A study of cellulose dissolution in ionic liquid-water brines

Weiqing Su
Abstract

A series of morpholinium salts were prepared in order to investigate their efficacy in dissolution of cellulose. These ionic liquids were prepared under normal bench-top experimental conditions rendering these ionic liquids well suited for applied research in industrial scale. Most of the ionic liquids prepared were halide free, but contained approximately 60000 ppm water due to their hygroscopicity. It was found that [AMMorp][OAc]-brine and [AMMorp][HSO₄]-brine, at 120 °C in 20 min, can dissolve 26 wt% and 8 wt% cellulose, respectively. In case of [BMMorp][OAc], [BMMorp][OAc]-brine was not able to dissolve cellulose and addition of some amount of halogen-containing ionic liquid was required to dissolve cellulose. The combination of 70% [BMMorp][OAc] with 23.3% [BMMorp][Br] and 6.7 wt% water enabled the dissolution of 6 wt% cellulose without any pretreatment, at 80 °C for 24 h. Similarly, 86.7 % [BnM Morm][OAc] with 7% [BnMMorp][Cl] and 6.3 wt% water could dissolve 22 wt% cellulose at 120 °C in 20 min. The organic electrolytic solutions of ionic liquids with various investigated amines could not dissolve cellulose at high temperature, while the solutions containing ethanol and 2-butanol could dissolve 2 wt% and 4 wt% cellulose respectively at 70 °C in 24 h. The optical microscopy images unraveled the behavior of cellulosic fibers in different solvent systems. Importantly, recovered ionic liquid still showed a strong ability for dissolution of cellulose. Due to their efficacy in dissolution of cellulose in the presence of high amount of water, these ionic liquids can be potentially applied in industry for processing of cellulose.
List of abbreviations, ordered by appearance in the text

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Iα</td>
<td>A triclinic structure</td>
</tr>
<tr>
<td>Iβ</td>
<td>A monoclinic structure</td>
</tr>
<tr>
<td>NMMO</td>
<td>N-methylmorpholine-N-oxide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NO</td>
<td>N-oxide group of N-methylmorpholine-N-oxide</td>
</tr>
<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>CF&lt;sub&gt;11&lt;/sub&gt;</td>
<td>Cellulose powder</td>
</tr>
<tr>
<td>PF</td>
<td>Paraformaldehyde</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>TEAC</td>
<td>Triethylammonium chloride</td>
</tr>
<tr>
<td>ILs</td>
<td>Ionic liquids</td>
</tr>
<tr>
<td>TSILs</td>
<td>Task specific ionic liquids</td>
</tr>
<tr>
<td>AmimCl</td>
<td>3- Allyl-1- methyl-imidazolium chloride</td>
</tr>
<tr>
<td>EohmimCl</td>
<td>1-(2-Hydroxyethyl)-3-methyl imidazolium chloride</td>
</tr>
<tr>
<td>EDA</td>
<td>Electron donor acceptor mechanism</td>
</tr>
<tr>
<td>β</td>
<td>The ability to make hydrogen bond</td>
</tr>
<tr>
<td>BmimCl</td>
<td>3-Butyl-1- methyl-imidazolium chloride</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>C&lt;sub&gt;m&lt;/sub&gt;mimCl</td>
<td>1-Butyl -3-methyl-imidazolium chloride</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;mimCl</td>
<td>1-Hexyl -3-methyl-imidazolium chloride</td>
</tr>
<tr>
<td>C&lt;sub&gt;8&lt;/sub&gt;mimCl</td>
<td>1-Octyl-3-methyl-imidazolium chloride</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;mimOAc</td>
<td>1-Ethyl -3-methyl-imidazolium acetate</td>
</tr>
<tr>
<td>C&lt;sub&gt;4&lt;/sub&gt;mimOAc</td>
<td>1-Butyl -3-methyl-imidazolium acetate</td>
</tr>
<tr>
<td>TMG</td>
<td>1,1,3,3-Tetramethylguanidine</td>
</tr>
<tr>
<td>MCC</td>
<td>Microcrystalline cellulose</td>
</tr>
<tr>
<td>TMGPr</td>
<td>1,1,3,3-Tetramethylguanidine propionate</td>
</tr>
<tr>
<td>TMGOAc</td>
<td>1,1,3,3-Tetramethylguanidine acetate</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>BDMTDACl</td>
<td>Benzylmethyl tetradecyl ammonium chloride</td>
</tr>
<tr>
<td>TEMAM</td>
<td>Triethylmethylammonium</td>
</tr>
<tr>
<td>TBMAM</td>
<td>Tributylmethylammonium</td>
</tr>
<tr>
<td>C&lt;sub&gt;m&lt;/sub&gt;mpyCl</td>
<td>3-Methyl-N-butylpyridinium chloride</td>
</tr>
<tr>
<td>BDTAC</td>
<td>Benzylmethyltetradecyl ammonium chloride</td>
</tr>
<tr>
<td>TFSAm</td>
<td>Bis(trifluoromethylsulfonyle)amide</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>m.p.</td>
<td>Melting point</td>
</tr>
<tr>
<td>t-BuOK</td>
<td>Potassium tert-butoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>NMBA</td>
<td>N,N-dimethylethanolamine</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-pyrrolidinone</td>
</tr>
<tr>
<td>2-Pyr</td>
<td>2-Pyrrolidinone</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>BMMorpOAc</td>
<td>N-butyl-N-methyl-morpholinium acetate</td>
</tr>
<tr>
<td>BMMorpBr</td>
<td>N-butyl-N-methyl-morpholinium bromide</td>
</tr>
<tr>
<td>(ΔE)</td>
<td>Energy difference</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>Name</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------------------</td>
</tr>
<tr>
<td>AMMorpOAc</td>
<td>N-allyl-N-methyl-morpholinium acetate</td>
</tr>
<tr>
<td>BnMMorpOAc</td>
<td>N-benzyl-N-methyl-morpholinium acetate</td>
</tr>
<tr>
<td>BnMMorpCl</td>
<td>N-benzyl-N-methyl-morpholinium chloride</td>
</tr>
<tr>
<td>AMMorpBr</td>
<td>N-allyl-N-methyl-morpholinium bromide</td>
</tr>
<tr>
<td>AMMorpHSO4</td>
<td>N-allyl-N-methyl-morpholinium bisulfate</td>
</tr>
<tr>
<td>AMMorpOH</td>
<td>N-allyl-N-methyl-morpholinium hydroxide</td>
</tr>
<tr>
<td>[AMMorp]_2CO_3</td>
<td>N-allyl-N-methyl-morpholinium carbonate</td>
</tr>
<tr>
<td>[AMMorp]_3PO_4</td>
<td>N-allyl-N-methyl-morpholinium phosphate</td>
</tr>
<tr>
<td>AMMorpH_2PO_4</td>
<td>N-allyl-N-methyl-morpholinium dihydrogen phosphate</td>
</tr>
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1. Introduction

With the modernization of third world countries and increasing in industrialization all over the world, the consumption of fossil resources are peaking. Consequently it is estimated that meaningful resources of fossil oil will be used up after 50 years which will result in a global energy crisis in near future. Hence, world community immediately needs to find alternatives to replace fossil oil mainly from bio-renewable and sustainable materials. Biofuels can provide a sustainable alternative to fossil fuels. The products from cellulose have been widely used in many industries viz. papermaking, construction industry, agriculture, plastic and electronics [1]. Cellulosic ethanol produced from non-food sources such as trees and grass, can constitute a major part of biofuels [2]. However, to exploit the fullest potential of the cellulose, its dissolution is extremely important. A large array of research has been devoted for the development of suitable system for cellulose dissolution as it will lead to more and more useful products from cellulose. In future, cellulose will play an important role for renewable materials.

1.1 Structure of cellulose

Cellulose is the richest biopolymer and renewable resource on the earth. Cellulose can be obtained from byproduct of agricultural products, like cornhusk, rice straw, wheat straw and sugarcane bagasse and also can be obtained from animals and bacteria as well as some amoebas [3]. Most of these resources contain cellulose. As an example, wood species typically contain 40-50 % of cellulose, 10-30 % hemicellulose and 20-30% lignin. The most cellulose rich species is cotton which contains almost 100 % cellulose [4]. Cellulose consists of crystalline and amorphous regions. Different growth conditions lead to various micro-fibril structures of native cellulose due to biosynthesis by the plants themselves. Nevertheless, the structure of cellulose comprises primarily two anhydroglucose rings (C₆H₁₀O₅)n, the n from 100000 to 150000 (where n is dependent on the source of the raw material) that are coupled with oxygen covalent bond, the oxygen links C1 of one glucose with C4 of another anhydroglucose ring [5]. Additional links are intra-chain and intermolecular hydrogen bonds between hydroxy groups and oxygen of the adjoining ring or adjacent molecules. All these make the cellulose a linear structure containing stacking of multiple cellulose chain. Thousands of these types of structure are repeated and form a rigid and relatively stronger network; either the intra- or inter-chain hydrogen bonding network renders the cellulose a very stable biopolymer. Therefore, a large amount of anhydroglucose rings are linked together. So cellulose consisting of a large number of linearly linked β(1→4) linked D-glucose units [6], the structure of cellulose is shown at Figure 1.

![Figure 1: Structure of cellulose [5]](image-url)
Cellulose commonly is divided into four types polymorphs of crystalline cellulose (I,II,III,IV). Cellulose I has two different polymorphs which form native samples, a triclinic structure (Iα) and a monoclinic structure (Iβ). Although the Iα and Iβ have the same atom skeleton, different hydrogen bonding patterns occur. They can co-exist with different percent proportions in cellulose I according to the various cellulose sources [7]. The Iα generally dominants in algae and bacteria, however there are more Iβ than Iα in senior cell wall species and Iβ dominates in plants and in tunicates [8]. Iα is meta-stable and more reactive than Iβ, and, therefore Iα can be convert to Iβ in alkaline solution when using hydrothermal treatments at 260 °C (high temperatures) in suitable solvents under helium gas. Iα polymorph is more common in the algae and bacteria and the aim of many researchers is to completely convert Iα to Iβ which still has not been achieved up until now [9-10]. Nishiyama and his co-workers found that Iα and Iβ have different lattice planes and different geometry and in the basis of these results it can be speculated that hydrogen bonding of Iα is weaker than that of Iβ. Thus, Iα can thermally degrade at lower temperatures and has a lower stability [11-12].

Cellulose II can be obtained from cellulose I when subjected to a treatment with ionic liquids and other solvents upon dissolution of cellulose I. Generally speaking, most of the cellulose II is formed during the regeneration process by ionic liquids, also obtained after treatment with aqueous sodium hydroxide [13]. Cellulose II has a monoclinic structure and arranges in anti-parallel sheets. Through aqueous ammonia treatment of cellulose I or II yet another cellulose polymorph can be obtained: cellulose III. Whose intra and inter hydrogen bonds are similar to cellulose II, but, the chains are similar to cellulose I which is parallel [14].

Cellulose is extremely difficult to deconstruct using common technologies due to the stiff bio-molecules and long inter and intra hydrogen bond chains of cellulose. Thus cellulose is insoluble in water and the other organic solvents such as ethanol, acetone and benzene; All previously mentioned properties of cellulose cause challenge upon dissolution of cellulose although cellulose can be dissolved in several complex solvents, such as Cu(NH₃)₄(OH)₂, [NH₂CH₂CH₂NH₂]Cu(OH)₂, [NH₂CH₂CH₂NH₂]Zn(OH)₂, ([Pd(NH₂(CH₂)₂NH₂)](OH)₂ and so on [15-16]. If the desire is to dissolve cellulose, the most important thing is to disrupt hydrogen bonding of cellulose and then get various derivatives of cellulose from different processes. As a further technology development, several different processes for the treatment of cellulose exist. Currently, the most important and dominant process used to produce cellulose fibers is the viscose processing technology, called the “viscose process”.

1.2 Dissolution of cellulose processes

1.2.1 Viscose process

In 1855, the first “artificial silk” was produced by Georges Audemars. Unfortunately, his process is hardly commercialized. First commercial viscose rayon was successfully produced in 1905 and since then viscose rayon is dominating the global fiber market [17]. The schematic diagram of viscose process is shown at Figure 2. Pulp and sodium hydroxide (NaOH) are added to the slurry tank, cellulose is steeped by sodium hydroxide inside slurry tank and the cellulose is converted into alkali cellulose. Most of the pulp can be dissolved in the slurry tank, whereas the residual hemicellulose and low
molecular weight cellulose are removed by the filter press. After several processes such as pressing, shredding, the “white crumb” was formed. The white crumb should be stay at aging drum to be oxidized and depolymerized by contacting with air. The depolymerization can produce short chain lengths providing manageable viscosity to the spinning solution. Then the aged white crumb is transported to xanthator. Xanthation will occur upon addition of carbon disulphide (CS₂) into xanthator. The carbon disulphide reacts with alkali cellulose to form cellulose xanthate. Inorganic impurities are also to be formed due to reaction of the carbon disulphide with the alkaline medium which gives yellow color to the mixture. The product from white crumb now changed to “yellow crumb” [18].

The yellow crumb is passed to the dissolved hopper whereupon it is dissolved in aqueous caustic solution. However, the yellow crumb cannot be dissolved completely, because there are blocks of unxanthated hydroxyl groups inside of crystalline regions of cellulose and, as a result, the mixture becomes very viscous. Through ripening, filtration and de-aeration, the solution is transferred to spinning where it is mixed with sulfuric acid (H₂SO₄) and other additives. When the solution comes in contact with the sulfuric acid, the xanthate groups are converted to unstable xantheic acid groups which loose carbon disulphide to form the filaments or rayon fibers [18]. During the process carbon disulphide is released and can be recycled.

Although viscose process is widely employed in the fibers industry, this technology needs a large amount of fresh water and uses very corrosive chemicals such as sodium hydroxide and sulfuric acid. Moreover, carbon disulphide can cause serious nervous system problems on human beings [19].

![Figure 2: Processes diagram of viscose process](image)

**1.2 NMMO (N-methylmorpholine-N-oxide) process**

The other fiber production technology industrialized in the world is the so called NMMO process. NMMO (Figure 3) is synthesized of a tertiary amine N-methylmorpholine with hydrogen peroxide (H₂O₂). NMMO as a solvent for dissolving cellulose was commercialized in the early 1990s. It can dissolve cellulose and produce Lyocell fibres. However, this technology causes high fibrillation of fibres [20]. A lot of studies has been done for the improvement the fiber quality, viz, addition of some...
surfactants as additives to the precipitation bath, adjusting pH during the washing process and dried fiber treated with swelling media-dimethylsulfoxide, ZnCl$_2$, NMNO or cross-linking agents (mono and bifunctional hydroxyl group containing compounds) [21]. NMNO process is based on the water-NMNO-cellulose system (3-phase diagram of the components). The cellulose dissolution state depends on the amount of NMNO and water. It has been shown that only a narrow region works: 17 % to 23 % water, 60 % to 68 % NMNO, whereupon up to 23 % cellulose can be dissolved [22].

Although NMNO process was used in industry for a few decades, there is not a very clear mechanism for dissolution of cellulose and the structure of cellulose–water–NMNO solutions. However, Gagnaire et al. had proved that there is not cellulose derivatization in cellulose–water–NMNO solutions using nuclear magnetic resonance (NMR) [23]. Other acceptable interpretation is that there is a stronger dipolar N–O group in NMNO and oxygen of N–O group prefers to break hydrogen bonds for forming hydroxylated compounds. Thus, the cellulose can be dissolved by the NMNO due to the cleavage of inter- or intra-molecular hydrogen of cellulose. Nevertheless, upon presence of water in the NMNO-cellulose mixture, there is a competition between water and cellulose to contact with oxygen of NO groups, since hydrogen of water is more hydrophilic than cellulosic OH hydrogen. Also, the oxygen of NO group is likely to prefer the hydrogen of water, resulting in cellulose being more soluble in low concentration of water in 3-phase diagram [24]. Further, the type of N–O in NMNO also influences the solubility of cellulose. Roseneau et al. proved that there are two different types of N–O in NMNO molecules. In solvents with negligible solvent–solute interaction, about 95% of the NMNO molecules showed a typical chair conformation with an axial N–O while 5% had an equatorial N–O at room temperature. Other conformations, such as boat and twist, those are energetically largely disfavored. If increasing the concentration of water in the NMNO solution, the percentage of NMNO molecules with an axial N–O was reduced from 95% to 75 %. On the other hand, the percentage of NMNO molecules with an equatorial N–O was increased to 25 % from 5 %, the dissolution capacity of NMNO for dissolving cellulose will be reduced [25].

NMNO provides a simple physical technology to produce cellulose fibers, films, food casings, membranes, sponges, beads and others without hazardous by-products [26]. However, the NMNO process gives rise to several side reactions which can cause deconstruct of NMNO, modify the performance of product, consume more stabilizers, and cause thermal runaway reactions of the NMNO process [27]. The fibrillation trend of cellulose and the whole process requires complex safety technologies. These factors still limit the further expansion of the process [28].

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{N}^+ & \quad \text{O}^-
\end{align*}
\]

**Figure 3:** Structure of N-methylmorpholine-N-oxide
1.2.3 LiCl/dimethylacetamide (DMAc) process

Besides the viscose process and NMMO process, LiCl/DMAc as a solvent to dissolve the native cellulose had been reported by Turbak et al. [29]. The cellulose with a degree of polymerization (DP) 100-4000 can be dissolved in this solution. The influence of temperature and water in LiCl/DMAc/cellulose system were evaluated by Ramos et al. [30]. The results showed that a higher concentration of cellulose can be dissolved at 5 °C than at 25 °C under identical conditions which indicated that lower temperatures improve the dissolution of cellulose. As the temperature is relative with ion pair concentration of LiCl/DMAc, lower temperatures increase the ion pair concentration. If the concentration of water is increased in the system, higher amount of LiCl is needed to dissolve same amount of cellulose.

However, LiCl/DMAc system can dissolve cellulose without any additive at temperatures higher than 100 °C. When temperature is reduced to 80 °C, some additives such as azototropic methanol or isopropanol [31-32] and adipic anhydride [33] should be added, since the reaction velocity will be accelerated by adding these additives. Although, there are several different methods to dissolve cellulose used LiCl/DMAc, in a typical solvent exchange procedure the process is as follows: first the cellulose is immersed into water, then exchange of water by the acetone takes place, further, by DMAc. This solvent exchange procedure is generally called as ‘activation’ [34]. Also, a series of the solvent systems with a different proportion of LiCl/DMAc for cellulose powder (CF11), paraformaldehyde (PF)/DMSO, triethylammonium chloride (TEAC)/DMSO have been used to fabricate cellulose hydrogels directly [35].

Evidently, the mechanism of ‘activation’ is not very clear till now and several presumptions have been made about how LiCl/DMAc systems dissolve cellulose. Chrapava et al. concluded that the intermolecular hydrogen bonds of cellulose can be broken by LiCl/DMAc mixture. Moreover, one anhydroglucose unit needs two LiCl units in the reaction resulting in two intermolecular hydrogen interactions. Otherwise the cellulose does not seem to be dissolved [34]. Ishii et al. investigated the molecular mobility of cellulose in different solvents with LiCl [36], and they found that mobility of DMAc-treated cellulose is faster than the others and the DMAc-treated cellulose have large surface roughness.

1.2.4 Alkali/urea/thiourea process

On the assumption that alkali cellulose could be produced and may be dissolved in other solvents except carbon disulphide, alkali/urea/thiourea process was invented. Generally, the alkali is sodium hydroxide. It is reported that cellulose can be dissolved in a solution of 9.5 wt% NaOH/4.5 wt% aqueous urea at low temperatures [37]. It has been demonstrated that the intramolecular hydrogen bonds of cellulose were destroyed by the alkali/urea solution, as aqueous alkali solution can disrupt the chain packing of original cellulose and reform new hydrogen bonds, while urea can reduce aggregation of cellulose molecules [38]. Many studies demonstrated that when decreasing the temperature, the solvent dissolution capability of different aqueous alkali/thiourea systems was increased strongly [39]. This means that lower temperatures represent an advantage in terms of cellulose dissolution. If NaOH complex solvent was pre-cooled to –10 °C, the highest solubility for cellulose was attained [40].
Zhang et al. found out the optimal ratios of NaOH/urea/H₂O and NaOH/thiourea/H₂O solvents composition to dissolve cellulose, corresponding to 6:4:90 and 9.5:4.5:86, respectively [41]. However, Qi et al. discovered another method using a two step process to dissolve the cellulose at -5°C. After the initial treatment of cellulose with 12%-18% NaOH about 4%-6% thiourea was added to afford a clear solution [38]. Despite the fact that these solvents system possess a higher solubility capacity for cellulose and were rather inexpensive and less toxic, other problems remain: High alkalinity and the fact that the solvent cannot be recycled thus leading to serious environmental problems.

1.2.5 Ionic Liquids (ILs) process

Another type of solvent system used to dissolve the cellulose is represented by ionic liquids (ILs). (Room-temperature) Ionic liquids are commonly defined as fused salts or ionic salts comprised of cations and anions, and having melting points below 100 °C. ILs have attracted huge amount of research attention due to their specific physicochemical properties, viz., low melting point, high thermal stability, low flammability and negligible vapor pressure [42]. When ionic liquids which incorporate functional groups designed to impart to them particular properties or reactivities, it is called task-specific ionic liquids (TSILs) [43]. ILs are used in various chemical fields, such as catalysis, synthesis, separation, analysis, and energy supply [44]. ILs can often be dissolved in polar solvents such as acetone, dichloromethane (DCM) and methanol. This renders the recycling of ILs plausible after the reaction. They can also offer advantages like atom economy of process, safety and higher efficiency than conventional volatile organic solvents and importantly environmental compatibility [45]. As examples of common ILs, imidazolium and pyridinium derivatives are considered as among most common. On the other hand, e.g. the derivatives from phosphonium, tetraalkylammonium and guanidine have also been used for some special purposes, such as medicine, electrolyte and analysis [46, 47, 48, 49].

**Figure 4** illustrates typical cations and anions used in ionic liquids [50].

**Figure 4** illustrates typical cations and anions used in ionic liquids, the substitutes of R₁ could any alkyl and alkenyl group. Different anions in combination with the same cation can generate different ILs with different physical and chemical properties. Tsunashima et al. reported that the unsaturated phosphonium ionic liquids have lower melting point, high thermal stability, lower viscous and higher conductive than the saturated phosphonium ionic liquids [51].

In 1934, Graenacher et al. pointed out that 1-ethylpyridinium chloride can dissolve cellulose [52]. Swatloski et al. studied the dissolution of cellulose in imidazolium based
ionic liquids. They used the 3-buty1-1-methyl-imidazolium cation, combined with Cl−, PF$_6^-$, Br−, SCN−, and BF$_4^-$ anions. The results showed that only the Cl−, SCN− and Br− anions containing ionic liquids have the ability to dissolve cellulose at 100–110 °C. They also proved that microwave heating is more effective than conventional heating in dissolution of cellulose in these ionic liquids [53]. In 2005, a novel ionic liquid 3-allyl-1-methyl-imidazolium chloride [Amim][Cl] was synthesized by Zhang et al.. This novel ionic liquid can dissolve cellulose without any pretreatments [54]. Luo et al. synthesized a new ionic liquid 1-(2-hydroxyethyl)-3-methyl imidazolium chloride [Eohmim][Cl] thus combining –OH groups to the imidazolium cation and found that this ionic liquid performs better in the dissolution of cellulose (6.8 wt% at 70 °C) [55].

Why do these ionic liquids dissolve cellulose? According to electron-donor-acceptor (EDA) mechanism, imidazolium cation is an electron acceptor and chloride anion as an electron donor. Thus, the ionic liquid could interact with oxygen and hydrogen of OH bonding of cellulose. For the [Eohmim][Cl] ionic liquid, OH group also interacts with the hydrogen bonding of cellulose, thus increasing the capacity of ionic liquid to dissolve cellulose. The amorphous region of cellulose was initially dissolved, followed by reaction of ionic liquid with the crystalline part of cellulose. Ionic liquid molecules then penetrated the capillaries and interstices of the cellulose structure and caused further breaking of H-bonding leading to dissolution of cellulose [56]. Fukaya et al. made a series of 1,3-dialkyl-imidazolium formate ionic liquids [57]. These ionic liquids had a low viscosity, polarity and were free of halogen. All these ionic liquids had a potential to dissolve cellulose due to their low viscosity and high hydrogen bond basicity β (0.99) (the ability to make hydrogen bond) when compare with the chloride anions ionic liquids, such as 3-allyl-1-methyl-imidazolium chloride [Amim][Cl] (β 0.83) and 3-buty1-1-methyl-imidazolium chloride (β 0.84) [Bmim][Cl].

As, the structure of cellulose is composed of inter and intra molecular hydrogen bonds, the higher hydrogen basicity of ionic liquids can weaken inter and intra molecular hydrogen bonds of the cellulose, causing the dissolution of cellulose [57]. The regenerated cellulose products can be obtained by adding anti-solvent, such as water, ethanol and acetone into the solution. The mechanism of regeneration involves the addition of an anti-solvent, such as water to the dissolution solution, thus extracting ionic liquids into the aqueous phase. The water molecules form hydrodynamic shells around the ionic liquid molecules inhibiting the direct interactions between cellulose and ionic liquid molecules. Further, the ionic liquids can be recovered by vacuum evaporation [58]. Depending of the requirements for the final product, different regeneration processes are designed leading to different forms such as films, beads, gels [59].

### 1.2.5.1 Imidazolium based ionic liquids

It has been found that that imidazolium based ionic liquids display a high efficiency for dissolution of cellulose. Swatloski et al. studied ionic liquids which containing 1-buty1-3-methylimidazolium cations [C$_4$min] $^+$ combined with a range of anions, from small hydrogenN-bond acceptors Cl to large non coordinating anions [PF$_6^-$], also including Br−, SCN−, and [BF$_4^-$]. They found that the cellulose was dissolved without pretreatment in these ionic liquids. Table 1 summarizes the dissolution of cellulose under various parameters in different imidazolium based ionic liquids [53].
Table 1: Dissolution of cellulose in different imidazolium-based ionic liquids [53]

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Method</th>
<th>Amount of Cellulose (wt %) dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][Cl]</td>
<td>Conventional heat (100°C)</td>
<td>10 %</td>
</tr>
<tr>
<td></td>
<td>(70 °C)</td>
<td>3 %</td>
</tr>
<tr>
<td>[C₄mim][Cl]</td>
<td>Conventional heat (80°C)</td>
<td>5 %</td>
</tr>
<tr>
<td></td>
<td>and sonication</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][Cl]</td>
<td>Conventional heat (100°C)</td>
<td>slightly soluble</td>
</tr>
<tr>
<td>[C₄mim][Br]</td>
<td>Microwave</td>
<td>6 %</td>
</tr>
<tr>
<td>[C₄mim][SCN]</td>
<td>Microwave</td>
<td>6 %</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>Microwave</td>
<td>insoluble</td>
</tr>
<tr>
<td>[C₆mim][Cl]</td>
<td>Conventional heat (100°C)</td>
<td>5 %</td>
</tr>
</tbody>
</table>

Because [C₄mim][Cl] possesses the ability to dissolve higher concentration of cellulose quicker than traditional solvents, they speculated that [C₄mim][Cl] is a highly effective in breaking the extensive hydrogen bonding in cellulose due to presence of chloride ions. However, the larger alkyl chains attached to imidazolium ionic liquids like [C₆mim][Cl] and [C₈mim][Cl] are less efficient in dissolving cellulose. Erdmenger et al. studied the effect of alkyl chain length on 3-alkyl-1-methyl-imidazolium cation combined with chloride anion on dissolution of cellulose and pointed out that there is no regular regulation for the solubility of 3-alkyl-1-methyl-imidazolium chloride with its alkyl chain length [59]. Alkyl chain with less than six carbon units and odd-numbered alkyl chain length is more efficient in the dissolution of cellulose than even number of alkyl chain length, but the C₄ chain length has the highest solubility for cellulose [60].

Recently, 1-butyl-3-methylimidazolium acetate [C₄mim][OAc] ionic liquid illustrated better dissolution capacity of cellulose. Wu et al. have demonstrated that dissolved power of 1-butyl-3-methylimidazolium acetate [C₄mim][OAc] for chitin is more efficient than [Amim][Cl] or [C₄mim][Cl]. It is reported that the BASF company being one of the pioneers in industrial usage of ILs, has turned to [C₂mim][OAc] to dissolve cellulose on an industrial scale because of its better physicochemical properties, such as low toxicity, lower corrosiveness as well as lower melting point and viscosity. Also, importantly, the favorable biodegradability profile should be emphasized [61].

Sun et al. tested the solubility of [C₂mim][OAc] in softwood (southern yellow pine) and hardwood (red oak) after mild grinding [62]. It was found that [C₂mim][OAc] is a better solvent than [C₄mim][Cl] for the dissolution of these wood samples, but hard wood is easier and faster to be dissolved than soft wood. The factors affecting of dissolution of wood were the particle size of wood (powder mesh), pretreatment with microwave and ultrasound. They also showed that after complete dissolution of wood in [C₂mim][OAc], proper reconstitution using acetone/water (1:1 v/v) solvents afforded the carbohydrate free lignin and cellulose rich materials.
1.2.5.2 Guanidine based ionic liquids

King et al. developed a new generation of ionic liquids derived from 1,1,3,3-tetramethylguanidine (TMG) which obtained by treating TMG with a series of carboxylic acids, such as formic, acetic and propionic acids. They successfully prepared 9 ionic liquids with various acids. All of these ILs are studied for their dissolved capacity for microcrystalline cellulose (MCC). They found that 1,1,3,3-tetraethylguanidine propionate, 1,1,3,3-tetraethylguanidine acetate and 1,1,3,3-tetraethylguanidine formate showed the good dissolution for the 5 wt % of MCC at 100°C within 18 h [63].

1.2.5.3 Ammonium ionic liquids

Several solvent systems containing ammonium salts, such as DMSO/ tetrabutyl ammonium fluoride (TBAF) [64], benzylidemethyl (tetradecyl) ammonium chloride dihydrate (BDMTDAACL2H2O) [65] and trimethylbenzyl ammonium hydroxide (Triton B) [65] were developed for the dissolution of cellulose. Kohler et al. prepared a series of triethylmethylammonium (TEMAM) and tributylmethylammonium (TBMAM) based ionic liquids as shown in Table 2. Among those, TEMAM formate ([CH3N(CH2CH3)3]-[HCOO]) and TBMAM formate ([CH3N(CH2CH2CH2CH3)3][HCOO]) could dissolve cellulose. It was also shown that an addition a small amounts of formic acid helped to reduce the melting point and increased the dissolution velocity of cellulose [67].

<table>
<thead>
<tr>
<th>No.</th>
<th>Cation</th>
<th>Anion</th>
<th>Color</th>
<th>Melting point ( °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEMAM</td>
<td>HCOO</td>
<td>colorless</td>
<td>155</td>
</tr>
<tr>
<td>2</td>
<td>TEMAM</td>
<td>ClCH2COO</td>
<td>white</td>
<td>130</td>
</tr>
<tr>
<td>3</td>
<td>TEMAM</td>
<td>Cl2CHCOO</td>
<td>white</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>TEMAM</td>
<td>Cl3CCOO</td>
<td>white</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>TBMAM</td>
<td>HCOO</td>
<td>yellow</td>
<td>&lt;20</td>
</tr>
<tr>
<td>6</td>
<td>TBMAM</td>
<td>ClCH2COO</td>
<td>white</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>TBMAM</td>
<td>Cl2CHCOO</td>
<td>colorless</td>
<td>&lt;20</td>
</tr>
<tr>
<td>8</td>
<td>TBMAM</td>
<td>Cl3CCOO</td>
<td>yellow</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

The solubility of cellulose with a DP in the range from 290 to 1200 was studied among 3-methyl-N-butylpyridinium chloride [C3mpy][Cl], BDMTDACl and 1-N-butyl-3-methylimidazolium chloride [C4mim][Cl]. They found that the amount of dissolved cellulose decreased with increasing DP of the sample. Different ILs have different amounts dissolution of cellulose, the ionic liquid [C4mpy][Cl] is more effective than [C4mim][Cl] in terms of dissolution of cellulose. BDMTDACl could dissolve the lowest amount of cellulose (5 wt %), but it has the advantage of the lowest melting point of
1.2.5.4 Phosphonium based ionic liquids

Phosphonium ionic liquids have several advantages than imidazolium and ammonium ionic liquids in terms of thermal and chemical stability. Tsunashima et al. have demonstrated a series of phosphonium ionic liquids based on triethylbutylphosphonium (P2224+), triethylpentyl-phosphonium (P2225+), triethyl (methoxy-methyl)phosphonium (P222(101)+) and triethyl[2-ethoxy-methyl] phosphonium (P222(201)+) cations combining with trifluoromethylsulfonyl amide (FSA) anion. All these ionic liquids have low melting points compared to imidazolium and ammonium ionic liquids. When combined with bis(trifluoromethylsulfonyl) amide (TFSA) anion, these ionic liquids show lower viscosities and higher conductivities than those combined with FSA anion [69]. Introduction of methoxy group in phosphonium cations improve transport properties of the ionic liquids because the methoxy group can donate an electron which reduces the positive charge of cation [70]. The unsaturated phosphonium ionic liquids have lower melting points, lower viscosity, high thermal stability and higher conductivity than the saturated phosphonium ionic liquids [51].

Abe et al. reported that tetrabutylphosphonium hydroxides containing a certain amount water which dissolved cellulose [71]. They pointed out the 30-50 wt% water in this ionic liquid dissolved 15 wt % cellulose rapidly at room temperature and suggested the hydroxide anions of ionic liquid interacted with protons of hydroxyl group of cellulose.

1.2.5.5 Pyridinium based on ionic liquids

Early 1934, Granenacher applied for patent for cellulose solution which pointed out that benzylpyridinium chloride has a capacity to dissolve the cellulose [52]. Though 3-methyl-N-butylpyridinium chloride [C₄mpy][Cl] can dissolve a higher percent of cellulose (approximately 38 wt%), [C₄mpy][Cl] and the reagents degraded during the reaction with cellulose, so this ionic liquid does not render a successful candidate for cellulose processing [68].

1.2.5.6 Influence of water in ionic liquid on cellulose dissolution

Almost all reports on dissolution of cellulose in ionic liquids clearly indicated the negative influence of water on dissolution of cellulose in ionic liquids [52-63]. It is considered that more than 0.5 mole fraction of water in ionic liquid significantly reduced the solvent properties of ionic liquid and resulted in a system that could not dissolve cellulose [58]. This mainly happens due to possible competition between ionic liquid and water for accessible active functional groups of the cellulose. The strong interaction of cellulosic hydroxyl group with water molecule inhibit the interaction of ionic liquid with cellulose and result in non-dissolution of cellulose in ionic liquid.

The water is found to be one of the major impurities in ionic liquids, especially in hydrophilic ionic liquids. In normal bench-top laboratory conditions, one should expect high content of water than those prepared in glove box and with the use of high vacuum
pumps. Also, water can be readily absorbed in ionic liquid from atmosphere during storage or experiments. Most of these reports insist the dryness of ionic liquid for optimum dissolution of cellulose. However, these stringent requirements of dryness can create great difficulty in terms of cost in their application in industrial scale. Thus, it is highly important to develop new ionic liquids which can dissolve cellulose even under high water content conditions.

2. Experimental methods

In this work, several analytical technologies were used, viz. Karl Fischer titration method, ion chromatography (IC), rotary evaporation system, optical microscopy and nuclear magnetic resonance (NMR) spectroscopy. A brief introduction of these systems is described as below.

2.1 Ion chromatography

Ion chromatography (IC) is a rapid analytical method used for quantitative analysis of aqueous samples in parts-per-million (ppm) or even less. Many ions can be analyzed quantitatively (such as chloride, bromine, and common cations like sodium and potassium) using conductivity detectors of IC. IC represents one kind of liquid chromatography that contains different ion-exchange resins in column to separate atomic or molecular ions based on their interaction with the resin. The mixture of Na₂CO₃ or NaHCO₃ is commonly used as the mobile phase, upon which the eluent suppressor supplies H⁺ to neutralize the anion and retain or remove Na⁺ [72]. Most IC equipments contain a pump, injector, filter, column electrolytic suppressor and detector, as shown in Figure. 6. For the anion determination, the column used in this study was ANX-99-8511, IC Sep AN1, Peek 4.6mm 250mm. The active length of the anion suppressor column was 100 mm long.

![Figure 5: The operational principle of an ion chromatography](image)

2.2 Optical microscopy

Microscopy is a technology for magnification of small specimen which cannot be seen with naked eye. The principle of microscopy is using multiple-lens (compound microscopes) through diffraction and reflection to get a magnified visual image. As the
development of technology, the modern optical microscopy often has accessories such as with a camera, computer, high-end fluorescence detector and so forth. The efficient illumination and all these add-ons make the microscopy more efficient, provide high resolution and high-quality images about the specimen [73]. An optical microscopy (AXIOSKOP 40) was used to investigate the dissolution of cellulose.

![Optical Microscope](image)

**Figure 6**: A photograph of optical microscope

### 2.3 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is an important characterization tool to verify the structure and quality of chemicals. NMR spectroscopy being used for determining the content of sample and structures of an atom or molecules, due to their magnetic nuclei in a magnetic field can absorb and re-emit electromagnetic radiation under the application of an applied magnetic field. NMR spectroscopy also can provide detailed state and chemical shift of molecules which help scientists to confirm physical and chemical properties of their products. In our case, proton nuclear magnetic resonance spectroscopy was used for determination of proton skeleton of products. Normally, protons are spinning in randomly orientation. Once an external magnetic field is applied, protons will spin either parallel or anti parallel it, the protons with parallel spin has lower energy than one with anti parallel spin. Hence, an energy difference (ΔE) between the parallel and anti parallel states will be created. The signal in NMR spectroscopy results from the difference and is proportional to the population difference between the states [74].
2.4 Karl-Fischer titration method

Karl Fischer titration is an analytical method which designed to determine the water content in a variety of products. The principle is based on the quantitative reaction of water with iodine and sulfur dioxide, which used a primary alcohol (methanol) as solvent and an organic base (pyridine) as buffering agent. The reaction was described as below.

\[
\begin{align*}
I_2 \cdot \text{Pyr} + SO_2 \cdot \text{Pyr} + \text{Pyr} + H_2O & \rightarrow SO_3 \cdot \text{Pyr} + 2\text{PyrH} \cdot I^-

SO_3 \cdot \text{Pyr} + \text{CH}_3\text{OH} & \rightarrow \text{PyrH} + \text{CH}_3\text{SO}_4
\end{align*}
\]

Where Pyr represents pyridine.

The product, SO₃-Pyr reacts further with the methanol to form the methylsulfate anion. There are two different techniques for determination of water content to Karl Fischer: Volumetric and Coulometric titration. Volumetric Karl Fischer Titration, where a solution containing iodine is added using a motorized piston burette and where iodine is generated by electrochemical oxidation in the cell. The selection of the appropriate technique is based on the estimated water content in the sample [75].

3. Experimental section

3.1 Materials

Most of the chemicals were purchased from Sigma Aldrich Ltd., such as N-methyl morpholine, \textit{N,N}-dimethylethanolamine (DMEA), dimethylformamide (DMF), \textit{N}-methyl pyrrolidinone (NMP), \textit{N,N}-dimethylbenzylamine, 2-pyrrolidinone, \textit{N,N,N',N'}-tetramethyl guanidine(TMG), allyl bromide, benzyl chloride, 1-bromobutane. Amines and alkyl halides were redistilled before further use. Acetic acid (100%), formic acid (100%), sodium acetate (≥ 99.0%), potassium acetate (≥ 99.0%), potassium tert-butoxide (≥ 98.0%), potassium carbonate (≥ 99.5%), potassium phosphate monobasic (≥ 99.0%), potassium phosphate tribasic (≥ 98.0%) sodium bisulfate (≥ 95.0%) and sodium
hydroxide (≥99.8%) were purchased from Merck. Ethanol (≥99.5%) and n-butanol (100%) were purchased from Solveco Ltd. Amberlite IR-400 OH resin was purchased from Sigma Aldrich Ltd. Cellulose was obtained from Aditya Birla Domsjö AB (dissolving, sulfite cellulose).

3.2 Preparation of ionic liquids

3.2.1 Preparation of N-butyl-N-methyl-morpholinium bromide [BMMorp][Br]

In 250 mL three neck round bottom flask, redistilled N-methylmorpholine (1 eqv) and 1-bromobutane (1.5 eqv) were added to acetonitrile (10 vol). The solution was stirred at 70 °C for 24 h under nitrogen atmosphere (Scheme 1). The flask was then brought to room temperature and placed in a freezer at 4 °C for 12 h. White crystals were slowly forming which were filtered and recrystallized with tetrahydrofuran (THF) and isopropanol. The resulting white solid was dried and stored in desiccator. M.P.: 208 °C

$^1$H NMR: (400 MHz, CDCl$_3$): δ (ppm) = 0.98 (t, 3H), 1.46 (m, 2H), 1.78 (m, 2H), 3.62 (s, 3H), 3.67 (m, 2H), 3.86 (m, 4H), 4.09 (m, 4H)

![Scheme 1](image)

Scheme 1: Preparation of N-butyl-N-methyl-morpholinium bromide

3.2.2 Preparation of N-butyl-N-methyl-morpholinium acetate [BMMorp][OAc]

3.2.2.1 Using sodium acetate

[BMMorp][Br] (1.0 eqv) and sodium acetate (1.5 eqv) were put into round-bottom flask in different solvents (dichloromethane, methanol, ethanol, water, n-butanol) and stirred vigorously at room temperature for 24 h (Scheme 2). The solid was filtered through funnel, solvent is removed under vacuum. A viscous colorless liquid slowly changed to a semi-viscous liquid.

![Scheme 2](image)

Scheme 2: Preparation of N-butyl-N-methyl-morpholinium acetate

3.2.2.2 Two-step approach
[BMMorp][Br] (1eqv) and potassium tert-butoxide (1.5 eqv) were added together in ethanol (10 vol) in conical flask. The solution was stirred for 24 h at room temperature (Scheme 3). The solid obtained was filtered and washed several times with ethanol. To ethanolic solution, acetic acid (1.5 eqv) was added and solution was stirred vigorously for 24 h. The ethanol was then removed on a rotary evaporation. The product was dissolved in dichloromethane and filtered to remove undissolved potassium bromide. Evaporation of dichloromethane resulted in a semi-viscous fluid.

![Scheme 3](image)

**Scheme 3**: Two step approach for preparation of N-butyl-N-methyl-morpholinium acetate

### 3.2.2.3 Ion Exchange method

10.0 g Amberlite IRA-400(R-OH) in deionized water was loaded in a glass column. 100 mL solution of 1.0 M KOAc solution was then passed through the column with flow rate around 1mL/ min. The column was then thoroughly washed with deionized water till the pH of the eluent was same as that of deionized water.

[BMMorp][Br] (3.5 0g, 0.296 M) was dissolved in 50 mL deionized water. The solution was loaded to the column carefully. The column was then eluted with deionized water as an eluent with a controlled flow rate of 1 mL/min. Around 10 mL of eluent solution was collected in each test tube and analyzed by ion chromatography. The solution in test tubes containing pure [BMMorp][OAc] was evaporated under vacuum and dried to obtain colourless liquid.

\[
\text{1H NMR: (400 MHz, CDCl3): } \delta \text{ (ppm) } = 0.98 \text{ (t, 3 H), 1.44 (m, 2H),1.74 (m, 2H),1.89 (s, 3H), 3.56 (s, 3H),3.73 (m, 2H), 3.83 (m, 4H), 4.02 (m, 4H)}
\]

### 3.2.3 Preparation of N-allyl-N-methyl-morpholinium bromide [AMMorp][Br]

In 250 mL round bottom flask, N-methylmorpholine (1 eqv) and allyl bromide (1.5 eqv) were added to acetonitrile (10 vol). The solution was stirred at 70 °C for 24 h (Scheme 4). The flask was then brought to room temperature and placed in a freezer at
4 °C for 12 h. Pale white crystals were slowly forming which were filtered and recrystallized with tetrahydrofuran and isopropanol. The resulting pale white solid was dried and stored in desiccator. M. P.: 182 °C.

$^1$H NMR: (400 MHz, CDCl3): δ (ppm) = 3.56 (s, 3H), 3.77 (m, 4H), 4.05 (m, 4H), 4.68 (d, 2H), 5.79 (d, 1H), 5.91 (d, 1H), 6.02 (m, 1H)

![Scheme 4: Preparation of N-allyl-N-methyl-morpholinium bromide](image)

3.2.4 Synthesis of different N-allyl-N-methyl-morpholinium salts

**Step 1:** [AMMorp][Br] (1.0 eqv) was dissolved in ethanol and a small amount of deionized water which then treated with 1.5 eqv of metal salts (sodium acetate, potassium carbonate, potassium phosphate tribasic, potassium phosphate monobasic, sodium bisulfate and sodium hydroxide), stirred vigorously at room temperature for 24 h (Scheme 5), in order to obtain corresponding N-allyl-N-methyl-morpholinium acetate [AMMorp][OAc], N-allyl-N-methyl-morpholinium carbonate [AMMorp]$_2$[CO$_3$], N-allyl-N-methyl-morpholinium phosphate [AMMorp]$_3$[PO$_4$], N-allyl-N-methyl-morpholinium dihydrogen phosphate [AMMorp][H$_2$PO$_4$], N-allyl-N-methyl-morpholinium bisulfate [AMMorp][HSO$_4$], N-allyl-N-methylmorpholinium hydroxide [AMMorp][OH] respectively. The solid was filtered through funnel and solvent was removed under vacuum. Different viscous yellow liquids were obtained. These liquids were further purified through ion exchange method.
Step II: 10.0 g Amberlite IRA-400(R-OH) in deionized water was loaded in a glass column. 100 mL solution of 1.0 M metal salts passed through the column with flow rate around 1mL/min. The column was then thoroughly washed with deionized water till the pH of the eluent was same as that of deionized water.

The yellow liquid obtained from step I was dissolved in 50 mL deionized water. The solution was loaded to the column carefully. The column was then eluted with deionized water as an eluent with a controlled flow rate of 1 mL/min. Approximately 6 mL of eluent solution was collected in each test tube and further analyzed by ion chromatography or NMR. The solution in test tubes containing pure [AMMorp]n[X]n− was evaporated under vacuum and dried to obtain yellow liquid.

N-allyl-N-methyl-morpholinium acetate
1H NMR: (400 MHz, CDCl3): δ (ppm) = 1.93 (s, 3 H), 3.43 (s, 3 H), 3.69 (m, 4 H), 4.01 (m, 4 H), 4.54 (d, 2 H), 5.74 (d, 1 H), 5.83 (d, 1 H), 5.98 (m, 1 H)

3.2.5 Preparation of N-benzyl-N-methyl-morpholinium chloride [BnMMorp][Cl]

In 250 mL round bottom flask, N-methylmorpholine (1 eqv) and benzyl chloride (1.5 eqv) were added to acetonitrile (10 vol). The solution was stirred at 70 °C for 24 h (Scheme 6). The flask was then brought to room temperature and placed in a freezer at 4 °C for 12 h. The white crystals were filtered and recrystallized with tetrahydrofuran and isopropanol. The resulting white solid was dried and stored in desiccator. m.p.: 253 °C.

1H NMR: (400 MHz, CDCl3): δ (ppm) = 3.54 (s, 3 H), 3.76 (m, 4 H), 4.01 (m, 4 H), 5.32 (s, 2 H), 7.47 (m, 3 H), 7.68 (m, 2 H)
3.2.6 Synthesis of N-benzyl-N-methyl-morpholinium acetate [BnMMorp][OAc]

[BnMMorp][OAc] was synthesized in three steps. In the first step, sodium hydroxide was added to [BnMMorp][Cl] in methanol and the solution was stirred at room temperature for 1 h. White precipitate sodium chloride was removed by filtration. In the second step, acetic acid was added to the filtrate. The solution was stirred again at room temperature for 1 h. After evaporation of methanol, the product was dissolve in acetone and remaining inorganic salt was removed. Finally the product was further purified by the ion exchange method. The product was dried under vacuum at 80 °C for 3 h. The product was analyzed by ion chromatography and 1HNMR.

1HNMR: (400 MHz, CDCl3): δ (ppm) = 1.98 (s, 3 H), 3.44 (s, 3H), 3.71 (m, 4H), 3.99 (m, 4H), 5.15(s, 2H), 7.44(m, 3H),7. 61(m, 2H).

3.3 Regeneration of cellulose

After dissolution cellulose, small amount of the mixture was put into the glass slide and pressed the mixture with cover slip, making a thin film. After cooling the film which
was washed several times with distilled water, then the film was dried under 80°C for 10 min. Finally a white dry film was obtained.

3.4 Recovery of ionic liquids

The completely dissolved cellulose was diluted with 5-fold amount of methanol and kept for 1 h. When the color of cellulose was changed to white, the regenerated cellulose was separated with solution by filtration. The cellulose was isolated as hard beads (Figure 16a). The methanol was evaporated under vacuum for 3 h, getting a concentrated liquid which was analyzed by 1HNMR and used to dissolve cellulose again.

4. Results and discussion

Various ionic liquids, mainly imidazolium cation based ionic liquids have been used for the dissolution of cellulose. However, in spite of momentous efforts, only a few ILs could efficiently dissolve cellulose. Although the so called NMMO process was successfully industrialized for the dissolution of cellulose, very few reports exist that describe the dissolution of cellulose in morpholinium cation based ionic liquids. Thus, it was interesting to study the effect of morpholinium cation based ionic liquids on the dissolution of cellulose, followed by regeneration of cellulose fibers.

Herein, we report our initial findings of dissolution of cellulose in different morpholinium cation based ionic liquid brines. In this study, [BMMorp][Br], [AMMorp][Br], [BnMMorp][Cl] were synthesized as starting materials. [BMMorp][OAc], [AMMorp][OAc], [BnMMorp][OAc] were synthesized and analyzed for their efficacy on the dissolution of cellulose. Most of these ionic liquids contained approximately 6 wt% water. As the [AMMorp][OAc]-brine has shown a strong ability to dissolve cellulose, a series of N-allyl-N-methyl-morpholinium salts with different anions were also synthesized and analyzed for their efficacy on the dissolution of cellulose, viz. [AMMorp][HSO₄], [AMMorp][OH], [AMMorp][CO₃], [AMMorp][PO₄] and[AMMorp]-[H₂PO₄].

4.1 Synthesis of ionic liquids

4.1.1 Synthesis of N-butyl-N-methyl-morpholinium salts

[BMMorp][Br] was prepared in accordance with usual synthetic methods where upon N-methylmorpholine was treated with butyl halide in acetonitrile. The product was obtained as a white solid and recrystallized with 2-propanol and THF. The purity of the product was determined by 1HNMR. Since the acetate anion has been found to have a positive impact on the dissolution of cellulose, we then focused our efforts on the synthesis of [BMMorp][OAc].

4.1.1.1 Effect of solvent on the yield of [BMMorp][OAc]

Initially we tried to synthesize [BMMorp][OAc] using anion metathesis reaction wherein [BMMorp][Br] was treated with sodium acetate in dichloromethane. No metathesis was resulted in dichloromethane. Moreover, the use of water as solvent could afford only 4% [BMMorp][OAc]. Thus, we decided to use alcohols as solvent.
Methanol as solvent resulted in 32% yield of the product while ethanol as solvent improved the yield further to 75%. Importantly, n-butanol as a solvent increased the yield of product to 90%. Thus, it is evident that alcohols are more favorable for metathesis reaction of bromide with acetate anion (Figure 8). We also attempted a two step approach in which [BMMorp][Br] was first treated with a strong base potassium tert-butoxide followed by addition of acetic acid. Nevertheless, the method failed to give high yield of [BMMorp][OAc].

![Figure 8: The yield of [BMMorp][OAc] using different solvents.](image)


### 4.1.1.2 Ion Exchange method

In order to obtain high purity [BMMorp][OAc], we changed our strategy to ion exchange approach for the synthesis of [BMMorp][OAc]. Amberlite IR 400 (OH) resin was employed for this purpose. The resin was first charged in the glass column. The solution of sodium acetate was then slowly run through the resin bed. The pH of eluent was slowly changed from 14 to 8 which indicated the complete conversion of OH groups with acetate groups. The dilute aqueous solution of [BMMorp][Br] was then slowly charged onto the resin bed. The purity of eluent collected in each test tube was analyzed by Ion chromatography. The test tubes containing pure [BMMorp][OAc] were mixed and evaporated under vacuum at 70 °C for 3 h to remove water molecules and obtained pure [BMMorp][OAc] as viscous liquid.

![Figure 9: Pure [BMMorp][OAc]](image)

### 4.1.3 Synthesis of N-allyl-N-methyl-morpholinium salts
Wu et al. have synthesized a novel IL 1-allyl-3-methylimidazolium chloride [Amim][Cl] which combined with allyl group which have lower melting point, lower viscosity when compared to other ILs substituted by saturated alkyl containing the same number of carbon atoms [76]. A series of N-allyl-N-methyl-morpholinium salts were synthesized. N-allyl-N-methyl-morpholinium bromide was synthesized as starting material. The ionic liquids based different anions were obtained through two stages. Initially, N-allyl-N-methyl-morpholinium salts were afforded by to anion metathesis reaction. Pure N-allyl-N-methyl-morpholinium salts were obtained by the ion exchange method. [AMMorp][OAc] was analyzed by ion chromatography and 1H NMR, the others ionic liquids were determined by ion chromatography. The purity of other ionic liquids was determined by ion chromatography. The results showed that there was no bromide present in all these ionic liquids (detection limit $\geq 0.1$ ppm).

### 4.1.4 Synthesis of N-benzyl-N-methyl-morpholinium acetate

Pernak et al. synthesized N-benzyl-N-methyl-morpholinium salts using anion exchange reaction by two step method, but the yield was 90.5% [77]. In this work, in order to get higher purity of [BnMMorp][OAc], three step method was used. Initially, we followed the reported procedure to obtain [BnMMorp][OAc] which passed through the column at last step. However, we could not obtain the pure [BnMMorp][OAc], the yield was only 92.5% through our three step method.

### 4.1.5. Determination of the amount of water in ionic liquids

As water acts an anti-solvent for ionic liquids and can extract ionic liquids into the aqueous phase as the water molecules form hydrodynamic shells around the ionic liquid molecules inhibiting the direct interactions between cellulose and ionic liquid molecules [58]. Therefore, it is very important to know the exactly amount of water in synthesized ionic liquids. In this case, the amount of water in several ionic liquids was measured by Karl Fischer titration method.

The analysis showed that (Table 3) the amount of water present in ionic liquids was between 5-7 wt%. Fortunately, most of tested ionic liquids could dissolve cellulose with high content of water. This means that high amount of water in these ionic liquids would have not negative impact their dissolution ability for cellulose. It is no doubt that a large amount of water can extract ionic liquid, but further experiments are needed to determine the upper limit of water in ionic liquids which can allow dissolution for cellulose in these ionic liquids.

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>Weight Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMMorp][OAc]</td>
<td>6.63</td>
</tr>
<tr>
<td>[AMMorp][OAc]</td>
<td>4.95</td>
</tr>
<tr>
<td>[AMMorp][HSO_4]</td>
<td>7.13</td>
</tr>
<tr>
<td>[BnMMorp][OAc]</td>
<td>6.25</td>
</tr>
</tbody>
</table>
4.2 Dissolution of cellulose

The newly synthesized ILs were further probed for the dissolution of cellulose. In a typical procedure for the dissolution studies, ionic liquid and certain amount cellulose were charged in the 10 mL vial under nitrogen atmosphere and then placed into oil bath at different temperatures for different time scale. The dissolution of cellulose was analyzed visually and using optical microscopy. Different ionic liquids were investigated in terms of their ability to dissolve cellulose.

4.2.1 Dissolution of cellulose in N-butyl-N-methyl-morpholinium acetate- brine

Though, acetate ions are found to increase the solubility of cellulose in ionic liquid [78-82], [BMMorp][OAc]-brine unable to dissolve cellulose against our expectation (Table 3). As it has been seen that halide ions are good hydrogen bond acceptors and their presence facilitates the dissolution of cellulose [55], we decided to employ the mixture of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water for the dissolution of cellulose. We started our study with addition of 2 wt% cellulose to the ionic liquid mixture and heated at 80 °C for 24 h. To our surprise, this mixture could dissolve the cellulose giving a transparent solution. Further addition of 2 wt% cellulose in the solution with continued heating at 80 °C for 24 h resulted in a transparent solution leading to dissolution of 4 wt% of cellulose. Addition of 2 wt% of cellulose to the solution had the same fate. However, the solution now turned viscous enough to restrict the stirring of the solution (Table 4). Increasing the amount of cellulose by 2 wt% did not result in its dissolution as it was suspended on the top of the viscous paste of ionic liquid and cellulose. Thus, the mixture of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water could to dissolve 6 wt% of cellulose. The heating of solution of 6 wt% cellulose in mixture of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water at 80 °C for 24 h also resulted in similar viscous paste of IL and cellulose. Thus, stepwise addition of cellulose is not essential for the efficient dissolution of cellulose.

Table 4: Dissolution of cellulose N-butyl-N-methyl-morpholinium salt-brines

<table>
<thead>
<tr>
<th>Ionic Liquid-brines</th>
<th>Time (h)</th>
<th>Cellulose (wt %)</th>
<th>Temp. (°C)</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMMorp][OAc]-brine</td>
<td>24</td>
<td>2</td>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water</td>
<td>24</td>
<td>6</td>
<td>80</td>
<td>++</td>
</tr>
</tbody>
</table>

[a] "++" symbol indicates dissolution;[b] "—" symbol indicates no dissolution.

4.2.2 Dissolution of cellulose in organic electrolytic solutions

Recently, Rinaldi reported a new approach of dissolving cellulose in organic electrolyte solutions containing small fraction of ionic liquid in order to circumvent several drawbacks such as slower dissolution due to high viscosity of ionic liquids and the high cost of ionic liquids [83]. Hence, we investigated the dissolution of cellulose in N-butyl-N-methyl-morpholinium based ionic liquids with few organic amines and protic solvents as additive. The amount of additives has been varied from 2 wt% - 100 wt%.
The organic amines studied as additives were N-methylmorpholine, $N,N,N',N'$-tetramethyl guanidine, $N, N$-dimethylethanolamine, $N, N$-dimethylbenzylamine, 2-pyrrolidinone, $N$-methylpyrrolidinone. The protic solvents used were dimethylformamide, ethanol and 2-butanol.

4.2.2.1 The influence of amines

In a typical procedure, 2 wt% cellulose was mixed with mixture of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water. A series of organic amines were used as additives in dissolution of cellulose, such as $N$-methylmorpholine, $N,N,N',N'$-tetramethylguanidine, $N,N$-dimethylethanolamine, $N,N$-dimethylbenzylamine, 2-pyrrolidinone and $N$-methyl- pyrrolidinone. 2 wt% of organic amine was added to it respectively. The solution was then heated at 80 °C for 24 h. If there is no dissolution of cellulose, more organic amine was added until 100 wt%. It was found that none of the organic amines from the concentrations of 2 wt%-100 wt% were able to dissolve cellulose, nevertheless, the viscosity of the solutions were gradually reduced with increasing amount of amine. Thus, all of these amines acted as an anti-solvent in the dissolution of cellulose in morpholinium based ionic liquid mixture.

4.2.2.2 Effect of protic solvents

Interesting results were obtained when protic solvents were employed as additives with ionic liquid mixture for dissolution of cellulose. As shown in Table 5 and Table 6, in presence of 2 wt% ethanol, the ionic liquid mixture could dissolve 2 wt% cellulose after heating at 70 °C for 24 h giving a white viscous paste. However, further addition of 2 wt% of cellulose did not lead to the dissolution. Thus, we increased the amount of ethanol by 2 wt%, no dissolution was achieved. Increasing the amount ethanol resulted in the same fate.

In case of 2-butanol, introduction of 2 wt% of 2-butanol in ionic liquid mixture could able to dissolve up to 4 wt% of cellulose leading to a white paste. Increasing the amount of cellulose by 2 wt% with increasing amount of 2-butanol did not lead to the further dissolution cellulose. Thus, 2-butanol found to be more efficient than ethanol in terms of dissolution of cellulose in morpholinium cation based ionic liquid mixture. Dimethylformamide, however, was unable to assist in the dissolution of cellulose in the studied ionic liquid mixtures.

Table 5: Dissolution of cellulose in 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water in presence of ethanol

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Ethanol (wt %)</th>
<th>Cellulose (wt %)</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>24</td>
<td>2</td>
<td>2</td>
<td>++</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>4</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>6</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>10</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>20</td>
<td>4</td>
<td>—</td>
</tr>
</tbody>
</table>
Table 6: Dissolution of cellulose in 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] with 6.7 wt% water in presence of 2-butanol

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>2-Butanol (wt %)</th>
<th>Cellulose (wt %)</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>24</td>
<td>2</td>
<td>2</td>
<td>++</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>2</td>
<td>4</td>
<td>++</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>4</td>
<td>6</td>
<td>—</td>
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<tr>
<td>70</td>
<td>24</td>
<td>6</td>
<td>6</td>
<td>—</td>
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<td>70</td>
<td>24</td>
<td>10</td>
<td>6</td>
<td>—</td>
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<tr>
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<td>50</td>
<td>6</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>100</td>
<td>6</td>
<td>—</td>
</tr>
</tbody>
</table>

[a] "++" symbols indicate dissolution; [b] "—" symbols indicate no dissolution

4.2.3 Dissolution of cellulose in N-allyl-N-methyl-morpholinium salt-brines

Wu et al. reported that 1-allyl-3-methylimidazolium chloride [Amim][Cl] can dissolve 5 wt% cellulose without any pretreatment or activation within only 20 min [76]. The allyl group in ionic liquids can accelerate the velocity of dissolution of cellulose. A series of ionic liquids based on N-allyl-N-methyl-morpholinium cation were synthesized and used to dissolve the cellulose. The results were shown at Table 7. Oil bath was preheated to preset temperature then vials were put into oil bath. Only
[AMMorp][OAc]-brine presented a strong ability to dissolve cellulose, which can dissolve 12 wt% cellulose in 20 min at 80 °C and gave a transparent gel. Although [AMMorp][HSO₄]-brine can dissolve 4 wt% cellulose under identical conditions, when the vial was cooled to room temperature, the mixture of ionic liquid and cellulose got stiff. However, if temperature was increased to 120 °C, [AMMorp][OAc]-brine and [AMMorp][HSO₄]-brine can dissolved 26 wt% and 8 wt% cellulose in 20 min respectively. The others N-allyl-N-methyl-morpholinium salt-brines have been shown their non-ability to dissolve cellulose at 80°C for 24 h.

Figure 10 shows the photographs of cellulose before and after heating in [AMMorp][OAc]-brine. The color was changed during dissolution of cellulose by increasing the weight of cellulose and increasing the temperature. Pale yellow color was shown in the mixture of 2 wt% cellulose with [AMMorp][OAc]-brine (Figure 11a). When 12 wt% cellulose was added, the color of mixture was changed to deep brown and it was look like a transparent deep brown gel (Figure 11b). Very viscous gel (Figure 11c) was observed after adding 26 wt% cellulose in [AMMorp][OAc]-brine at 120 °C. It is obvious to see that addition of more cellulose to ionic liquid-water brines resulted in higher viscosity of the mixture and thus, high temperature could reduce viscosity of the mixture which can accelerate the further dissolution of cellulose.

Table 7: Dissolution of cellulose in N-allyl-N-methyl-morpholinium salt-brines

<table>
<thead>
<tr>
<th>Ionic Liquid-brines</th>
<th>Time (h)</th>
<th>Cellulose (wt %)</th>
<th>Temp. (°C)</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AMMorp][OAc]-brine</td>
<td>20min</td>
<td>12</td>
<td>80</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>100</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>120</td>
<td>++</td>
</tr>
<tr>
<td>[AMMorp][HSO₄]-brine</td>
<td>20min</td>
<td>4</td>
<td>80</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>100</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>120</td>
<td>++</td>
</tr>
<tr>
<td>[AMMorp][OH]-brine</td>
<td>24</td>
<td>2</td>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>[AMMorp]₃[PO₄]-brine</td>
<td>24</td>
<td>2</td>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>[AMMorp][H₂PO₄]-brine</td>
<td>24</td>
<td>2</td>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>[AMMorp]₂[CO₃]-brine</td>
<td>24</td>
<td>2</td>
<td>80</td>
<td>—</td>
</tr>
</tbody>
</table>

[a] "++" symbols indicate dissolution; [b] "—" symbols indicate no dissolution.

Figure 10: The photographs of 26 wt% cellulose dissolved in [AMMorp][OAc]-brine
Figure 11: Different weight of cellulose dissolved in [AMMorp][OAc]-brine at different temperature, the images taken after cooling. (a) 2 wt% cellulose at 80°C; (b) 12 wt% cellulose at 80°C; (c) 26 wt% cellulose at 120°C

4.2.4 Dissolution of cellulose in \(N\)-benzyl-\(N\)-methyl-morpholinium acetate-brine

Pernak et al. prepared a series of \(N\)-benzyl-\(N\)-methyl-morpholinium salts using an anion exchange reaction. The thermal stability, toxicity and ability of dissolution of cellulose for all these morpholinium ionic liquids were analyzed [77]. They found that 90.5\% \([BnMMorp][OAc]\) had a best ability which dissolved 1wt\% microcrystalline cellulose. We synthesized 86.7 \% \([BnMMorp][OAc]\) with 7\% \([BnMMorp][Cl]\) and 6.3 wt\% water and tested the ability of dissolution of cellulose. To our surprised, the synthesized \([BnMMorp][OAc]\)-brine had a good ability to dissolve cellulose. Almost 4 wt\% cellulose was dissolved in 20 min at 80°C. When temperature was increased to 100°C and 120°C, 16 wt\% and 22 wt\% cellulose was dissolved respectively within 20 min, as shown at Table 8.

Table 8: Dissolution of cellulose in 86.7 \% \([BnMMorp][OAc]\) with 7\% \([BnMMorp][Cl]\) and 6.3 wt\% water

<table>
<thead>
<tr>
<th>Ionic Liquid-brine</th>
<th>Time (min)</th>
<th>Cellulose (wt %)</th>
<th>Temp. (°C)</th>
<th>Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.7 % ([BnMMorp][OAc]) with 7% ([BnMMorp][Cl]) and 6.3 wt% water</td>
<td>4</td>
<td>80</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>100</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>120</td>
<td>++</td>
<td></td>
</tr>
</tbody>
</table>

[a] “++” symbols indicate dissolution

4.2.5 Analysis of cellulose solution using optical microscopy

4.2.5.1 Analysis of cellulose solution using optical microscopy in \([BMMorp][OAc]\)-brine

The effect of solvents on cellulose fiber structure and the dissolution of cellulose fibers were analyzed by optical microscopy. As shown in Figure 12 A, when cellulose is soaked in water, the cellulosic fibers were clearly seen in microscopic images. Importantly, when cellulose is dissolved in the solution of 70\% \([BMMorp][OAc]\) and 23.3\% \([BMMorp][Br]\) and 6.7 wt\% water and in solution of 70\% \([BMMorp][OAc]\) and 23.3\% \([BMMorp][Br]\) and 6.7 wt\% water with 2 wt\% 2-butanol, fibers were difficult to observe in the microscopic images, which clearly indicated the efficiency of these systems in dissolving cellulose (Figure 12 B, E). In none of the cases, the ballooning of
fibers was seen. In case of 2 wt% cellulose in solution 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] and 6.7 wt% water with 6 wt% 2-pyrrolidinone, cellulosic fibers were seen to fragmented in smaller fibers upon heating at 80 °C (Figure 12 C). However, fiber structure remained intact when the derivative of methyl derivative pyrrolidinone was used as an additive (Figure 12 D).

Figure 12: Optical micrograph of fibers in different solvent systems. (A) Cellulose soaked in water, (B) 2 wt% cellulose in 70% [BMMorp][OAc] with 23.3% [BMMorp][Br] and 6.7 wt% water, (C) 2 wt% cellulose in solution of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] and 6.7 wt% water with 6 wt% 2-pyrrolidinone, (D) 2 wt% cellulose in solution of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] and 6.7 wt% water with 4 wt% N-methyl-2-pyrrolidinone, (E) 2 wt% cellulose in solution of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] and 6.7 wt% water with 2 wt% 2-butanol, (F) 2 wt% cellulose in solution of 70% [BMMorp][OAc] and 23.3% [BMMorp][Br] and 6.7 wt% water with 20 wt% ethanol.
The effect of ionic liquid [BMMorp][OAc]-brine with increasing in temperature on the cellulosic fiber structure was also studied using optical microscopy. **Figure 13** shows microscopic images of 2 wt% cellulose in [BMMorp][OAc]-brine at different temperatures: room temperature, 40°C, 60°C, 80°C, 100°C. It can be clearly seen from the microscopic images that with increase in temperature, swelling of more and more of the fibers took place. The solvent seems to be penetrating inside fibers causing not only swelling the fibers but also the outer edges of the fibers found to be distinctly pale as compared to brighter edges at room temperature.

![Microscopic images of 2 wt% cellulose in [BMMorp][OAc]-brine at different temperatures](image)

**Figure 13**: Microscopic images of 2 wt% cellulose in [BMMorp][OAc]-brine at different temperatures: (a) Room temperature, (b) 40°C, (c) 60°C, (d) 80°C, (e) 100°C.

### 4.2.5.2 Analysis of cellulose solution using optical microscopy in N-allyl-N-methyl-morpholinium salt-brines

Cellulosic fiber structure were analyzed by optical microscopy in a series of N-allyl-N-methyl-morpholinium salt-brines, microscopic images showed that the cellulose can
be dissolved wherein [AMMorp][OAc]-brine and [AMMorp][HSO₄]-brine. It is clear to see that there is no cellulose fiber structure in these microscopic images (Figure 14 b, c, d) when compared with the microscopic image (Figure 14 a) which presents microscopic image of cellulose in [AMMorp]₂[CO₃]-brine where cellulose fiber structure was clearly seen. As the increasing temperature, more and more cellulose was dissolved in [AMMorp][OAc]-brine or [AMMorp][HSO₄]-brine. Figure 14 b, c, d show the different percent cellulose in [AMMorp][OAc]-brine under different temperature, but no cellulose fiber structure was seen in both of them.

![Microscopic images of cellulose in different ionic liquid-brines.](image)

**Figure 14**: Microscopic images of cellulose in different ionic liquid-brines. (a) 2 wt% cellulose in [AMMorp]₂[CO₃]-brine at 40 °C; (b) 4 wt% cellulose in [AMMorp][OAc]-brine at 80 °C; (c) 12 wt% cellulose in [AMMorp][OAc]-brine at 80 °C; (d) 26 wt% cellulose in [AMMorp][OAc]-brine at 120 °C.

### 4.2.5.3 Analysis of cellulose solution using optical microscopy in [BnMMorp][OAc]-brine

It was reported that N-benzyl-N-methyl-morpholinium acetate has the ability to dissolve 1 wt% cellulose at 100 °C. However, To our surprised, 86.7 % [BnMMorp][OAc] with 7% [BnMMorp][Cl] and 6.3 wt% water was synthesized by three steps which can dissolved 16 wt% cellulose under 100 °C and 22 wt% cellulose at 120 °C. Microscopic images of cellulose were shown at **Figure 15**. Cellulosic fiber structure can be observed (Figure 15 b) when 24 wt% cellulose dissolved in 86.7 % [BnMMorp][OAc] with 7% [BnMMorp][Cl] and 6.3 wt% water at 120 °C.
4.3 Regeneration of cellulose

Regenerated cellulose can be obtained during the recovery of ionic liquids. When the gel material was subjected to methanol, the ionic liquids were extracted by the molecular solvent. At the same time the gel material was changed to white beads (Figure 16 a). A pale yellow thin film was obtained after using glass slide and cover slip for cellulose restructuring. A colorless film was obtained after the film was washed several times using distilled water (Figure 16 b). However, this film was not stable. When drying the colorless film at 80 °C for 10 min, a white cellulose film was obtained.

4.4 Recovery of ionic liquids

A solution was obtained after filtration during the regeneration of cellulose, which contained an ionic liquids and the anti-solvent (Figure 17 b). In this work, methanol was added into the gel material as the anti-solvent. Methanol was evaporated under vacuum and the residual was analyzed by means of 1HNMR. On the basis of the NMR data, no decomposition was observed upon cellulose dissolution-regeneration cycle in [AMMorp][OAc]. For further investigation of the dissolution ability of this ionic liquid for cellulose, recovered [AMMorp][OAc] was used in another cycle. 4 wt % cellulose was quickly dissolved at 80 °C in 20 min. Thus, the recovered [AMMorp][OAc] still possessed
a strong ability to dissolve cellulose. The Figure 17 shows the extracted ionic liquid in methanol and recovered ionic liquid.

![Figure 17: Recovery of ionic liquids. (a) recovered ionic liquid; (b) extracted ionic liquid in methanol.](image)

5. Conclusions

In conclusion, a series of morpholinium cation based ionic liquids were prepared by different synthetic methods in normal bench-top laboratory conditions. Amongst various investigated solvents during the anion metathesis of bromide ion to acetate ion, n-butanol was found to be the most efficient solvent. However, the pure [BMMorp][OAc] could only be obtained via the ion exchange method. As a consequence, the other ionic liquids were also synthesized applying the ion exchange method as the last step.

Qualitative cellulose dissolving experiments with morpholinium ionic liquids showed that [AMMorp][OAc]-brine expressed strong efficacy for dissolution of cellulose without any pretreatment. Among a series of N-allyl-N-methyl-morpholinium salt-brines, only [AMMorp][OAc]-brine and [AMMorp][HSO₄]-brine showed the ability to dissolve cellulose, but [AMMorp][HSO₄]-brine express the lower power for dissolution of cellulose when compared to [AMMorp][OAc]-brine. This again demonstrated the superior ability of acetate-based morpholinium ionic liquids to dissolve cellulose, in comparison to the corresponding evaluated alternatives containing other anions. The combination of [BMMorp][OAc]-brine with [BMMorp][Br] and [BnMMorp][OAc]-brine with [BnMMorp][Cl] were also found to be cellulose dissolving solvent, which showed the effect of halide ions during dissolution process of cellulose.

Different substituent group in acetate-based morpholinium ionic liquids also impact the ability of dissolution of cellulose. Among these ionic liquids, the allyl group demonstrated a stronger positive effect for cellulose dissolution than either benzyl or butyl group. Extraction and recovery of [AMMorp][OAc] was carried out and the recovered [AMMorp][OAc] demonstrated a strong ability to dissolve cellulose. The regenerated cellulose showed a good physical stability as a dried film.

The use of different additives to cellulose dissolving mixture of [BMMorp][OAc] with [BMMorp][Br] and water showed very interesting results. None of the investigated
amines were able to assist the dissolution of cellulose; rather they acted as an anti-solvent. Importantly, ethanol and 2-butanol helped in dissolving cellulose to certain extent. Micrographic studies of various samples indicated that certain solvent systems bring about fragmentation of the cellulosic fibers while other keeps the cellulosic fiber intact at high temperature. The absence of fibers in the micrographic image of the cellulosic solution gave an indication of cellulose dissolution in the solution. Micrographic studies of dissolution of cellulose in [BMMorp][OAc]-brine suggested that the fibers were more expansively swelled with increase in temperature of the solution indicating greater penetration of solvent with rise in temperature.
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7. References

8. Appendixes – NMR

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Current Data Parameters

NAME: MethylEster
EXPERIMENT: 1H-NMR

F2 - Acquisition Parameters

Date: 26110808
Time: 15.21
INSTRUMENT:Bruker

F2 - Processing Parameters

SI: 399.600 MHz

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Bruker

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