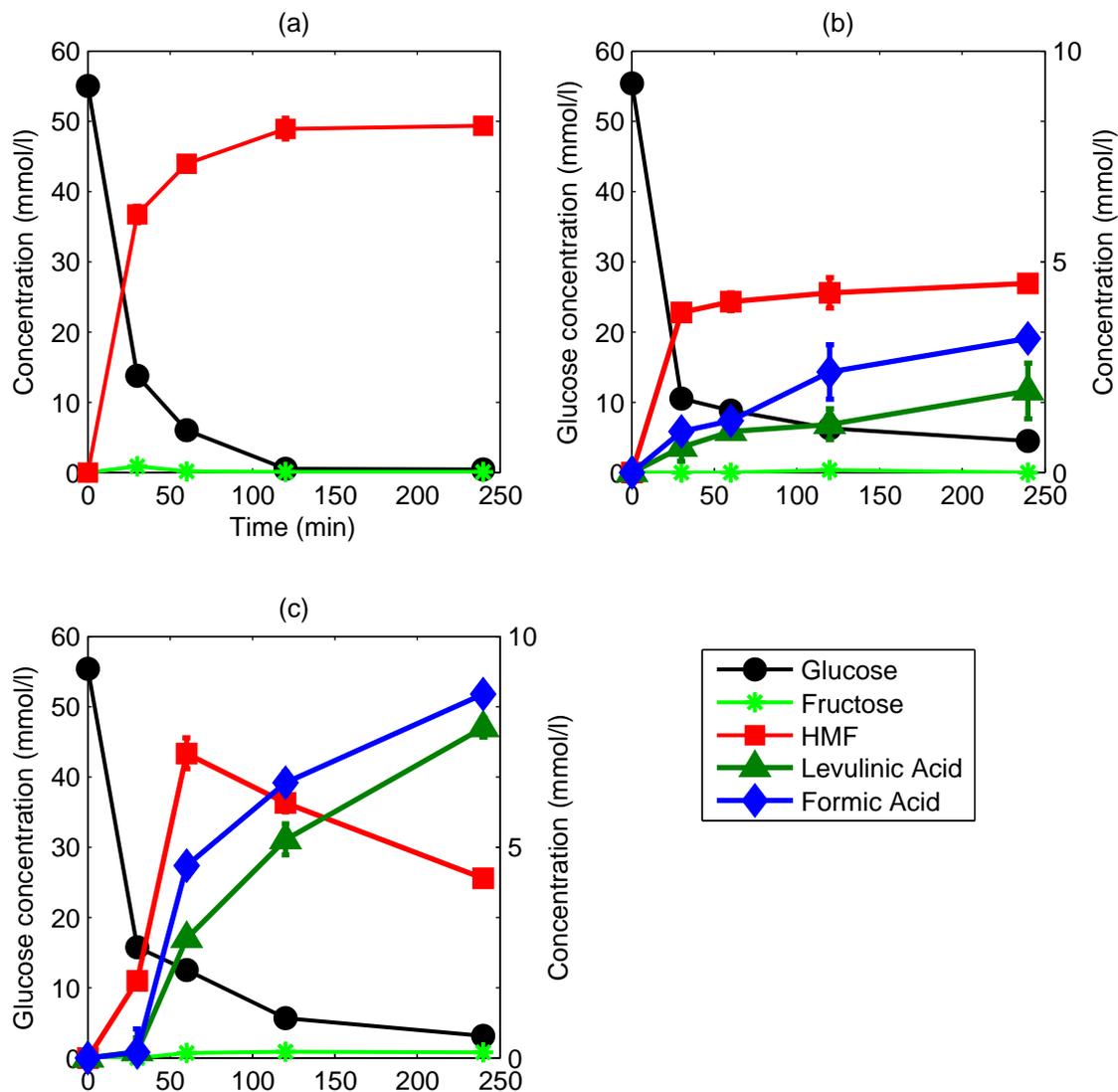


Figure 3.11: The consumption of Glucose and the evolution of products from the Catalytic Dehydration of Glucose at 100 °C using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in (a) $[\text{bmim}]\text{Cl}$, (b) ChCl-CA and (c) ChCl-OA . In (b) and (c), the product concentrations are plotted on the secondary y-axis.

tion reactions [73] In our work, it was also seen that the activity of glucose in the eutectics with and without the catalyst were identical, which confirms the inactivity of the catalyst. Furthermore, experiments have been described in Chapter IV, which solidify our hypothesis on the solvent species present in solution and their (in)ability to complex with the catalyst.

Ionic Liquid	β
[bmim]Cl	0.92
ChCl-Ph	0.42
ChCl-CA	0.53
ChCl-OA	0.42

Table 3.4: A comparison of the hydrogen bond basicity represented by the Kamlet Taft parameter, β , of the eutectics to [bmim]Cl

Though the isomerization to fructose from glucose could not be successfully carried out in the QAS-based eutectics, the effect of the acidity of the solvents still has similar effects on product distribution. In addition to ChCl-CA and ChCl-OA, the additional eutectics introduced in Section 3.3.2 were also studied. Figure 3.12 shows the conversion and yield data for the catalytic dehydration of glucose after 4 h at 100 °C. It is once again seen that with increasing solvent acidity, the selectivity to HMF decreases. The HMF undergoes acid hydrolysis resulting in the formation of levulinic and formic acid in ChCl-BA, ChCl-CA and ChCl-OA, while these hydrolysis products are not seen in ChCl-Ph.

Experiments were also carried out using FeCl_3 as a Lewis Acid. The results, shown in Figure 3.13 for ChCl-OA at a reaction temperature of 100 °C, are very similar to the ones carried out using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, with low yields of HMF. However, hydrolysis of HMF takes place more readily in $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

In summary, it was observed that in all the QAS-based eutectics, the conversion of glucose was almost complete. However, the yields of HMF and its hydrolysis products were very low, irrespective of the Lewis Acid catalyst used. It is believed that while in [bmim]Cl the catalyst complexes with the solvent, this is not feasible in the eutectics

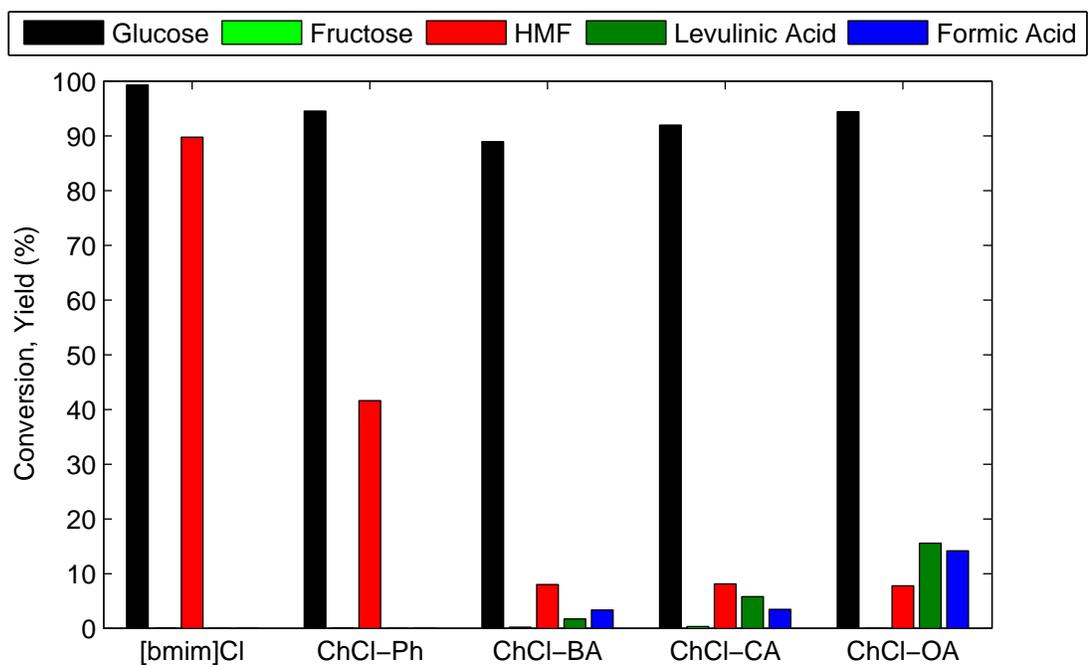


Figure 3.12: Product Yields and Glucose Conversion at $T = 100\text{ }^{\circ}\text{C}$ and $t = 240\text{ min}$ for [bmim]Cl, ChCl-Ph, ChCl-BA, ChCl-CA and ChCl-OA in the Catalytic Dehydration of Glucose. The acidity of the solvents increase from left to right. While product yields are not high, it is observed that increasing acidity has similar implications in reaction pathways and product distributions as was observed in the Dehydration of Fructose.

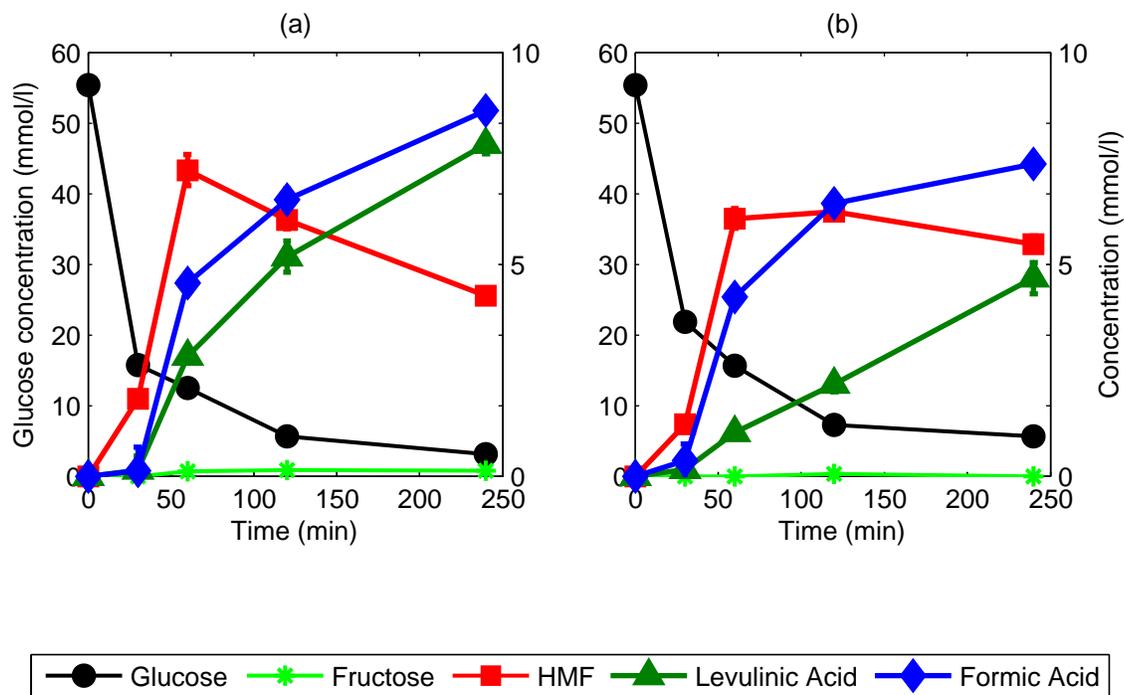


Figure 3.13: Comparison of Glucose consumption and product evolution from the Catalytic Dehydration of Glucose using two different Lewis Acid (a) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and (b) FeCl_3 at a temperature of $100\text{ }^\circ\text{C}$. Both catalysts show similar activity. In both cases, pathways for the isomerization of glucose into fructose is inactive leading to low HMF production. However, the acid hydrolysis of HMF takes place more readily in $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

due to the unique structure of the solvent itself. Consequently, the isomerization of glucose into fructose, which is an important pathway in the formation of HMF and subsequently levulinic acid, is not catalyzed in the QAS-based eutectics. This leads to low yields of HMF. Further proof of this hypothesis is provided in Chapter IV. However, even in this case, the acidity of the eutectics plays a role in affecting the reaction pathways. It is observed that eutectics with lower acidities like ChCl-Ph tend to have higher selectivities towards HMF, and in solvents with higher acidities, like ChCl-OA, HMF readily hydrolyses to levulinic and formic acids. It is also important to note that the mechanism of isomerization described in this study is applicable only to homogeneous Lewis Acids. Since the focus of this study was the solvent system, there hasn't been an in-depth study into different catalysts. It is believed that heterogeneous alternatives will be successful in enabling this isomerization, and it is expected that it will still be possible to select between these eutectics when one product is desired over the other.

3.5 Hydrolysis and Dehydration of Sucrose

The study of sucrose as a potential feedstock is of increasing importance. In countries like Brazil where sugarcane is inexpensive and plentiful, cane sugar, which is primarily sucrose, is a preferred feedstock for biofuel production. Since 2008, BP has invested in technologies to convert cane sugar into butanol, another biofuel [74]. In order for ILs as a biomass conversion technology to be competitive, they must be able to handle a variety of feedstocks.

Sucrose is a disaccharide, consisting of glucose and fructose monosaccharides bound by a glycosidic bond. Being molecules studied earlier in this work, the study of sucrose represents a natural increase in complexity in our study of biomass conversion. In studying solvents for the conversion of sucrose, it is important to investigate their ability to hydrolyze the glycosidic bond, and break the disaccharide

into the constituent monosaccharides, in addition to their ability to dehydrate the monosaccharides. Once again, the experimental and analytical methods developed in Chapter II were used. Experiments were carried out at a temperature of 100 °C in stirred batch reactors. The reactions were carried out with and without the Lewis Acid catalyst $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and the effect of the catalyst on the product distribution was studied. In each case, the initial sucrose loading was 0.29 mmol, and 0.15 mmol catalyst was used in studies that involved the use of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The activities of the QAS-based eutectics were compared to the activity of $[\text{bmim}]\text{Cl}$.

Figure 3.14(a) shows the results of the reaction carried out in $[\text{bmim}]\text{Cl}$. The ratio of the moles of reactant/product to the moles of sucrose are plotted on the y-axis. At time $t = 0$, the reaction mixture contains equal number of moles of glucose and fructose per mole of sucrose. After a reaction time of 4 h in the absence of a catalyst, it is observed that most of the fructose is consumed, while glucose remains unconsumed. It is also observed that approximately one mole of HMF is formed without any other products. This indicates that in $[\text{bmim}]\text{Cl}$, the hydrolysis of sucrose does take place. On hydrolysis, the dehydration of fructose proceeds to produce HMF. While in the absence of any catalyst, glucose remains unreacted, in the presence of a Lewis Acid catalyst, glucose is consumed too, and the mole ratio of HMF to sucrose approaches 2. This implies that while fructose can easily dehydrate to make HMF, in the presence of the catalyst, glucose can now undergo catalytic dehydration to HMF as described in Chapter II. The pathways with and without a catalyst are shown in Figure 3.15. Since the yield of HMF in the absence of a catalyst is almost 100 %, it follows that the only path to make humins are from glucose.

In ChCl-Ph , even in the absence of a catalyst, the hydrolysis of sucrose takes place, and fructose is converted to HMF. The glucose however does not remain unreacted. While some of it is converted to HMF, a majority of the glucose is converted to humins. In the presence of a catalyst, the concentration of HMF marginally increases,

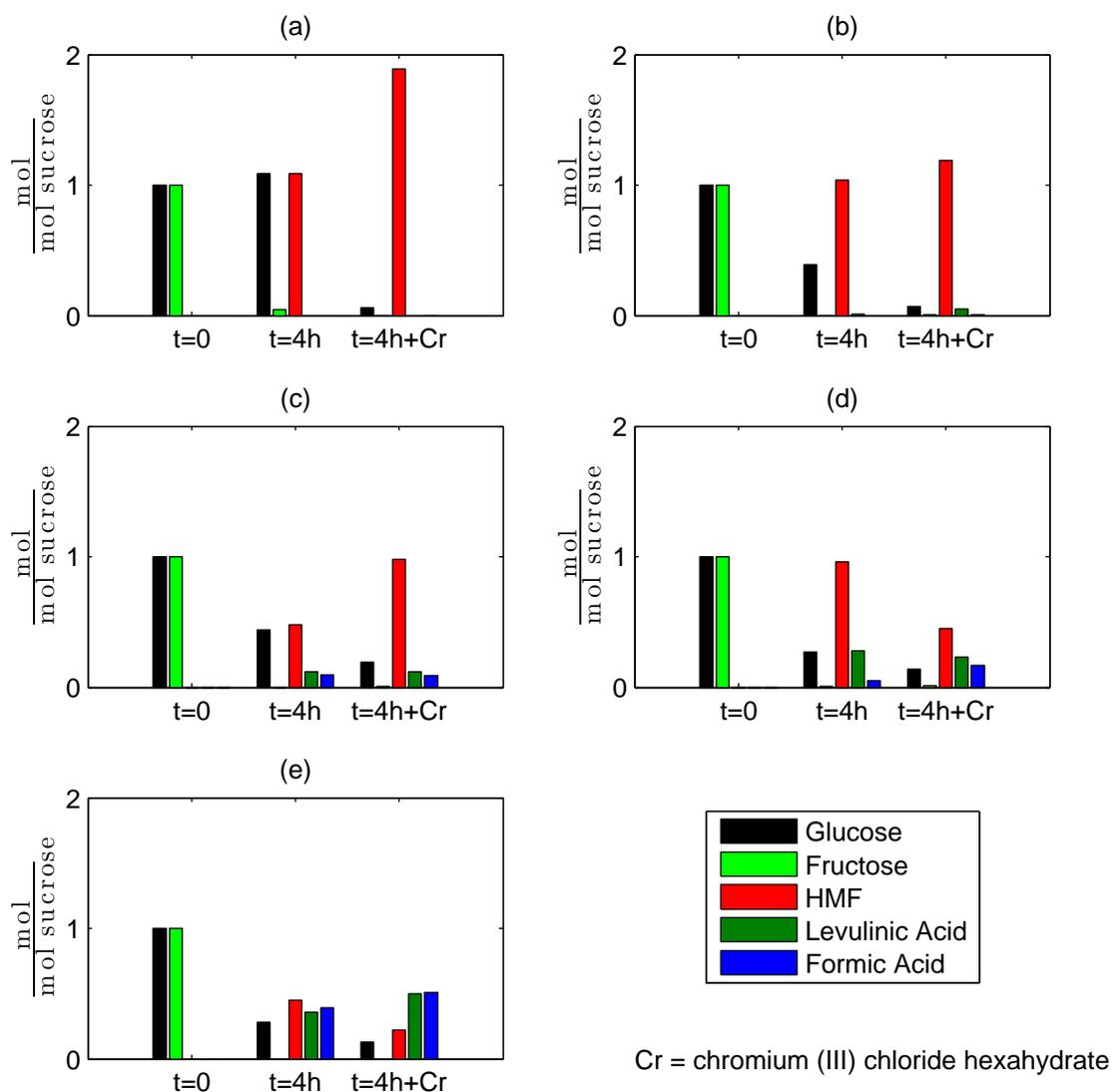


Figure 3.14: The results of the hydrolysis and subsequent dehydration of sucrose in different solvents are shown here. The reactions were carried out at 100 °C, first without a catalyst (labeled as 't=4h'), and then in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (labeled as 't=4h+Cr'). The product distributions at 4 h normalized to the number of moles of sucrose are shown here. The results shown here depict activity in different solvents: (a) [bmim]Cl (b) ChCl-Ph (c) ChCl-BA (d) ChCl-CA and (e) ChCl-OA.

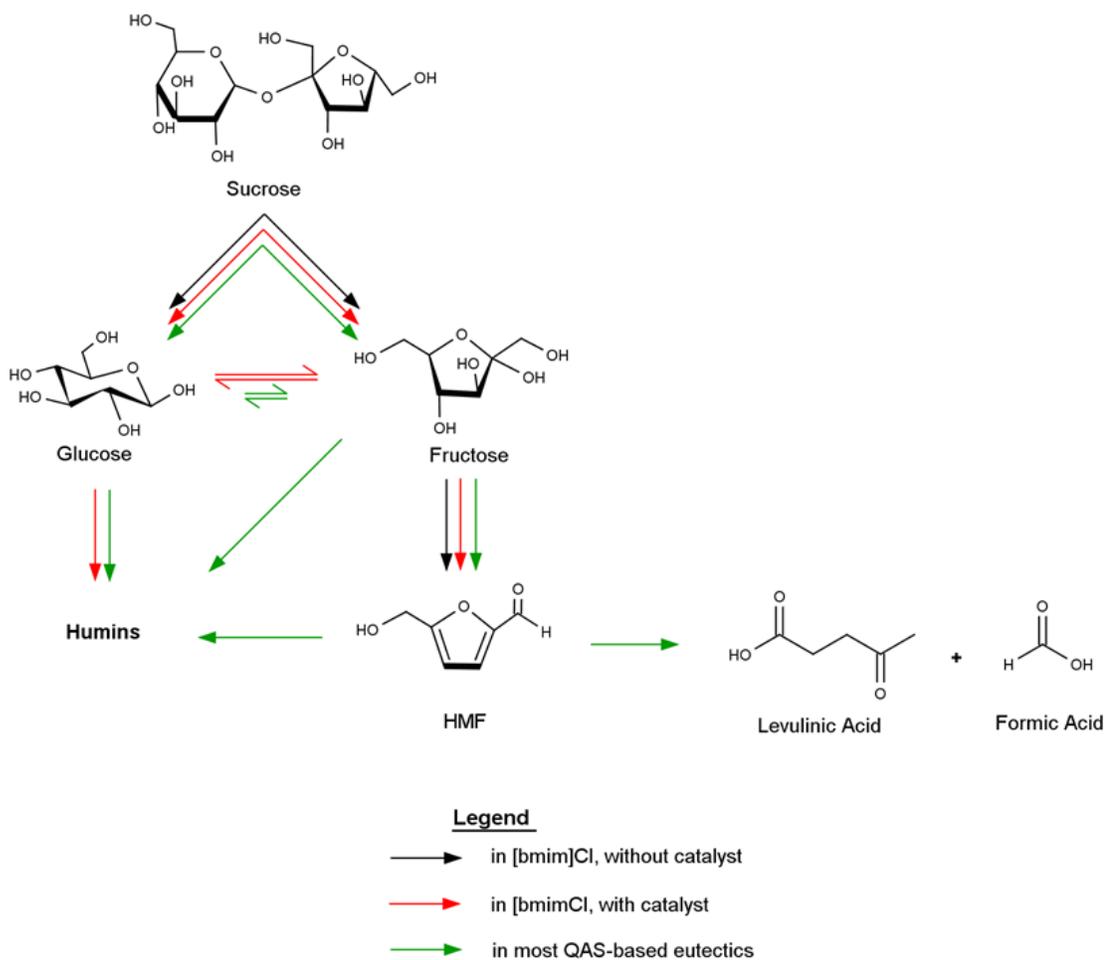


Figure 3.15: Reaction pathways in the hydrolysis of sucrose and the subsequent dehydration of its monosaccharides in [bmim]Cl and the QAS-based eutectics. Pathways in both catalyzed and non-catalyzed scenarios for [bmim]Cl are shown here. In green are the pathways observed in the eutectics. However, the hydrolysis of HMF is not observed in ChCl-Ph.

while the consumption of glucose is accelerated. Similar behavior is seen in less acidic solvents like ChCl-BA as well (Figure 3.14(c)). In both cases, very little levulinic and formic acids are seen. When the acidity of the solvent increases, like in ChCl-CA and ChCl-OA, the addition of the catalyst accelerates both the consumption of glucose, as well the hydrolysis of HMF - to a higher extent in ChCl-OA than in ChCl-CA.

3.6 Conclusions

In this chapter, QAS-based eutectics were explored as inexpensive and environmentally friendly alternatives to imidazolium-based ILs like [bmim]Cl studied in Chapter II for the conversion of biomass feedstock. Like the ILs, these eutectics have favorable physical properties like low melting point and low vapor pressure. The eutectics are also easy to synthesize, often by preparing a physical mixture of commodity chemicals. In addition, one of the goals of this work was to develop property-activity relationships that might lead to insights into selecting solvents for targeted chemistries. The ability of these solvents to convert various biomass feedstock was tested starting with simple sugars like fructose. Reaction pathways from the sugars were examined, and the differences in reaction pathways in different solvents were studied.

The acidity of the solvents was found to be a factor that controlled reaction pathways. This property of the eutectics could be easily controlled by affecting the partners that make up the eutectic. By manipulating this, it was possible to selectively produce HMF or levulinic acid - two molecules that have been identified to be value-added chemicals from biomass. The study of the reaction pathways also showed that solvents with higher acidity favored the production of levulinic and formic acids formed by the acid hydrolysis of HMF, whereas those with lower acidity usually stabilized HMF and hence led to higher selectivity towards it.

Different feedstocks were tested in these solvents. With fructose, it was possible

to achieve high yields and selectivities towards the products as mentioned above. The dehydration of glucose was attempted with a homogeneous Lewis Acid catalyst ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$). It was found that while the catalyst isomerized glucose into fructose in $[\text{bmim}]\text{Cl}$, the isomerization did not take place in the QAS-based eutectics. This caused low product yield and higher yields of humins. When sucrose was used as a feedstock, it was found that all solvents were capable of breaking the glycosidic bond, and forming the two monosaccharides glucose and fructose. The behavior of each these monosaccharides in the solvents are as observed before.

Therefore, QAS-based eutectics have the potential to be a less expensive alternative to imidazolium-based ILs. They exhibit easily tunable properties that can be tailored to specific reactions and products. However, in this study, it was shown that homogeneous Lewis Acid catalysts cannot be used in the eutectics to isomerize the glucose into fructose - an important reaction in this network. It has been hypothesized that the reason for this is the inability of the eutectics to complex with the Lewis Acid. This hypothesis will be explored more deeply in Chapter IV. It is believed that this mechanism for isomerization is only applicable to homogeneous catalysts. While this study focused on solvent behavior and selection, heterogeneous catalysts, which offer other advantages like easy separation from the reaction mixture, needs to be developed to perform this isomerization. The insights on solvent selection gained in this study can then be applied to developing new solvent and catalyst system capable of effectively converting biomass into valuable products.

CHAPTER IV

Influence of Solvent Species: Low Melting Quaternary Ammonium Salts

4.1 Introduction

Ionic liquids based on the quaternary ammonium cation have been one of the first ILs to have been reported in literature when the synthesis of ethyl ammonium nitrate was reported in 1914 [26]. However, most of the following work concentrated on the use of molten salts for high temperature electrochemistry. Detailed studies of the synthesis and characterization of the tetra-*n*-alkylammonium salts were then described in the 1960s [75]. The most common synthetic approach was a reaction between the trialkylamine of the desired carbon number and a corresponding salt with the desired anion. A few organic reactions were reported, for example, the use of tetra-*n*-hexylammonium benzoate for kinetic studies [26]. Alkali chloraluminates then came to dominate the field, but were not adopted widely due to their instability in water. However, imidazolium and pyridinium-based ILs with alternate anions (halides, hexafluorophosphates, acetates, etc.) were then synthesized in the 1990s and were found to be much more stable in water [76].

Since then, research in imidazolium-based ILs have taken off as has been well documented in Chapters II and III. This is applicable not just to typical organic

reactions, but to biomass conversion as well. It has however, been pointed out that one of the first ILs to report the production of HMF from fructose was a quaternary ammonium-based one, with tetraethylammonium bromide yielding 75 % HMF [37]. There is a need to move away from imidazolium-based ILs since, as has been mentioned before, they are expensive to synthesize and toxic. In addition to imidazolium-based ILs, pyridinium-based and phosphonium-based ILs have been studied, but they too have disadvantages similar to the imidazolium-based ILs. A number of ILs are being currently used for various applications like imidazoles for acid scavenging [77], amine-appended imidazolium ILs for CO₂ capture [78], etc. It has been suggested that low-melting ammonium and phosphonium salts that are already being used currently for other applications might be viable options for transitioning away from imidazolium-based ILs [79]. In fact, the authors have tabulated several low melting salts along with their melting points. This is an attractive option since these salts already have additional uses, and hence don't have to be synthesized specially for usage as a solvent. Even when synthesis of new quaternary ammonium salts is desired, environmentally friendly methods that utilize simple ammonium salts, dialkyl carbonates along with imidazolium-based ILs have been developed [80]. Compared to the conventional methods which use amines and alkyl halides, these methods use non-volatile and relatively benign materials.

The goals of this study were two-fold. The first was to be able to use the strategy outlined above of utilizing compounds that have other primary functions as solvents. These were then applied to the problem of biomass conversion. The widely-available, but oft-forgotten quaternary ammonium-based ILs were chosen, and the reactions studied in earlier chapters, i.e., the dehydration of the biomass feedstocks fructose, glucose and sucrose, were examined. In studying these reactions, it was intended to definitively test the hypothesis that was put forth in Chapter III, that the low hydrogen bonding ability of those solvents were due to the fact that in the formation

of eutectics, the hydrogen bonding sites were used up by the partners, and this led to the inhibition of the isomerization reaction of glucose into fructose. In order to test this hypothesis, which formed the second goal of this study, the activity of these low-melting quaternary ammonium salts in the uncatalyzed dehydration of fructose and the catalyzed dehydration of glucose are compared. If HMF yields from the catalyzed dehydration of glucose are equal to or greater than the uncatalyzed dehydration of fructose, then our hypothesis is true. Additionally, studying the effect of the Lewis acid catalyst $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ on the dehydration of glucose will also provide insights on the behavior of the solvent, and on the effect of the solvent species in solution.

4.2 Choice and Characterization

Among the various low melting quaternary ammonium salts available, Methyl-trioctylammonium chloride (Q8881Cl) was chosen. This salt is widely used as a phase transfer catalyst. As a component of Stark's catalyst, Q8881Cl is used in the environmentally-friendly synthesis of adipic acid, which is used in the synthesis of nylon [81]. Unlike many of the low melting quaternary ammonium salts tabulated in literature [79], the melting point of Q8881Cl is <100 °C, around 75 °C. Furthermore, the salt is immiscible in water. This has benefits in process development, since one of the products of the dehydration reaction that is being attempted in this study, is water.

In order to determine the upper limit of operability of our reactions, the thermal stability of the salt was investigated by the use of the Thermogravimetric Analyzer (TGA). Analysis was carried out under N_2 at a heating rate of 5 °C/min. The results are shown in Figure 4.1. From the weight loss curve, the onset temperature of decomposition, T_{onset} can be determined as the intersection of the baseline weight after drying and the tangent to the decomposition curve. The temperature at which decomposition starts is determined as the start temperature, T_{start} . This

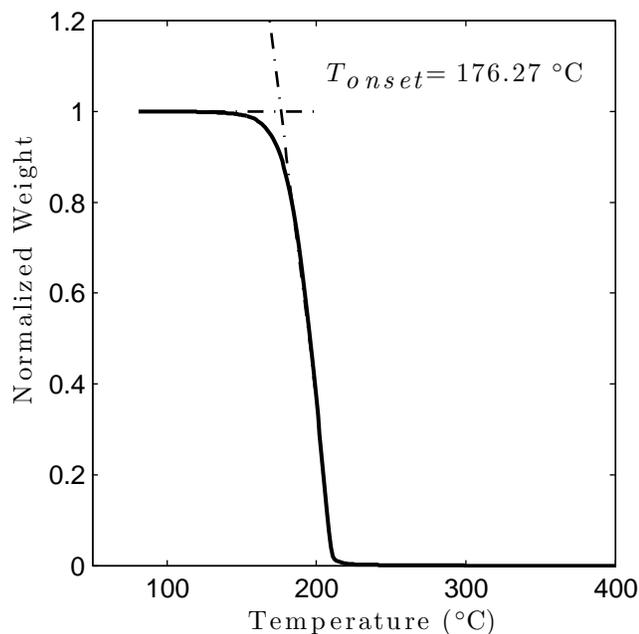


Figure 4.1: Normalized weight loss curve from the thermal decomposition of Q8881Cl under an inert atmosphere. From the curves, the onset temperature of decomposition and the temperature at which decomposition starts are determined.

analysis is commonly carried out in the determination of decomposition temperatures for substances [30]. For Q8881Cl, T_{onset} was determined to be 175.27 °C and T_{start} was determined to be 149.89 °C. While this determines the upper bound at which reactions can be carried out, experiments in this study are being carried out at much lower temperatures.

In addition to the thermal stability, the solvent properties of Q8881Cl were also measured. The measurements were carried out as described in Appendix B. As has been discussed in Chapter III, the hydrogen bond basicity of the solvent, i.e., the Kamlet-Taft parameter β is of particular importance here. The results of these calculations are shown in Table 4.1. This shows that the β value for Q8881Cl is much higher than the eutectics, but not as high as [bmim]Cl. This further supports our hypothesis about the involvement of partner species in the eutectics having a detrimental effect on the hydrogen bond basicity of the resulting solution. The activity

of Q8881Cl is now studied and is correlated to the hydrogen bond basicity. Based on these characterization results, an increase in the activity of the glucose isomerization can be predicted.

Ionic Liquid	β
[bmim]Cl	0.92
ChCl-Ph	0.42
ChCl-CA	0.53
ChCl-OA	0.42
Q8881Cl	0.85

Table 4.1: Table comparing the hydrogen bond basicity represented by the Kamlet Taft parameter, β , of different ionic liquids

4.3 Results and Discussion

The dehydration of the sugars fructose and glucose, along with the hydrolysis and subsequent dehydration of sucrose were studied here. The methods developed in Chapter II, discussed in detail in Appendix A.3 was used here to study the activity of the solvent. However, since Q8881Cl is immiscible with water, acetone was used to dilute the reaction mixture prior to HPLC analysis.

4.3.1 Dehydration of Fructose

From our work in Chapters II and III, it is known that the dehydration of fructose can proceed without a catalyst. Hence, the dehydration of fructose was first carried out in the absence of any catalyst. The experiments were carried out in 1 g IL with 0.27 mmol fructose at 100 °C. Figure 4.2 shows the results of these experiments. It can be seen that the consumption of fructose is accompanied by the production of HMF. The reaction is rather slow in the solvent with the reaction still incomplete after 8 h of reaction time. This is also reflected in HMF production which has a yield of 35 % at 8 h reaction time. This can be compared to reactions studied in other

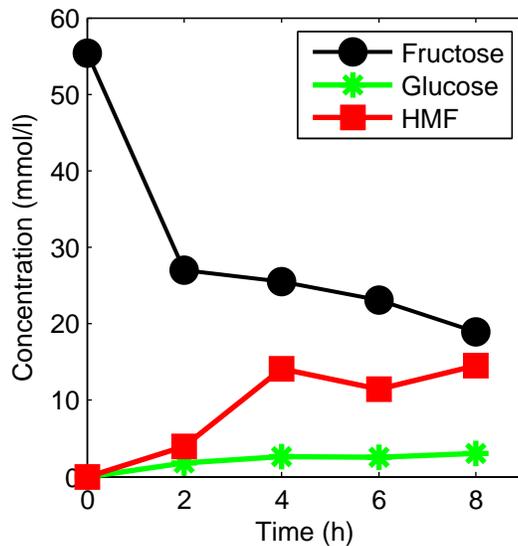


Figure 4.2: Time-series data showing the results of the dehydration of fructose in Q8881Cl in the absence of catalysts. The reactions were carried out at 100 °C.

solvents described earlier in Chapter III, where the ultimate fructose conversion and HMF yields were achieved in 1-2 h.

The slow reaction rate can be attributed to the acidity of the solvent. Since the solvent is not as acidic as the ones previously studied, the reaction proceeds more slowly. The presence of glucose indicates that since Q8881Cl is not acidic, in addition to dehydration to make HMF, fructose can also isomerize to glucose. In the solvents previously studied, this pathway did not exist for fructose. In addition to glucose and HMF, the formation of humins were also experimentally observed.

The yields of HMF and the conversion of fructose can be increased with the addition of catalysts. Experiments were conducted using 0.075 mmol each of H_2SO_4 , a Brønsted acid, and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, a Lewis acid as catalysts. The results of these experiments are shown in Figure 4.3. This shows an increase in yield and conversion respectively of HMF and fructose. The fact that this increased conversion and yield can be brought about by the use of either a Lewis or a Brønsted acid is further proof that low yields and conversions observed in the non-catalyzed case are due to the

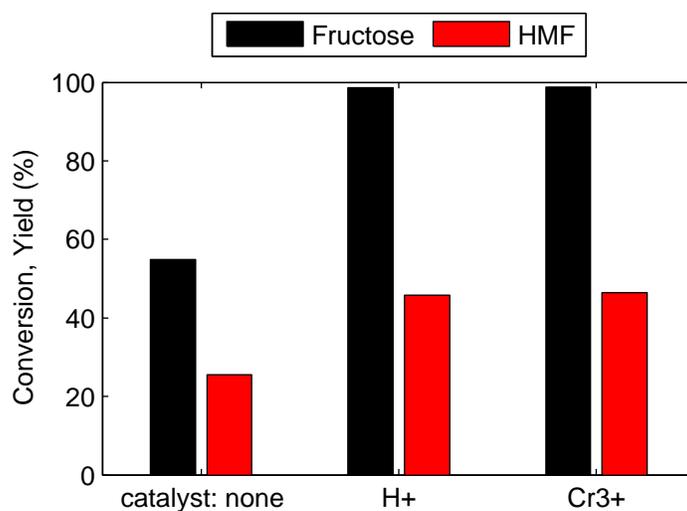


Figure 4.3: HMF yields and fructose conversion from the dehydration of fructose carried out in Q8881Cl in the presence of a Brønsted acid (H_2SO_4) and a Lewis Acid ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$). The catalyst loading in each case was 0.075 mmol. The reactions were carried out at 100 °C.

acidity of the solvent alone.

Though fructose conversion was almost complete on the addition of a catalyst, this did not translate to HMF yields greater than 46 %. It is interesting to note that the HMF yield in using either catalyst is the same. An increase in reaction time did not change the HMF yield as seen in Figure 4.4.

The reaction was also studied at higher temperatures to investigate the effect of temperature on the reaction. The results are shown in Figure 4.5. Again, no increase in HMF yields are seen, which suggests that the reaction is hindered not by kinetics, but by a competition among pathways, most possibly between the production of humins and the production of HMF from fructose.

4.3.2 Dehydration of Glucose

Analogous to the work in Chapter III, the dehydration of glucose was also carried out in Q8881Cl. As a blank, the reaction was first carried out in the absence of any

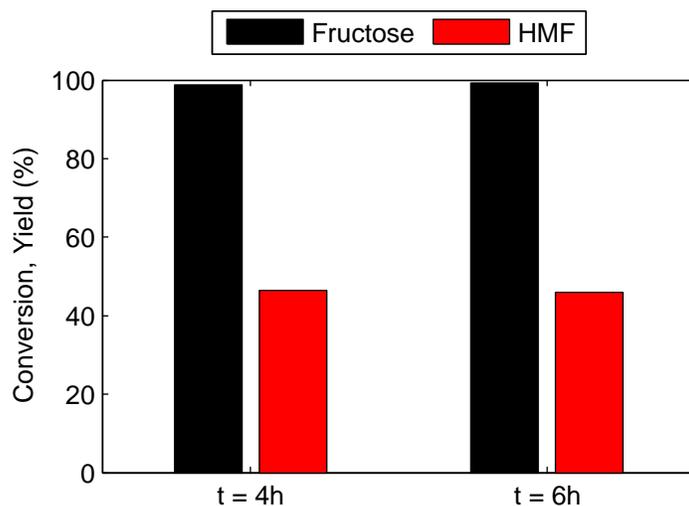


Figure 4.4: Effect of reaction time on HMF yields and fructose conversion in the dehydration of fructose carried out in Q8881Cl in the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The catalyst loading in each case was 0.075 mmol. The reactions were carried out at 100 °C.

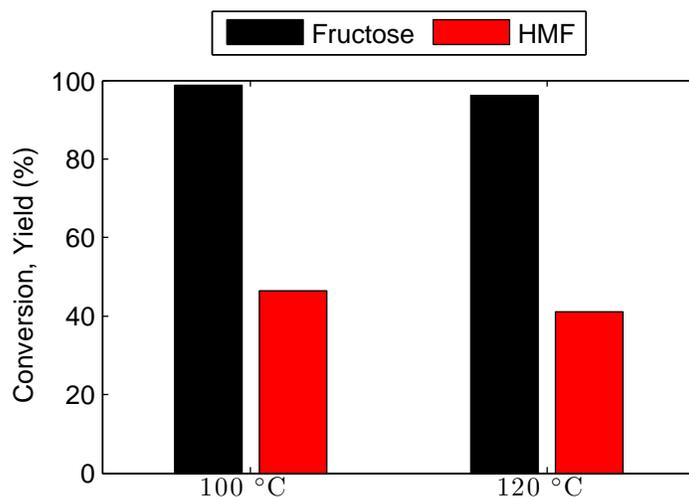


Figure 4.5: The effect of temperature on the conversion of fructose and HMF yield in the dehydration of fructose carried out in Q8881Cl in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The catalyst loading in each case was 0.075 mmol.

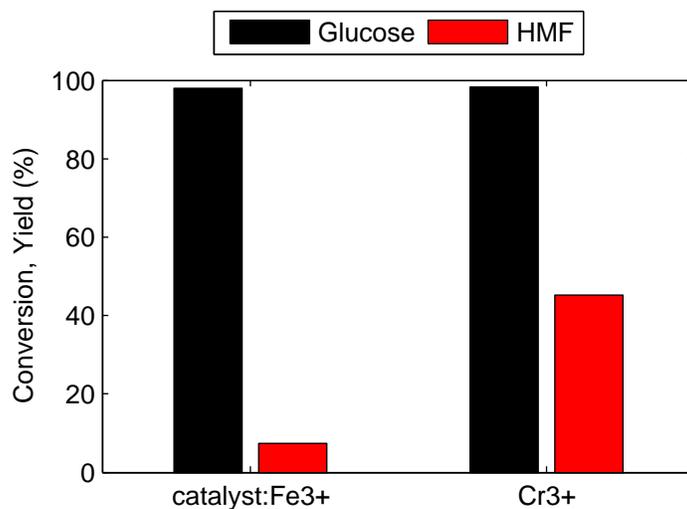


Figure 4.6: Glucose conversion and HMF yield observed during the catalytic dehydration of glucose using FeCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as catalysts. Reactions were run at 100 °C for 4 h.

catalyst. After a reaction time of 4 h, no activity was observed. Lewis acids were then used as catalysts for the reaction. FeCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were tried as catalysts. The reaction was run for 4 h at a temperature of 100 °C. Figure 4.6 shows the results of these experiments. It was observed that when FeCl_3 was used as the catalyst, the glucose conversion was very high, reaching 98 %. However, the HMF yields were low, around 7 %. No other products were observed on the HPLC. When $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was used as a catalyst, high glucose conversions were again observed, about 98 %. This was accompanied by much higher yields of HMF, 45 %. These results are similar to those observed in Chapter II in $[\text{bmim}]\text{Cl}$, and then in Chapter III in the eutectics, where FeCl_3 was an ineffective catalyst compared to $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ which was attributed to the inability of FeCl_3 to form dimers.

The catalytic dehydration of glucose was then studied in detail using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst. The results are shown in Figure 4.7. While the concentration of glucose in the reaction mixture rapidly decreases, the concentration of fructose is observed to first increase and then tail off. This shows that the reaction proceeds

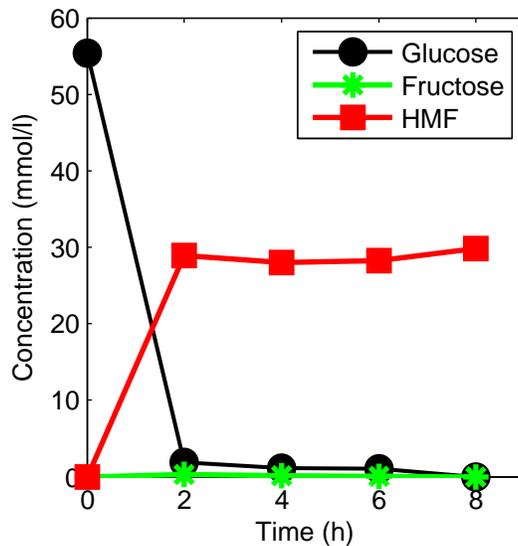


Figure 4.7: Time series data showing the reactants and products during the catalytic dehydration of glucose using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst. Reactions were run at $100\text{ }^\circ\text{C}$.

via the isomerization step, as was observed before in Chapters II and III. These concentration changes of the sugars are accompanied by a corresponding increase in HMF concentration. The final concentration of HMF is reached with a reaction time of 2 h, and the concentration does not change with additional reaction time. This indicates that HMF is a stable product in the solvent and does not decompose or that the hydrolysis of HMF does not take place.

Interestingly, the final yield of HMF is about 52 %, which, while consistent with the results from the dehydration of fructose seen in Section 4.3.1, is significantly lower than what was observed in earlier chapters in $[\text{bmim}]\text{Cl}$, but higher than what was observed in the eutectics. In the QAS-based eutectics, the low yield of HMF was attributed to the inhibition of the glucose-fructose isomerization reaction brought about by the lowering of the hydrogen bonding ability of the solvent. This was due to the hydrogen bonding sites being used up to make the solvent. This problem clearly does not exist in Q8881Cl since the reaction is being catalyzed as demonstrated in Figure 4.6. In the QAS-based eutectics, the production of humins was experimen-

tally observed immediately on quenching, with increasing amounts as the acidity of the solvent increased. However, in Q8881Cl, these condensation products are not immediately observed. When the cooled reaction mixture is allowed to sit at room temperature, the heavy products start to form. The addition of water was also found to accelerate the production of humins.

The plateauing of the HMF production curve suggests that the relatively lower yields is not simply because the reaction is slow, but is an effect of competing pathways. If it were because of a slow reaction, HMF yield would be steadily increasing and not plateauing. This can be further reinforced by studying the effect of temperature on the reaction. Here, the reaction was carried out at 120 °C. Figure 4.8 compares the yield of HMF at these temperatures. It is seen that increasing temperatures, in fact lowers HMF yields. <1 % yields of formic acid and levulinic acid are also observed. These results confirm the fact that there are competing pathways for glucose and suggests that at higher temperatures the breakdown of HMF and the production of humins via condensation reactions are accelerated. At lower temperatures, however, HMF is a stable product in the solvent, and it can be concluded that pathways for the formation of humins are from glucose, and the intermediate fructose.

4.3.3 Hydrolysis and Subsequent Dehydration of Sucrose

As with the work in Chapter III, the ability of a low melting QAS, Q8881Cl in this case, to convert a disaccharide like sucrose was studied. The ability of the solvent to cleave the glycosidic bond and then dehydrate the resulting hexoses were studied. The reactions were carried out both in the absence of and in the presence of a Lewis acid catalyst ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) at a temperature of 100 °C.

The results of the reaction performed in the absence of any catalyst are shown in Figure 4.9. The ratio of the moles of substance to the moles of sucrose is plotted on

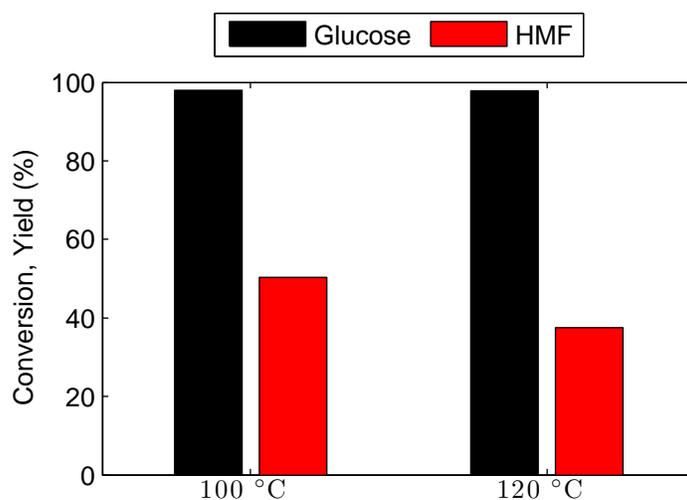


Figure 4.8: The effect of temperature on the conversion of glucose and HMF yield in the dehydration of glucose carried out in Q8881Cl in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The catalyst loading in each case was 0.075 mmol.

the y axis, and its behavior with time is followed. At the beginning of the reaction, glucose and fructose are present in equimolar quantities, and the molar ratio of each of the sugars starts off at 1. It is observed that with time, the amount of glucose remains almost the same, with the ratio hovering around 1. However, the concentration of fructose decreases, leading to lower molar ratios. The consumption of fructose is slow and the conversion levels off around 50 %. This is accompanied by a corresponding increase in the concentration of HMF in the reaction mixture. However, the yield of HMF is low. These results show that in Q8881Cl, the disaccharide can hydrolyze into monosaccharides, and the behavior of the monosaccharides is similar to what was observed in Sections 4.3.1 and 4.3.2, where in the absence of a catalyst, low conversions and yields of fructose and HMF respectively were observed. The behavior of the glucose monosaccharide of sucrose is similar to the blank behavior observed in Section 4.3.2.

The conversion of sucrose was then carried out in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst. The results of these experiments are shown in Figure 4.10. This indicates

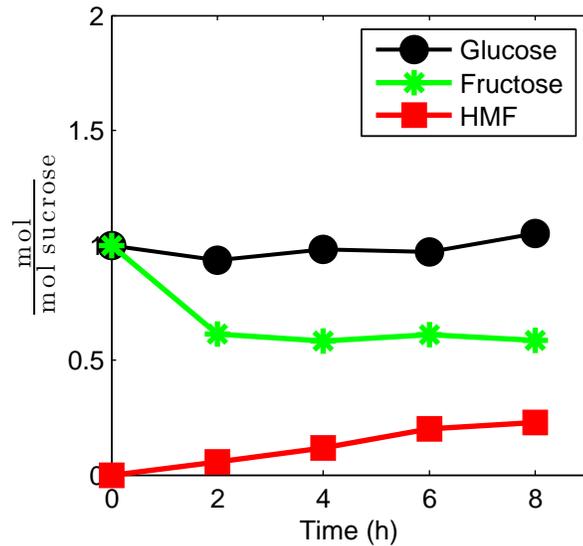


Figure 4.9: The concentration of the monomers of sucrose - glucose and fructose and HMF have been compared to the initial concentration of sucrose, and shown here as a function of time during the hydrolysis and subsequent dehydration of sucrose at 100 °C in the absence of a catalyst.

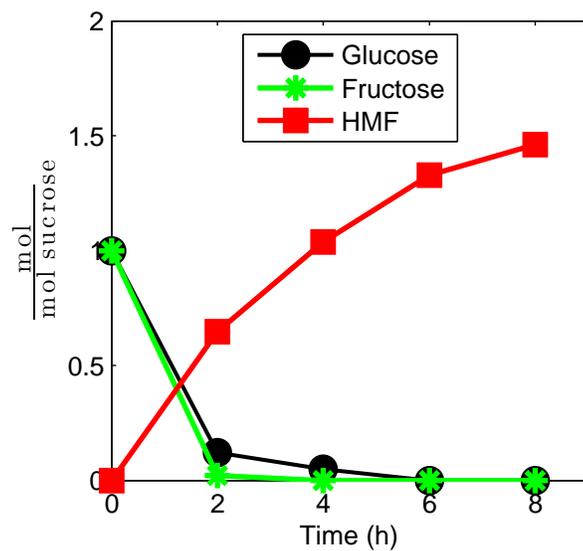


Figure 4.10: The concentration of the monomers of sucrose - glucose and fructose and HMF have been compared to the initial concentration of sucrose, and shown here as a function of time during the hydrolysis and subsequent dehydration of sucrose at 100 °C using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst.

that in the presence of the catalyst, the hydrolysis of the glycosidic bond again occurs and the resulting monosaccharides are consumed quickly, with their mole ratios dropping to zero by 4 h. The concentration of HMF consequently increases. However the mole ratio of HMF to sucrose does not reach its theoretical maximum of 2. In both the non-catalyzed and catalyzed conversions of sucrose, the production of humins as described in Section 4.3.2 was experimentally observed.

4.4 Conclusions

In this chapter, low melting single species quaternary ammonium salts were explored as solvents for the conversion of various biomass feedstock. The motivation for using these solvents is that while imidazolium-based ILs such as [bmim]Cl studied in Chapter II were effective solvents, they were expensive and toxic. While low-cost eutectics based on the quaternary ammonium cation, studied in Chapter III, showed the ability to tune product selectivities based on solvent characteristics, the inhibition of isomerization reactions was found to be a drawback. These low melting QAS solvents have the potential to alleviate these drawbacks.

Q8881Cl was chosen as a solvent, since it is already commercially available owing to its primary use as a phase transfer catalyst. In addition, it also has favorable physical properties - low melting point (<100 °C), and reasonable thermal stability, and chemical properties (high hydrogen bond basicity). Starting with fructose, the ability of the solvent to convert different feedstocks was tested in the solvent. While the low acidity of the solvent results in slow kinetics for the non-catalyzed dehydration of fructose, the addition of an acid - either Lewis or Brønsted, causes an increase in HMF yields. The insights developed in the work described in Chapter III were applicable to these solvents too. In particular, the effect of solvent acidity and hydrogen bonding were found to have a profound effect on product selectivities and reaction pathways. Unlike in the eutectics where the low hydrogen bonding ability resulted in

low HMF yields in glucose dehydration reactions, these solvents are single species like the imidazolium-based ILs and hence retain the hydrogen bonding ability required for isomerization reactions to take place. HMF is a stable product in this solvent, and the rate of production of humins is also slow, which has positive implications for process development. Similar results were also found in reactions with sucrose. In the absence of a catalyst, the hydrolysis of the disaccharide takes place, and the fructose undergoes a dehydration to HMF, albeit slowly, while glucose remains in the solution unreacted. However, in the presence of a catalyst, both the monosaccharides undergo dehydration reactions effectively to form HMF. In all cases, humins production is observed, but compared to studies with the eutectics, the amount of humins formed is lower.

In conclusion, low melting quaternary ammonium salts like Q8881Cl are attractive alternatives to the more common imidazolium ILs for the conversion of biomass feedstock. Unlike imidazoliums that have to be synthesized only for use as ILs, many of these salts are already produced on relatively large scales and have alternate uses, for e.g., the salt Q8881Cl, used in this study is used as a phase transfer catalyst.

CHAPTER V

Cellulose Hydrolysis and Subsequent Dehydration

5.1 Introduction

Cellulose as a biomass feedstock for the production of fuels and chemicals, is important since, being inedible, it does not compete with food resources. Additionally, the sources that are typically proposed for cellulosic biomass like switchgrass are perennial crops as opposed to feedstocks like corn and soybeans used for ethanol and biodiesel production. Hence, the conversion of cellulose is of utmost importance. ILs are especially a pertinent medium to study the conversion of cellulosic feedstock in, since they have the potential to maximize its utilization and conversion to value-added products.

The dissolution of cellulose was first reported in dialkylimidazolium ILs [35]. It has been found that smaller anions that accept hydrogen bonds like Cl^- and Br^- could dissolve cellulose while larger anions like PF_6^- could not, with the solubility going as $\text{Cl}^- > \text{Br}^- > [\text{PF}_6]^-$. This correlation has been confirmed by studies that have shown stronger interaction of the carbohydrate with the anion as compared with the cation [82]. It was also observed that increasing alkyl substitutions on the cation decreases the solubility of cellulose [35, 83]. The solubility of these macromolecules has been attributed to the C-H... π interactions with the IL [84]. Based on this, several ILs have been designed pairing π e^- rich aromatic systems with the imida-

zolinium cations, and these ILs have shown increased solubility of not just cellulose, but raw wood like spruce itself [85]. The increased π interactions and the associated hydrogen bonding between the solvent and cellulose leads to the breakdown of the crystallinity of the cellulose which has been confirmed with ^{13}C -NMR studies [86]. While most studies have focused dialkylimidazolium-based ILs, primarily [bmim]Cl for the conversion of cellulose, other imidazolium-based ILs with allyl groups have also been promising [51]. In addition to imidazolium ILs, other solvents like a mixture of N,N-dimethylacetamide and LiCl have also been found effective in dissolving cellulose [46].

The ability of ILs to solvate cellulose means that previously inaccessible routes for conversion of the carbohydrates can be applied. Innovative schemes like using an ionic liquid environment to carry out the pyrolysis of cellulose has been performed [87]. Various derivitization reactions have been demonstrated. In the absence of any catalysts, the homogeneous acetylation of cellulose has been shown [88]. Other reactions such as acylation and carbamylation of cellulose has also been demonstrated [89, 90]. More importantly, reactions along the scheme described in Chapter I have been demonstrated. The depolymerization/hydrolysis of cellulose has been carried out by various researchers using acid catalysts like sulfuric acid [38], and that of wood in trifluoroacetic acid [91]. One-pot synthesis of HMF from cellulose has been demonstrated using CrCl_2 and CuCl_2 as catalysts [44]. The use of microwave heating has been shown to increase the rates of both cellulose dissolution and the formation of HMF using CrCl_3 catalysts [43, 47]. A comparison of alkali and alkaline earth metals and transition metal catalysts for the conversion of cellulose found that transition metals were a much better choice [17]. Again of note is that most of the studies have focused on the usage of imidazolium-based ILs for cellulose conversion, with a few exceptions where N,N-dimethylacetamide and LiCl has been used [92], in the presence of metal chloride catalysts.

In the present study, the depolymerization and hydrolysis of cellulose and the subsequent dehydration of the resulting monosaccharides is studied in different ILs. Of particular interest are the activities of the quaternary ammonium-based eutectics introduced in Chapter III and the low melting quaternary ammonium salt introduced in Chapter IV, Q8881Cl. The activity in [bmim]Cl is studied and is used as a benchmark to compare the activity of the other solvents. From literature, the importance of hydrogen bonding on the dissolution and reactivity of cellulose in the solvents was understood, and the hydrogen bonding ability of the solvents were studied using the Kamlet-Taft parameters. These parameters were then correlated with the activity of the solvents. This strategy has been used before for imidazolium ILs [93]. The differences in cellulose depolymerization mechanisms between the different solvent classes were also studied using the number average DP as an indicator. It was found that though the eutectics predictably did not dissolve cellulose, they were successful in depolymerizing and hydrolyzing cellulose. The resulting sugars could also be converted to HMF, formic acid and levulinic acid, though the activity was kinetically limited.

5.2 Results and Discussion

5.2.1 Dissolution of Cellulose

In studying the ability of the solvents to process cellulose, the first step was to study the dissolution of cellulose in these ILs. To do this, ILs were melted, and maintained at a temperature of 100 °C in a well-stirred oil bath. Fixed amounts of cellulose were then added to the mixture, generally about 1 wt% of the IL. Stirring was then continued at the same temperature for 30 – 45 min, and the solution was then examined to see if the cellulose was dissolved. The results from these studies, using [bmim]Cl, Q8881Cl and ChCl-OA as representative examples, are described here. It was observed that [bmim]Cl solution was clear indicating that the cellulose

was completely dissolved. In Q8881Cl, it was observed that right after the addition of cellulose, the solution was turbid, but as stirring was continued, a clear solution started developing. However, a small amount of undissolved cellulose was observed. This indicates that it takes longer for the cellulose to dissolve. Studies to calculate the solubility limit were not carried out, so it is uncertain whether the presence of undissolved cellulose is due to a solubility limit or because of slow solvation. The IL is also more viscous than [bmim]Cl, leading to imperfect stirring conditions. However, in ChCl-OA, it was observed that the addition of cellulose resulted in a turbid milky white solution, and the turbidity remained with increasing time indicating that cellulose is completely insoluble in the solvent.

Based on our understanding of the dissolution process, these results are expected. As has been discussed in Section 5.1, the ability of a solvent to dissolve macromolecules like cellulose depends on its ability hydrogen bond with cellulose. This breaks the crystallinity of cellulose and hence dissolves it. Eutectics like ChCl-OA have low hydrogen bond basicities as can be seen in the value of their Kamlet Taft parameter, β . These values have been shown in earlier chapters, but have been reproduced in Table 5.1 for convenience. This means that eutectics like ChCl-OA, ChCl-CA cannot dissolve cellulose, while solvents with higher β values like [bmim]Cl and Q8881Cl can.

Ionic Liquid	β
[bmim]Cl	0.92
ChCl-Ph	0.42
ChCl-CA	0.53
ChCl-OA	0.42
Q8881Cl	0.85

Table 5.1: A comparison of the hydrogen bond basicity represented by the Kamlet Taft parameter, β , of different ionic liquids

5.2.2 Hydrolysis of Cellulose: Observed Kinetic Effects

Though it was found that the eutectics were unsuccessful in dissolving cellulose, the hydrolysis of the cellulose was attempted using a Lewis acid catalyst $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Protocols developed earlier and described in Appendix A were once again used in this study. In the presence of the Lewis Acid catalyst, it is not possible to stop the reaction at the products of hydrolysis, the simple sugars; the reaction proceeds with the dehydration of the resulting sugars. The results of these experiments are shown in Figure 5.1 where the product distribution at the end of 4 h reaction time is presented. The results are shown for reactions carried out in $[\text{bmim}]\text{Cl}$ and ChCl-OA which were used as representative examples of the most acidic eutectic and the neutral imidazolium IL. It is seen that in $[\text{bmim}]\text{Cl}$, HMF is the only product. In ChCl-OA , HMF is observed along with significant amounts of glucose and observable quantities of formic and levulinic acid. These results are significant since it was shown that even without the dissolution of cellulose, it is possible to hydrolyze cellulose and then dehydrate the resulting monosaccharides.

The results from the dehydration of glucose in ChCl-OA studied in Chapter IV, show that in this solvent, levulinic and formic acid is formed selectively at the expense of HMF. However, in this case, along with unconverted glucose in solution, the concentration of HMF was also lower than that of its hydrolysis products levulinic and formic acids. It was believed that these results might be the effect of the slow kinetics of the reaction. To test this, the hydrolysis experiments using $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were run for longer times up to 45 h with sampling at various intervals. The results of these experiments are shown in Figure 5.2. Here, the effect of time is shown for reactions carried out in ChCl-OA . It is seen that as the hydrolysis of cellulose proceeds, the concentration of glucose in solution increases. Some of this glucose undergoes a dehydration of HMF, but HMF itself leads to the formation of levulinic acid and formic acid. The concentration of HMF increases initially and then drops

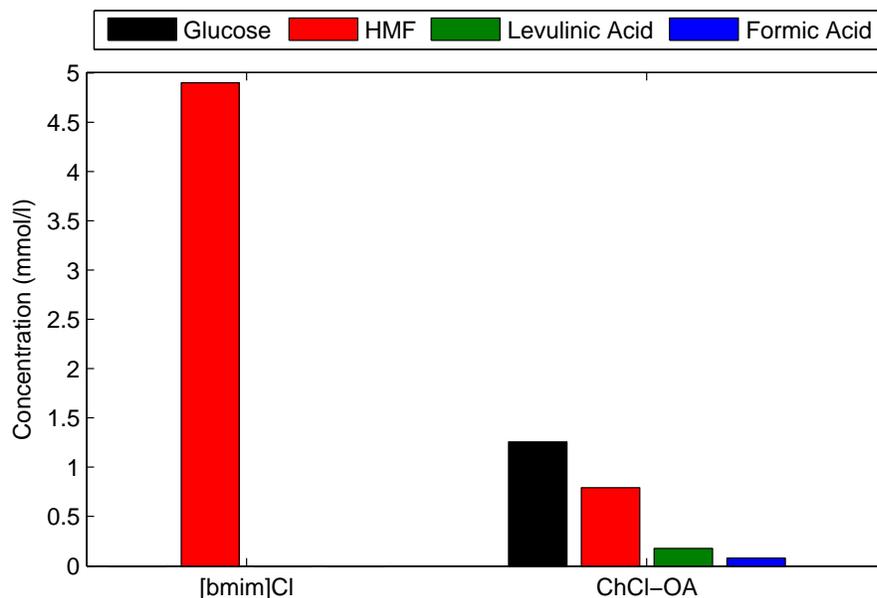


Figure 5.1: Product distribution from the hydrolysis and subsequent dehydration of cellulose at 100 °C in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in [bmim]Cl and ChCl-OA after 4 h of reaction time

off, while the concentrations of formic and levulinic acid increase. While glucose is consumed not only to make HMF, but also humins, its concentration remains fairly steady with only a slightly decreasing trend. This indicates that as the hydrolysis of cellulose proceeds, the concentration of glucose in solution is replenished. It is also noted that the trend observed in Chapter III, where HMF is not a stable product in ChCl-OA, but decomposes to produce levulinic and formic acids is seen here too.

This behavior is not seen not just in ChCl-OA, but in the other eutectics, and the low melting quaternary ammonium salt, Q8881Cl that have been studied so far as well. Figure 5.3 shows the product distribution of the reaction carried out at 100 °C for 45 h in [bmim]Cl, Q8881Cl, ChCl-Ph, ChCl-CA, and ChCl-OA. It is seen that in [bmim]Cl, HMF is the only product. HMF is also produced in Q8881Cl, but its concentration is lower than that observed in [bmim]Cl. These results are in agreement with the results of glucose dehydration in Q8881Cl seen in Chapter IV, where it was

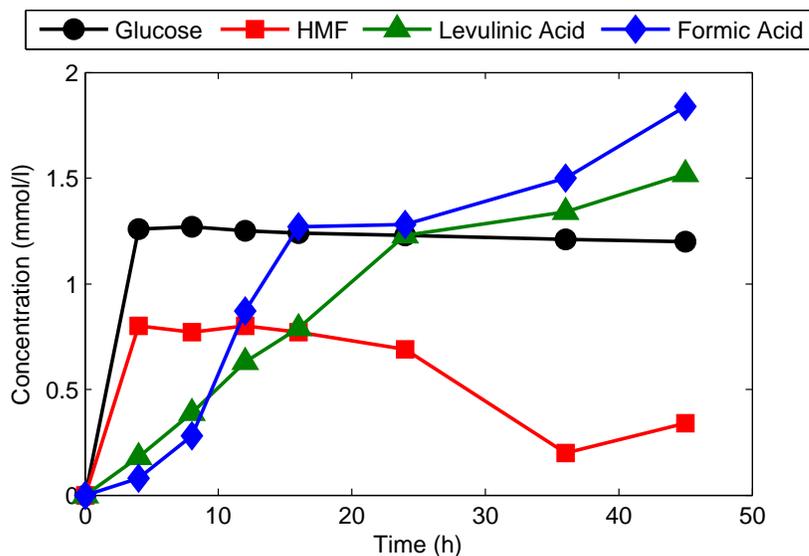


Figure 5.2: Results from the hydrolysis of cellulose carried out at 100 °C in ChCl-OA in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ for long times, up to 45 h

observed that while the Lewis acid was successful in catalyzing the isomerization of glucose and the subsequent dehydration, HMF yields were lower owing to competing side reactions.

In ChCl-Ph, lower concentrations of HMF are formed, and no levulinic and formic acids were observed. In ChCl-CA, significantly lower concentrations of HMF are accompanied by moderate concentrations of levulinic acid and formic acid. Though it was seen in Chapter IV, HMF is a stable product in ChCl-CA at shorter times, at long times, HMF decomposes into formic and levulinic acids. In ChCl-OA, as has been discussed earlier, levulinic and formic acids are selectively formed at the expense of HMF.

5.2.3 Depolymerization of Cellulose

It was suspected that the cause for the slow kinetics of the hydrolysis of cellulose in the eutectics compared to the imidazolium-based IL was their inability to dissolve cellulose. This can have an effect on the depolymerization and subsequent reaction of

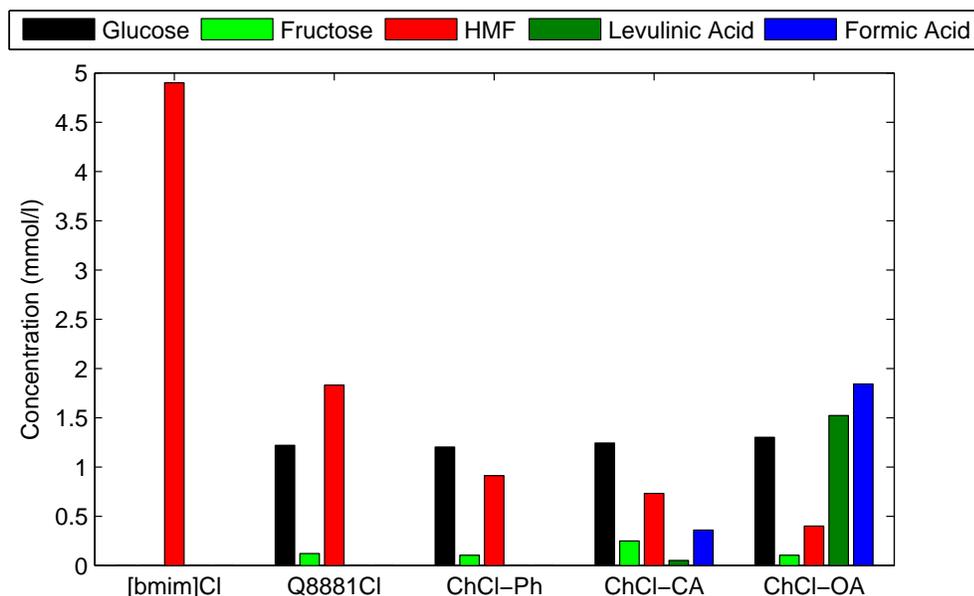


Figure 5.3: Product distribution when the cellulose hydrolysis and subsequent dehydration was carried out in all solvents for 45 h at 100 °C in $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

cellulose. To investigate this, it was decided to measure the degree of polymerization (DP) of cellulose in different solvents as a function of time. In addition to providing insights on the reason for the slow kinetics in eutectics, this study will also help understand the mechanism of depolymerization of a macromolecule like cellulose in different solvents.

In this study, as in Section 5.2.1, the solvent was first brought to reaction temperature of 100 °C in a stirred reactor vial immersed in a temperature-controlled oil bath. 1 wt% cellulose was then added and stirring was continued for 30 min. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was then added to begin the reaction. After the desired length of time, the reaction was quenched, and the reaction mixture was diluted with water. The number-average DP of the remaining cellulose was then determined as a ratio of the total glucosyl monomers present in solution to the ratio of the reducing end concentration. The total glucosyl monomer concentration was determined by the phenol-sulfuric acid method and the reducing end concentration was determined by

a modified 2,2'-bichinchoninate (BCA) method, both of which have been developed in literature [94]. The specifics of the method and the protocol has been detailed in Appendix C.

As a representative example, the results of these experiments carried out in two solvents are detailed here. [bmim]Cl and ChCl-OA were chosen here as they represent two extreme cases - [bmim]Cl is a neutral IL in which cellulose readily dissolves and the maximum hydrolysis and subsequent dehydration was observed, and ChCl-OA is the most acidic of the solvents studied and does not dissolve cellulose. These results are shown in Figure 5.4. The initial DP of the microcrystalline cellulose used here was 212. Each of the DP values have an uncertainty of ± 8 owing to the repeatability of the analytical protocol involved in the calculation of the DP. This value also agrees with the DP of other cellulose samples studied in literature [94]. In the absence of a catalyst, it was observed that there was no significant change in the DP after 1 h at 100 °C in [bmim]Cl. This means that the hydrolysis of cellulose does not take place without the catalyst being present. This agrees well with observations in literature, where no decrease in DP was observed, and recrystallization of dissolved cellulose was possible with changes in morphology only [35, 44]. On the addition of a catalyst, it is seen that the DP of cellulose falls off rapidly in [bmim]Cl from the initial value of 212 to its final value, around 11 in one hour. However in the case of ChCl-OA, there is a gradual drop off in the value of DP. These experiments were not carried out for long times like in Section 5.2.2 since the difference between the two solvents is evident.

These results shed some light on the differences in the mechanism of breakdown of cellulose and explain the reason for the slow kinetics observed in the eutectics. In [bmim]Cl, due to the breakdown of the crystallinity and subsequent dissolution of cellulose, the hydrolysis of the polymer is possible in the presence of the Lewis Acid catalyst. This also provides easier access to the resulting glucose monomers that can undergo the subsequent isomerization and dehydration to HMF. In ChCl-OA, the

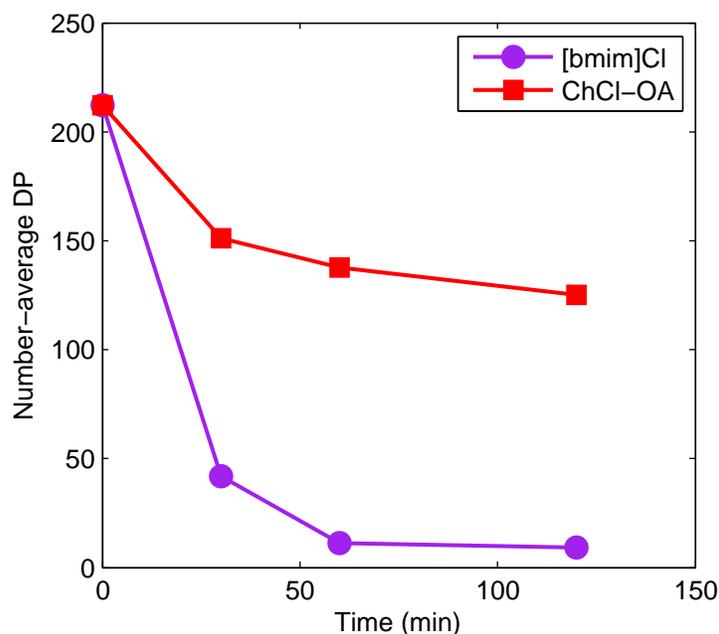


Figure 5.4: Comparison of the number-average Degree of Polymerization of Cellulose in different solvents as a function of time when the hydrolysis reaction is carried out at 100 °C in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

gradual decrease in DP suggests that cellulose is sequentially attacked by the solvent from the polymer ends. This limits access to the glucose monomers and combined with the inhibited isomerization reaction, results in slow kinetics of the hydrolysis/dehydration reaction. Nonetheless, these results show that even when cellulose is not dissolved by the solvent, it is still possible to depolymerize cellulose and the resulting monomers undergo subsequent dehydration reactions as expected.

5.3 Conclusions

The goal of this study was study the ability of the quaternary ammonium-based eutectics and the low melting quaternary ammonium salt previously used, to dissolve and then possibly aid in the conversion of cellulose to value-added products. From the understanding of the mechanism of cellulose dissolution, it was evident that the hydrogen bonding ability of the solvent is responsible for solvability. The hydrogen

bond basicity of the solvents were determined using the Kamlet-Taft β parameter, and it was possible to predict that cellulose was insoluble in the eutectics, and Q8881Cl, had a relatively higher β , but was still not as good as [bmim]Cl. This was found to have implications on solubility as well.

The hydrolysis and subsequent dehydration of cellulose was also studied in the different solvents with the help of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. It was found that though the eutectics could not dissolve cellulose, they were still successful in hydrolyzing cellulose and then making the hydrolysis products of the monosaccharide. However, it was found that the rate at which these reactions took place were much slower than what was observed in [bmim]Cl. Studying the degree of polymerization of the cellulose in solution provided valuable insights on the possible differences in the mechanisms of attack in the two solvents which could explain the difference in activity.

Thus, there is a case for the use of low-cost, non-toxic alternatives to imidazolium ILs for the conversion of cellulose. While some choices like Q8881Cl, which make use of materials that already have a primary usage, are more attractive than others (the eutectics) in terms of selectivity towards HMF, the eutectics provide a path to affect product selectivities.

CHAPTER VI

Conclusions and Future Work

6.1 Conclusions

The goal of this thesis was to develop new methods for the conversion of biomass to other value-added chemicals and fuels. In doing so, it was also desired to develop processes that were environmentally friendly and economical. The conversion of biomass feedstocks was attempted using ionic liquids as solvents. These being low melting salts, have insignificant vapor pressure, and thus minimize solvent losses and emissions, thereby providing a 'green' medium for chemical reactions. Perhaps the most attractive property for the conversion of biomass is their ability to dissolve macromolecules like cellulose that are naturally present in biomass. Having biomass in solution opens them up to a wide variety of reactions and efficient transformations that are impossible with other conversion techniques like pyrolysis and gasification. Most studies researching ILs for the conversion of biomass have been focused on the use of 1,3-dialkylimidazolium halides as solvents. While they display good solubility of cellulose and the conversion to value-added platform chemicals like HMF, they tend to be expensive and toxic. This makes the inevitable environmental release coupled with the high costs for industrially relevant quantities a difficult proposition. In this thesis, the development of solvents based on less expensive and less toxic materials, particularly based on the quaternary ammonium cation, for the conversion of biomass

feedstocks were targeted. Fundamental studies on solvent behavior and solute-solvent interactions were used to study the effect of different solvents in these reactions. The imidazolium-based ILs were used as a benchmark of activity to compare the reactivity newly developed solvents and the reaction pathways in them.

In Chapter II, the conversion of glucose was studied in the dialkylimidazolium IL, [bmim]Cl. The purpose of this study was two fold. One was to develop experimental protocols and analytical tools to study the reaction and the reaction network using a well-established solvent system. A stirred batch reactor for carrying out the reaction and then analyzing reaction mixtures on an HPLC proved to be the most successful. Using these protocols, a variety of parameters like catalyst, catalyst loading, temperature and time, that affect the dehydration of glucose were studied. The pathways in the dehydration of glucose proceeds first with an isomerization to fructose before the dehydration step to HMF. It was found that HMF was a stable product in the pathway, and glucose underwent a side reaction resulting in the formation of polymeric humins. The second goal of this study was to use these experimental results and build a phenomenological model to predict activity. A phenomenological model was built and MATLAB was used to solve mass balances, and determine rate parameters. While the model was fairly successful in predicting HMF yields, it was found that the model resulted in the overprediction of HMF yields. This was attributed to the assumptions made in the rate equations governing the formation of humins in the reaction network.

In Chapter III, deep eutectic solvents based on the quaternary ammonium salts were explored as possible alternatives to imidazolium ILs. The quaternary ammonium salt choline chloride was paired with different partner compounds to make the eutectics. The solvent properties of the eutectics were characterized, and the acidity and hydrogen bonding ability of the solvents were determined. The activity of these solvents in different reactions from the dehydration of simple sugars like fructose and

glucose to disaccharides were studied. It was found that it was possible to tune the selectivity of the products to either HMF or levulinic and formic acids based on the acidity of the partner. However it was found that the isomerization of glucose, a necessary pathway in the network, was inhibited in the eutectics. It was hypothesized that this was due to the low hydrogen bond basicity of the solvents since the hydrogen bonding sites are used up by the partners to make the solvent.

This hypothesis was tested in Chapter IV with the help of low melting single species quaternary ammonium salts. Q8881Cl was chosen as an example of such a solvent. The thermal stability of the solvent was characterized by TGA and the Kamlet Taft parameters, especially the hydrogen bond basicity, β was determined. It was found that Q8881Cl had a higher β value than the eutectics, but not as high as that of [bmim]Cl. This further supports the hypothesis regarding the effect of solvent species in solution and their contribution to the hydrogen bonding ability. The study of the conversion of fructose and glucose in Q8881Cl further confirmed that this increase in hydrogen bonding ability in these solvents can be correlated to an increase in the activity of isomerization reaction, with increased yields of HMF in the glucose dehydration reaction.

Finally, in Chapter V, the depolymerization of cellulose in these solvents is studied. The first step of the depolymerization process is the dissolution of cellulose. The dissolution of cellulose depends on the ability of the solvent to hydrogen bond with the cellulose, break its crystallinity, and hence dissolve it. This implies that the hydrogen bonding ability of the solvent plays an important role in its ability to dissolve cellulose. From our determination of the Kamlet Taft parameters, it was possible to predict the solvating ability of each of the solvents studied. It could then be predicted that solvents with higher β values like [bmim]Cl and Q8881Cl displayed higher ability to dissolve cellulose than the eutectics. This prediction was borne out in dissolution studies. On studying the hydrolysis of cellulose in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, it was

found that in spite of the low solubility of cellulose in the eutectics, it was still possible to hydrolyze cellulose and then dehydrate the resulting monosaccharides. However this reaction was much slower in the eutectics than in a solvent like [bmim]Cl. The reason for this was investigated by studying the mechanism of breakdown of cellulose by measuring the degree of polymerization of cellulose as a function of time. It was found that in [bmim]Cl, since the cellulose dissolves the monomers are readily available for attack by the Lewis acid which is responsible for the hydrolysis of the glycosidic bond and then the dehydration into HMF. In the eutectics, since the polymer is insoluble, the solvent attacks the end groups of the substrate sequentially. Thus the degree of polymerization of cellulose drops gradually, and thus the reaction is slower. It was also again observed that the acidity of the solvent played an important role in affecting the selectivity of the reaction towards either HMF in the case of less acidic solvents, and towards levulinic and formic acids in the case of the highly acidic solvents like ChCl-OA.

6.2 Future Work

The work done in this thesis explored quaternary ammonium salts and their eutectics for the conversion of biomass feedstocks, and in doing so provided insights into the solvent properties and behavior that are important in the selection of these solvents for the production of a variety of value-added platform chemicals, for e.g., HMF or levulinic acid needed to produce fuels and chemicals. While these solvents were found to be inexpensive compared to the traditionally used imidazolium ILs on a research scale, life cycle analyses of the two classes of solvents needs to be performed for an accurate comparison of the economic and environmental impact of the solvents. On the technical side as well, progress needs to be made in several key areas for the success of these materials. The purpose of this passage is to identify some of these areas.

6.2.1 Better catalysts for the isomerization of glucose

One of the key observations that were made with the work in the eutectics in Chapter III was the inhibition of the isomerization reaction of glucose. The reaction was carried out in the presence of a homogeneous Lewis acid catalyst. The mechanism of this isomerization as studied in the imidazolium ILs involves the coordination of the catalyst with the solvent using the hydrogen bonding to enable the isomerization. Due to the absence of these hydrogen bonding sites, the isomerization reaction is inhibited in the eutectics. It is believed that this mechanism is applicable to homogeneous catalysts. While the use of homogeneous catalysts negates any transport limitations, the use of these catalysts have two major disadvantages. The Lewis acid that has been found to be most effective is chromium chloride, which is not desirable due to its environmental concerns. Additionally, the use of heterogeneous catalysts will be more attractive due to its advantages in process design.

In a study of the effects of acid and base catalysts on glucose using high temperature water at 473 K as a solvent, it was found that heterogeneous catalysts like anatase TiO_2 and ZrO_2 were effective catalysts for the isomerization of glucose to fructose with [95]. It was found that the anatase titania acted as an acid catalyst while the zirconia acted as a base catalyst. Other solid acid catalysts like ZrP, Amberlyst 70 have also been used to make levulinic acids from carbohydrate feedstocks at much higher temperatures and pressures [96]. Examples like these suggest that further exploration of such catalysts with ionic liquids are required for the development of robust biomass conversion technologies.

6.2.2 Conversion of platform chemicals to value-added products: Hydrogenation of HMF

The work done in this thesis has focused on the development of better materials for the conversion of biomass feedstock like fructose, glucose, sucrose and cellulose into

platform chemicals like HMF and levulinic acid. While certain limitations exist in the use of these new materials, directions for improvement have already been identified in the previous section. For the adoption of these materials, it is necessary to be able to convert these platform chemicals into value added products. An example is the conversion of HMF to DMF. DMF, with an energy density of 30 MJ/L is considered a potential biofuel, comparable to gasoline [18]. In addition, studies in direct injection engines have shown that the combustion characteristics and emissions of DMF are comparable to gasoline [97], and hence represents a better choice than existing biofuels.

DMF has been produced from biomass feedstocks like fructose. Fructose has been dehydrated in water, and an organic solvent like 1-butanol has been used to extract HMF into the organic phase, before hydrogenolysis in the presence of a Cu-Ru/C catalyst [18]. The use of a pure ionic liquid phase for the hydrogenation or hydrogenolysis has been hampered by the limited solubility of molecular H₂ in ionic liquids. Similar to the reactions in water, studies have been carried out where the initial dehydration from the sugars has been carried out in mixtures of imidazolium-based 1-ethyl-3-methylimidazolium chloride ([emim]Cl) and acetonitrile. Pd/C catalysts and high hydrogen pressures were used to hydrogenate the HMF to DMF [40]. Preliminary experiments were carried out in our laboratory to perform the hydrogenation of HMF in a pure ionic liquid phase. The reaction was carried out in a batch hydrogenation reaction. The reaction conditions, and results are shown in Table 6.1 and are compared to studies in literature.

Solvent	Catalyst	P(bar)	T (°C)	t (h)	DMF Yield (%)
Butanol [18]	Cu-Ru/C	6.8	220	10	71
[emim]Cl+acetonitrile [40]	Pd/C	62	120	1	16
[bmim]Cl (<i>this study</i>)	Pd/C	55	120	4	4.3

Table 6.1: Comparison of the results of the hydrogenation of HMF to DMF in different solvents

It is seen that in organic solvents, high yields of DMF are seen with modest H₂ pressures, and high temperatures. With an IL-organic phase, much higher pressures are needed. In our study with a pure IL phase, low pressures showed no activity, and only small yields at high pressures. This behavior can be attributed to the low hydrogen solubilities, as well as higher viscosities of ILs that have been shown to lead to lower reaction rates [98]. Though the issue of H₂ solubility in ILs is a major stumbling block in designing conventional hydrogenation processes for the production of fuels like DMF, other promising routes for hydrogenation have been explored in literature, for e.g., the use of non-molecular hydrogen donors to carry out hydrogenation in aqueous/organic media at atmospheric pressures [99]. It is expected that analogous conversion methods can be employed in the ILs, especially the quaternary ammonium based ones.

The goal of this thesis was to provide a fundamental insight into the rationale behind the selection of solvents for the conversion of biomass. These insights were used to select ILs based on quaternary ammonium salts which were found to offer tunable selectivities to different products in the biomass conversion scheme. The property-performance relationships exemplified here will help design product-specific reaction systems. While further research still need to be made in a few critical areas, it is hoped that this work has pushed us closer to the development of environmentally and economically responsible processes for the production of renewably sourced fuels and chemicals.

APPENDICES

APPENDIX A

Methods for the Detection of Reactants and Products in Biomass Conversion

The objective of this passage is to discuss the various methods employed to determine the products of the reactions studied in this thesis. Among the different reactions studied here, the dehydration of sugars - glucose and fructose, is an important one. The reaction has been studied in detail in Chapters II, III and IV. The primary product of the dehydration is HMF. In the course of this work, different methods were used to detect the reactants and products.

A.1 UV-Visible Spectroscopy

HMF is naturally found in foods like milk, fruit juices and honey. However, in most of these heat treated or acidic foods, it is an undesired substance, and has been regulated. Online analyses of HMF content in foods has hence been a requirement. This has led to the development of various techniques for its quantification, the easiest of which is the use of a UV-Vis spectrometer. Historically, this process was developed to determine the quality of honey and monitor impurities due to HMF [100].

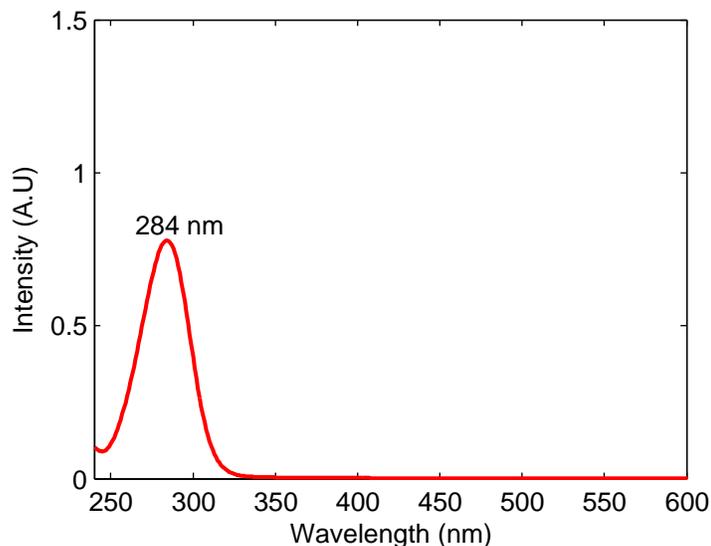


Figure A.1: Absorption spectrum of a 100 μM HMF sample taken using a UV-Visible spectroscope

HMF can be measured by measuring its absorbance at a wavelength of 284 nm. A representative example can be seen in Figure A.1 where the spectrum of a 100 μM HMF is shown.

This method offers reliable quantification of HMF. However, the low wavelength of detection makes it imperative that a quartz cuvette be used for detection. This results in an analytical method that is expensive, both monetarily and temporally. Due to reuse of quartz cuvettes, there is also increased chances of contamination of samples.

In Chapter II, the effect of increasing catalyst concentration on the reaction was studied. In such studies, increased catalyst concentrations interferes with HMF spectra at the lower wavelength region, which makes this method unreliable. In studies like the non-catalytic dehydration of fructose (studied in Chapters III and IV however, there are no interference effects from the solvent system.

One of the objectives of this work was to study the effect of solvents on reaction pathways. In order to achieve this, it was required to monitor the concentration of not just HMF, but also the reactants, intermediates and products. For all these reasons,

the use of UV-Vis spectroscopy was not a viable tool for analysis.

A.2 Derivatization of Reactants and Products

Due to the ubiquity of Gas Chromatographs, it was desired to use these instruments for the analysis of reaction samples from biomass conversion. However, the sugars and the resulting products are not volatile. It has been known that replacing the hydroxyl groups of the sugars with trimethylsilane groups, i.e., creating trimethylsilane derivatives of these sugars can be used to make volatile samples and quantify them in a GC [101]. Hexamethyldisilazane and trimethylchlorosilane have been used in this study as silylating agents.

In the undergraduate senior lab at the University of Michigan Chemical Engineering Department, an implementation of the silylation has been used for the derivatization of the products of transesterification of glycerol [102]. N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was used as the silylating agent in this work. This procedure was implemented, and is summarized here.

3 mL of pyridine was first added to a 4 mL vial. 200 μL of the carbohydrate sample was added, and the vial was shaken well. 100 μL of the pyridine-carbohydrate solution was then transferred to another vial which contained 0.15 mL of MSTFA. The sample was then allowed to rest for 20 min, followed by the addition of 1.2 mL of heptane. These samples were then transferred to GC vials for analysis.

In order to correctly identify and quantify samples, standards of glucose, fructose and HMF were prepared. The concentrations of these standards are listed in Table A.1. The standards were subjected to silylation as described above. The samples were analyzed using an Agilent GC fitted with a 60 m capillary column, and a Flame Ionization Detector (FID) detector. The retention times of the compounds are listed in Table A.2.

As can be seen, using this method, it was possible to successfully detect the sugars

Standard	Glucose (mM)	Fructose (mM)	HMF(mM)
1	70	70	250
2	140	140	500
3	280	280	1000

Table A.1: Glucose, Fructose and HMF standards analyzed in the silylation reactions

Compound	Retention Time (min)
Glucose	4.42
Fructose	4.43
HMF	7.72

Table A.2: Retention times for derivatized carbohydrate compounds analyzed on the GC

glucose and fructose, as well as the product, HMF. However, the retention time for glucose and fructose are very close to each other and in actual reaction mixtures, where these compounds are present together, deconvolution becomes a problem. It was also observed that additional products like levulinic and formic acid could not be detected in this method. For these reasons, the derivatization of carbohydrates were not employed in this study as an analytical tool.

A.3 HPLC Analysis of Reaction Mixtures

The analysis of reactants and products was attempted on the HPLC. Analysis was first attempted on a C-18 reversed-phase column maintained at room temperature. Both a UV-Vis and a differential refractive index detectors were used. While this was successful in identifying and quantifying glucose, fructose and HMF, levulinic and formic acids could not be identified using the UV-Vis detector. Analysis was then performed using a Phenomenex ROA ion exclusion column maintained at 60 °C. 0.005 N H₂SO₄ was used as a mobile phase and a flow rate of 0.5 ml/min was maintained through the column. A differential refractive index detector was used to quantify the amount of glucose, fructose, HMF, levulinic acid and formic acid in reaction samples. The retention times of these compounds are listed in Table A.3:

Compound	Retention Time (min)
Glucose	11.89
Fructose	13.21
Formic Acid	17.52
Levulinic Acid	20.69
HMF	39.79

Table A.3: Retention times for compounds analyzed on the HPLC

This method was successful in identifying and quantifying all the reactants and products in the reaction mixture. Peak separations between the sugar isomers were found to be adequate for quantification. Calibration of the instrument was carried out by the preparation of standards of all these compounds of known concentration. The results of these calibrations are shown in Figures A.2, A.3 and A.4. Reaction samples containing mixtures of these compounds resulted in separate peaks for each of these compounds. ILs, which were used as solvents in reactions did not cause any interference in analysis, often eluting before 10 min. This method has successfully been used throughout this work.

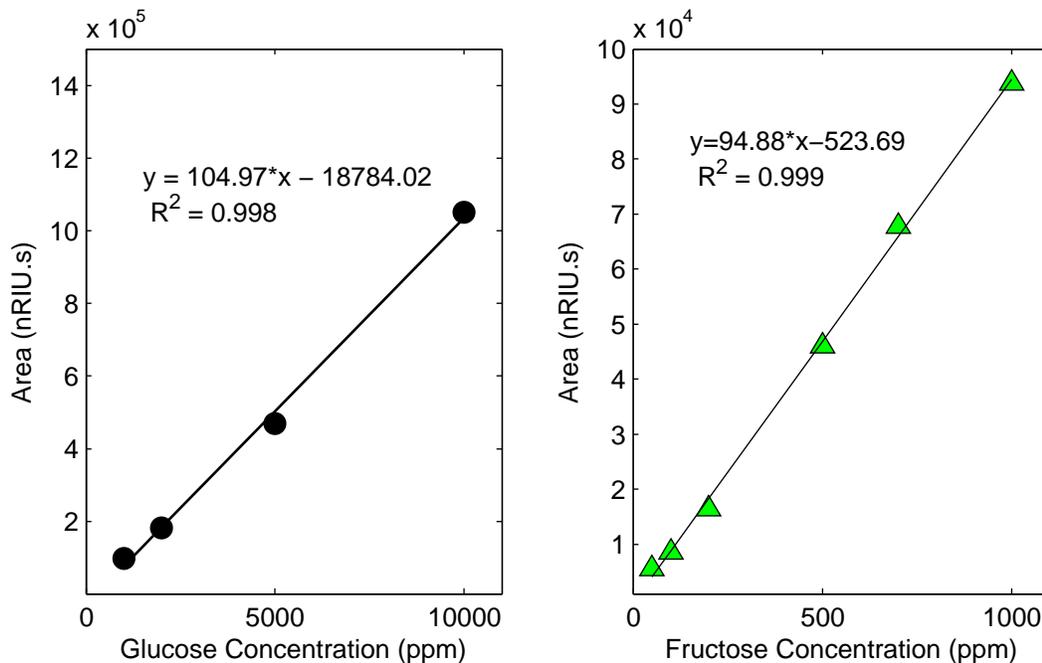


Figure A.2: Calibration curves for the detection of glucose and fructose using a differential refractometer on the HPLC

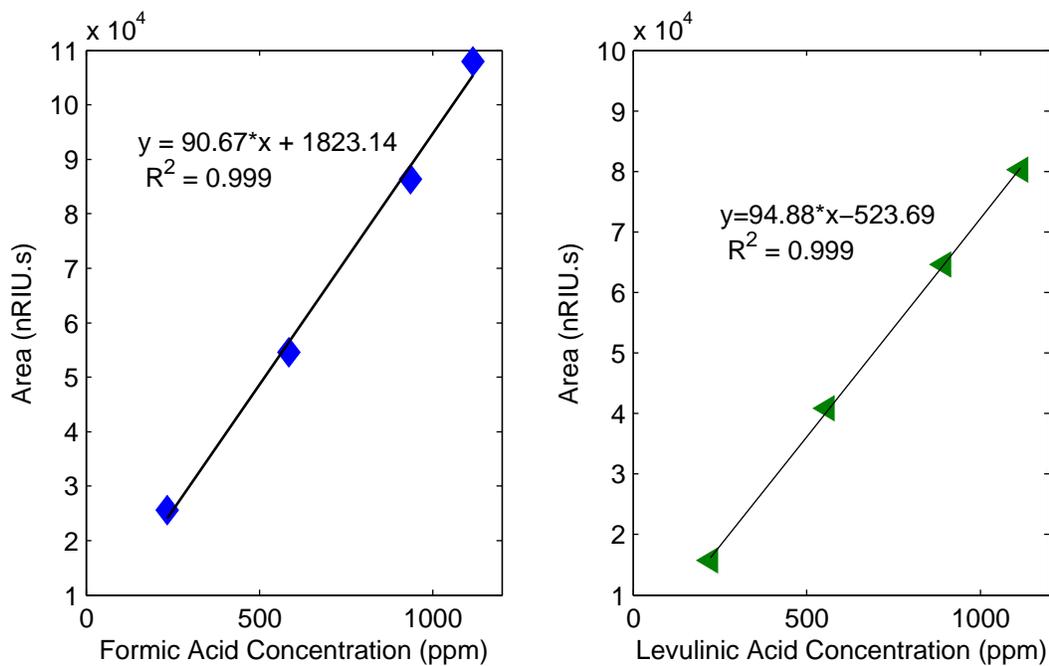


Figure A.3: Calibration curves for the detection of formic acid and levulinic acid using a differential refractometer on the HPLC

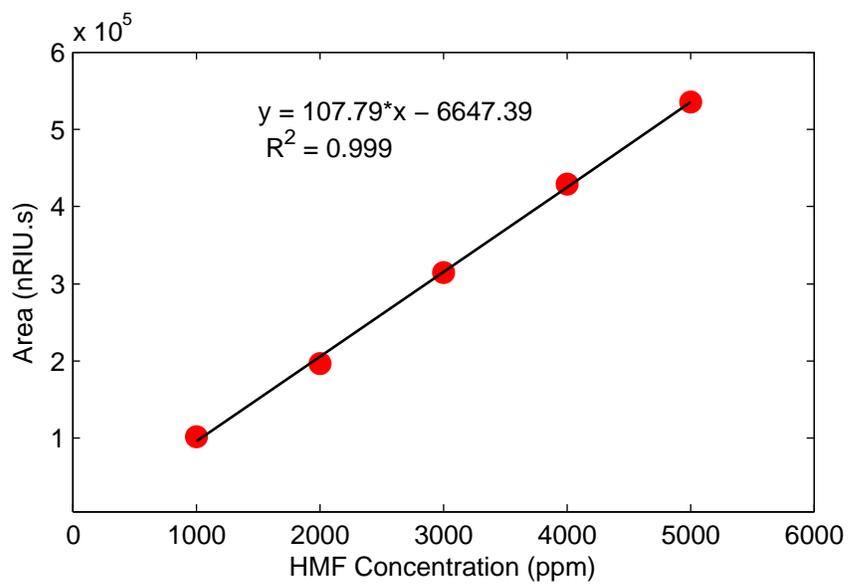


Figure A.4: Calibration curves for the detection of HMF using a differential refractometer on the HPLC

APPENDIX B

Determination of Solvent Parameters

The interactions of solvents with solutes are good indicators of their ability to affect chemical reactions. These interactions have an effect on the rates of reaction and the position of equilibriums in these chemical reactions. So, the study of solvents and how they interact with different substances is of particular importance, especially in our study where one of the primary goals is to design alternate solvents for the conversion of biomass. Due to the ubiquity of UV-Vis spectroscopic measurement methods and their ease of use, the use of solvatochromic compounds to measure solvent parameters. In this passage, the importance of the different parameters, and the methods of determining them are detailed.

The intermolecular interactions have been successfully described in literature by the work of Kamlet and Taft [103–105]. The effect of the Kamlet-Taft parameters, α , β and π^* can be correlated to many solvent effects using Linear Free Energy Relationships (LFER), and can be written as

$$P = P_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (\text{B.1})$$

where P is the solvent dependent process parameter, P_0 , s , a , b and d are coefficients derived from LFER analysis, and α represents the hydrogen bond donating ability

of the solvent, β the hydrogen bond accepting ability, and π^* the polarizability of the solvent. Each of these parameters can be determined experimentally. δ is an adjustment for the polarizability which depends on the class of solvent being studied and takes values of 0, 0.1 and 1 for aliphatic, polyhalogenated and aromatic solvents respectively [106]. The determination of α , β and π^* are discussed here.

B.1 Hydrogen Bond Basicity - β

For the determination of β , two sets of solvatochromatic indicators were chosen such that in solvents of varying polarity, and in the absence of hydrogen bonding, a linear relationship between their energies of absorbance exists. Then, in solvents where hydrogen bonding is present, the deviation from this linear relationship is measured, and the magnitudes of this deviation was taken as a measure of the hydrogen bond basicity.

To determine the hydrogen bond basicities of the ILs, it was decided to employ this method. In the study, one set of indicators that was used was 4-nitroaniline and N, N-diethyl-4-nitroaniline [103]. However, in our study, due to the unavailability of N, N-diethyl-4-nitroaniline, N, N-dimethyl-4-nitroaniline was used. This implied that the equations used in the original study could no longer be directly used, and had to be rederived. The methods employed in literature were closely followed in the derivation. Hexane, cyclohexane, toluene, benzene and dichloromethane were chosen as the non-hydrogen bonding solvents. With the energies of the absorbance maxima from the non-hydrogen bonding solvents, a regression line was drawn as shown in Figure B.1. Now, the absorbances of hydrogen bonding solvents, for e.g., acetone are measured. It is seen in Figure B.1 that this lies well below the regression line from the non-hydrogen bonding solvents. The difference between the energy of absorbance maxima of 4-nitroaniline as observed and that calculated from the regression line is used as the magnitude of deviation. As in the original study, the difference in energies

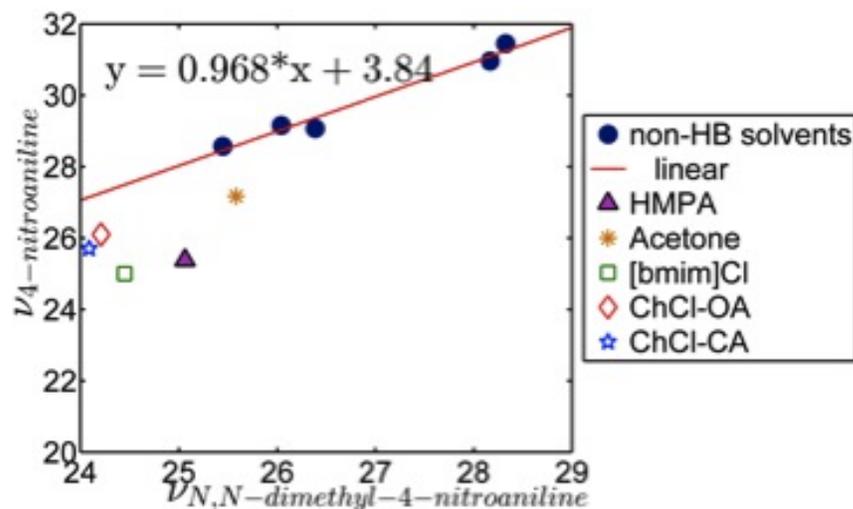


Figure B.1: Comparison of the spectral data for 4-nitroaniline and N,N-dimethyl-4-nitroaniline indicators in various hydrogen bonding, non-hydrogen bonding and ionic liquid solvents

for hexamethylphosphoramide (HMPA) is used as the basis for defining β , i.e.,

$$\beta = \frac{\Delta\nu_{\text{solvent}}}{\Delta\nu_{\text{HMPA}}} = \frac{\Delta\nu_{\text{solvent}}}{2.71} \quad (\text{B.2})$$

Using this method, the Kamlet-Taft parameter, β was measured for all the ILs studied in this thesis, and is shown in Table B.1.

Ionic Liquid	β
[bmim]Cl	0.92
ChCl-Ph	0.42
ChCl-CA	0.53
ChCl-OA	0.42
Q8881Cl	0.85

Table B.1: The Kamlet Taft parameter, β , measured for different ionic liquids

In this work, the Kamlet-Taft parameter, β was studied in more detail than any of the other parameters, since this was found to affect the reactivity in glucose dehydration studied in Chapter III and cellulose solubility studied in Chapter V.

B.2 Hydrogen Bond Acidity - α

The determination of the hydrogen bond acidity, α , follows a methodology similar to the development of the hydrogen bond basicity scale. The indicators used in this case are 4-nitroanisole and Dimroth's betaine/Reichardt's dye [104]. In the study, methanol is used as a standard, and has an α of 1. The results were reproduced (Figure B.2), and then used to determine the α parameter for a few of the ILs. As an example, these values for two ILs - [bmim]Cl and ChCl-OA are shown in Table B.2

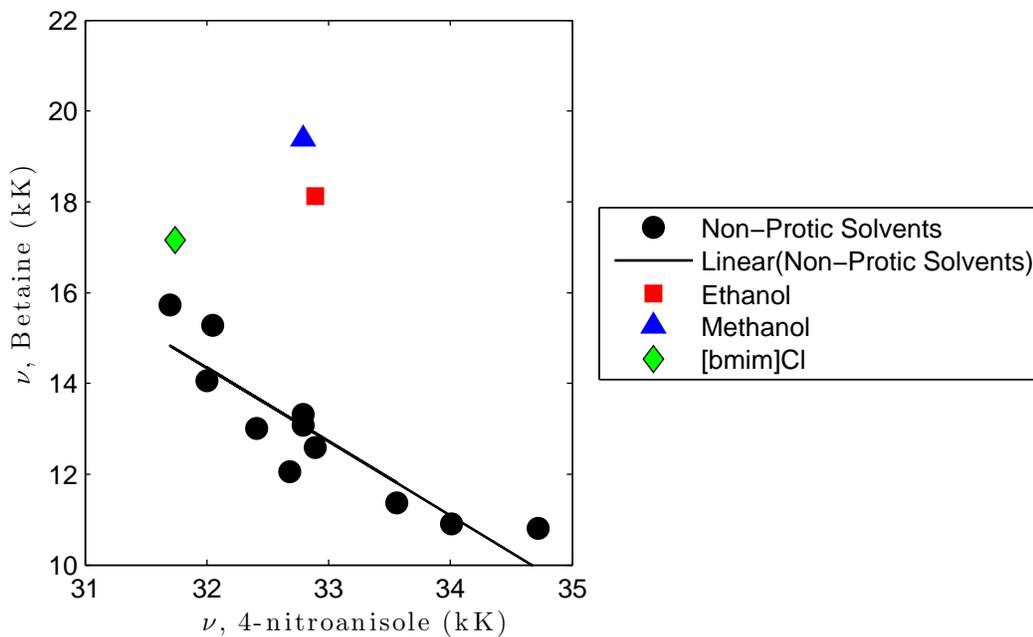


Figure B.2: Comparison of the spectral data for Betaine and 4-nitroanisole indicators in various non-protic, organic and ionic liquid solvents

Ionic Liquid	α
[bmim]Cl	0.42
ChCl-OA	0.23

Table B.2: The Kamlet Taft parameter, α , measured for different ionic liquids

B.3 Polarizability - π^*

Solvent polarity can be described as the ability of a solvent to solvate solutes, which depends on its interactions with the solute. Such interactions should exclude those that cause chemical reactions. These interactions can be best described by empirical parameters. The most popular are those involving solvatochromatic dyes where the effect of solvent polarity on the UV/Vis absorption spectra can be easily measured. Many such parameters exist, for e.g., the $E_T(30)$ scale which measures the energy of transition of the dissolved pyridinium N-phenolate betaine dye in a solvent, as shown in [107]. The Kamlet-Taft parameter, π^* differs from other parameters such as $E_T(30)$ in that it excludes the effect of hydrogen bonding effects of the solvents [105]. Several dyes have been identified with which π^* can be calculated. In this study, N,N-dimethyl-4-nitroaniline was used to calculate these values. Table B.3 tabulates the value of π^* of different solvents and compares them to those found in literature.

Solvent	π^*	π^* (literature)
Hexane	-0.07	-0.081
Toluene	0.49	0.53
Acetone	0.73	0.69
THF	0.62	0.58
[amim]Cl	1.13	1.17 [93]
[bmim]Cl	1.06	1.10 [93]
ChCl-OA	1.15	–

Table B.3: The Kamlet Taft parameter, π^* , measured for a variety of organic solvents and ionic liquids. All literature values are from [105] unless otherwise specified.

It is seen that the π^* values calculated in this study are close to the ones in literature.

APPENDIX C

Method for the Determination of the Degree of Polymerization of Cellulose

In the conversion of biomass, the hydrolysis and subsequent dehydration of cellulose is an important reaction. While the previously developed analytical methods using the HPLC are capable of analyzing the simple sugars and other products of these reactions, no information about the reactant is revealed. Measurement of the degree of polymerization (DP) of cellulose offers insight into mechanisms in which the polymer breaks down in different solvents.

The method for the determination of DP utilized here follows the work of Zhang and Lynd [94]. In this method, the number-average DP is measured by first measuring the total number of glucosyl monomers in the polymer and then dividing it by the number of chain ends. The procedure for doing this is described below.

C.1 Reducing End Determination

The BCA method has been employed here for the determination of the reducing end concentration. Solution A was first prepared by dissolving 0.971 g disodium 2,2'-bicinchoninate, 27.14 g sodium carbonate and 12.1 g sodium bicarbonate in 500 mL

deionized water. Solution B was then prepared by dissolving 0.624 g copper sulfate pentahydrate and 0.631 g L-serine in 500 mL DI water. Mixing equal volumes of Solutions A and B results in the BCA working solution. Solutions A and B were prepared in advance and stored in a refrigerator. The BCA solution was prepared fresh as and when required. The cellulose solution for which DP had to be determined was then prepared. This typically involved cellulose dissolved in an IL or eutectic.

1 mL of the BCA solution was added to 1 mL of the cellulose sample in a vial. The vials were mixed well and placed in an oil bath at 75 °C for 30 min. The solution was then cooled and the absorbance of the cooled solution was measured at 560 nm. If the samples contained undissolved or insoluble cellulose, the procedure was carried out as before, and after the cooling step, the solution was centrifuged, and the absorbance of the supernatant solution was measured at 560 nm. In order to correctly determine the concentrations of the sugars, glucose solutions with concentrations from 0 to 50 μM were used as standards. The calibration curve for the reducing end determination is shown in Figure C.1(a). It is in good agreement with literature [94].

C.2 Total Glucosyl Monomer Concentration

The phenol-sulfuric acid method developed by Dubois *et. al.* [108] has been adapted here. First, a 5 % phenol in water solution is prepared by adding DI water to phenol. This solution can again be stored in a refrigerator for future use. 1 mL of concentrated sulfuric acid is added to 1 mL of the cellulose solution and mixed well. After the solution is allowed to stand for 5 min, it is diluted with 10 mL of DI water. 2 mL of this diluted solution is then taken in a vial, and 1 mL of the 5% phenol solution is added followed by 5 mL of concentrated sulfuric acid. This mixture is allowed to stand for 10 min, mixed well and placed in an oil bath at 25 – 30 °C for 20 min. The absorbance of the solution is then measured at 490 nm. Calibration curves are prepared by using glucose solutions up to 500 μM . Figure C.1(b) shows

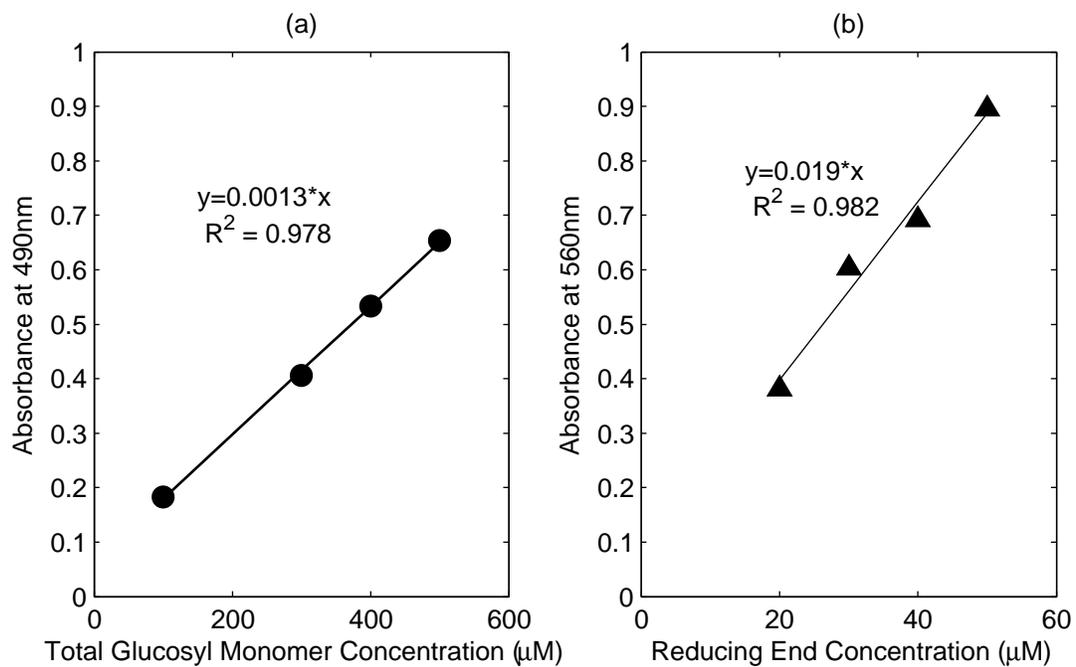


Figure C.1: Calibration curves for the determination of the (a) Total Glucosyl Monomer Concentration and (b) Reducing End Concentration

the calibration curves used in this study. Once again, the curves agree well with published data in literature [94].

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