Universidad de Valladolid

ESCUELA DE INGENIERÍA INDUSTRIALES

DEPARTAMENTO DE INGENIERÍA QUÍMICA Y
TECNOLOGÍA DEL MEDIO AMBIENTE

TESIS DOCTORAL:

STUDY OF THE IMPROVEMENT OF CELLULOSE PROCESSING USING IONIC LIQUIDS

Presentada por Cristina Jiménez de la Parra
para optar al grado de
doctora con mención internacional por la
Universidad de Valladolid

Dirigida por:
Doctora María Dolores Bermejo Roda
Profesora Doctora María José Cocero Alonso

UNIVERSIDAD DE VALLADOLID

ESCUELA DE INGENIERÍAS INDUSTRIALES

Secretaría

La presente tesis doctoral queda registrada en el folio Nº______

del correspondiente Libro de Registro con el Nº__________

Valladolid, a _______ de _________________ de 2016

Fdo. El encargado del Registro

María Dolores Bermejo Roda

Investigadora Ramón y Cajal del Departamento de Ingeniería Química
y Tecnología del Medio Ambiente
Universidad de Valladolid
y

María José Cocero Alonso

Catedrática del Departamento de Ingeniería Química
y Tecnología del Medio Ambiente
Universidad de Valladolid

CERTIFICAN QUE:

CRISTINA JIMÉNEZ DE LA PARRA ha realizado bajo su dirección el trabajo ***"STUDY OF THE IMPROVEMENT OF CELLULOSE PROCESSING USING IONIC LIQUIDS***", en el Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Escuela de Ingenierías Industriales de la Universidad de Valladolid. Considerando que dicho trabajo reúne los requisitos para ser presentado como Tesis Doctoral expresan su conformidad con dicha presentación.

Valladolid a _____ de_____________ de 2016.

Fdo. María José Cocero Alonso

Fdo. María Dolores Bermejo Roda

Reunido el tribunal que ha juzgado la tesis doctoral "***STUDY OF THE IMPROVEMENT OF CELLULOSE PROCESSING USING IONIC LIQUIDS***" presentada por Cristina Jiménez de la Parra y en cumplimiento con lo establecido por el Real Decreto 861/2010 (BOE 28.01.2011) ha acordado conceder por ______________________________la calificación de___________________________.

Valladolid, a de de 2016

PRESIDENTE SECRETARIO

1er Vocal 2do Vocal 3er Vocal

Contents

Abstract, Objectives and Content

Índice de contenidos

Abstract, objectives and content

ABSTRACT

In the last years there is a growing interest in the processing of cellulose and other biopolymers such as lignin, hemicellulose or chitin in order to use them as a raw material for obtaining materials, chemicals and fuels. Even when cellulose is the most abundant natural source of carbon, most of it is not currently processed due to the difficulty of dissolving it.

Traditionally, cellulose is mostly used for paper production using highly pollutant processes with strong acids and bases. In the last years there is a growing interest in using cellulose for material processing or as a source for producing chemicals and new process are under developments. Most of them are based on the fermentation of sugars from cellulose after an acid or enzymatic pre-treatment to obtain bioethanol, but this kind of processes present a number of limitations.

In 2002, the pioneer work of Swatloski and co-workers demonstrated that some ionic liquids were able to dissolve cellulose in high concentrations becoming a promising media for the processing of polymers, which created a large interest in industry.

In the **chapter 1** the state of the art of cellulose processing in ionic liquids is analyzed. In first place an introduction about cellulose, ionic liquids and the mechanism of dissolving cellulose in these solvents is presented. In the second part, an analysis of the new technologies developed in the field of biomass processing using ionic liquids is presented, paying special attention to the patents published and the companies involved on its development. These technologies have been divided into six main groups: dissolution and precipitation of cellulose; biomass fractionation; delignification or cellulose pretreatment for hydrolysis reactions or a fermentation process for the production of bioethanol; reactions to obtain bio-refining products and chemicals; preparation of cellulose composites and substitution reaction to obtain cellulose derivatives. Ionic liquids have generated a lot of interest as a clean alternative to the traditional polluting processes, both in industry and academia, owing to their capacity for dissolving biopolymers. The processes proposed are simple and relatively easy to implement being somehow limited by the high viscosity of the mixture biopolymer/IL and in some cases with the recoverability and recyclability of the IL. Since 2005 to the

present more than 70 patents related to the processing of biomaterials to form different chemicals and fuels as well as composite materials and substituted polymers, have been published. A great number of these patents are owned by companies such as BASF and Eastman Chemical Companies. Nevertheless, none of these processes is yet implemented at industrial scale.

The **second part** of this work is devoted to the determination of physical properties of cellulose dissolving ionic liquids. As ionic liquids are relatively new substances, physical properties determination and their modelling play an important role in almost every research related with ionic liquids, because in many cases these properties are unknown of determined with high uncertainty.

In **chapter 2**, the densities and viscosities of aqueous mixtures of two cellulose dissolving ionic liquids, 1-allyl-3-methylimidazolium chloride [amim][Cl] and 1-ethyl-3-methyl imidazolium acetate [emim][Ac], have been experimentally determined for water concentration up to approx. 35% water at atmospheric pressure and temperature range from 298.15 to 373.15 K. These two ionic liquids were selected because they are two of the most widely used for cellulose processing. Using density data molar excess volumes were calculated, resulting in negative values. Literature viscosity correlations were modified in order to describe the viscosity as a function of temperature and water concentration for both water concentrations lower than x_{H2O}=0.4 and for all the water concentration range. These modified equations were applied to correlate viscosity of water + ionic liquid viscosity data for other 1-alkyl-3-methylimidazolium chloride ionic liquids as well as for ethanol + 1-ethyl-3-methyl imidazolium acetate from literature obtaining a good reproducibility of the data.

In the **third part**, **chapter 3**, performed in the laboratories of QUILL in the Queen´s University of Belfast (UK), a new approach for improving cellulose processing using ionic liquids was undertook. The use of protic ionic liquid (PIL) was proposed. This kind of ILs has the particularities that can be easily recovered by distillation, recovering the constituting acid and base that can be later used to re-synthetize the PIL. After testing several acid and base, the optimum PIL among those investigated for cellulose processing was found to be that synthetized by mixing the strong base 1,4-diazabicyclo[4.3.0]non-5-ene and methoxyacetic acid [dbnH][MeOAc]. This PIL present a melting point of 30ºC and viscosities lower than those of imidazolium chloride ILs. This PIL was able to dissolve 10% cellulose in weight at only 40ºC in 3 h stirring and can be used to synthetize cellulose acetate.

In the **fourth part** of this work, the use of CO_2 as a co-solvent for viscosity reduction in biomass processing using ionic liquids is analyzed. To do so, the selected ionic liquid was the 1-butyl-3-methylimidazolium chloride [bmim][Cl]. This ionic liquid has been widely applied for biomass processing due to its high solubility but presents the inconvenient of its high viscosity and melting point.

In **chapter 4**, densities and viscosities of the ionic liquid 1-butyl-3-methylimidazolium chloride were determined and other properties as solubilities of CO_2 and melting points compiled from literature.

In **chapter 5** the influence of CO_2 in several reactions for cellulose processing is studied. The processes for cellulose processing considered in this chapter were hydrolysis and synthesis of cellulose acetate. In first place it was proved that CO_2 did not cause cellulose precipitation, it was tested by keeping a cellulose solution of [bmim][Cl] under CO_2 atmosphere for several days without observing cellulose precipitation. Similar results were obtained in hydrolysis with and without CO_2 atmosphere. This can be explained because in the hydrolysis process water was used as a reagent and the reduction of viscosity caused by water is higher than that caused by CO_2. Nevertheless at pressures of CO_2 higher than 45 bar a reduction in the hydrolysis was observed. The production of cellulose acetate was highly decreased when performed under CO_2 atmosphere. It was hypothesised that part of the acetylating reagent (acetic anhydride) could be in the CO_2 phase. Because under the P-T conditions used it present a solubility of 70% in mol in CO_2 phase. Nevertheless there are not data available of the influence of [bmim][Cl] in this equilibrium. The preliminary experiments performed in this work are not sufficient to explain the reason why the CO_2 is decreasing conversion in this reaction.

OBJECTIVES AND CONTENTS

The **objective** of this work is to develop solutions for the current challenges of the biomass processing in ionic liquids media. To do so the following specific objectives were proposed.

In the first place to make a detailed study of the state of the art in order to understand the process and identification its main limitations. To the realization of this objective was devoted the part 1 (chapter 1) of this work, in which the dissolution process of cellulose in ionic liquids is studied and the main industrial processes developed so far analyzed.

The second objective was to experimentally determine and model the main properties of the most frequently used ionic liquids for biomass processing. One ionic liquid of the imidazolium chloride family and other of the imidazolium acetate families were selected. As one of the main limitations of these ionic liquids was their high hygroscopicity, it was propose to determine the influence of water content in their densities and viscosities as well as to find a correlation for viscosity as a function of water content that may be of general use. This objective was worked in chapter 2.

The third objective was to find a solution of IL recyclability and try to dissolve cellulose under mild conditions. To do so the use of protic ILs was proposed. This objective was performed in collaboration with the team of prof. Seddon from the Queen´s University of Belfast (UK). It is proposed to find a protic IL able to efficiently process cellulose. Chapter 3 is dedicated to the accomplishment of this objective.

The last objective was to try to solve one of the main limitations of the process, the high viscosity of the ionic liquids, by using carbon dioxide as a co-solvent. It is well known that the use of molecular co-solvents can highly decrease viscosities of ionic liquids. This fact has widely used in biomass processing with ionic liquids using dimethylsulfoxide as a co-solvent. In this work, the use of carbon dioxide was proposed instead of using organic solvents. Carbon dioxide it is a green solvent without environmental limitations that can dissolved in ILs in concentrations as high as 70% in mol in some cases and decreasing its viscosity and melting points. CO_2 has the advantage that can be easily separated from the ILs without causing cross-contamination. To do so the IL [bmim][Cl] was selected due to its high capacity for biomass processing and its high viscosity and melting points.

This objective has been developed in chapter 4 and 5.

In chapter 4 the objective was to compile and determine experimentally some main physical properties of this IL such as melting points, viscosities, densities and CO_2 solubilities.

In chapter 5 the objective was to analyze the influence of CO_2 as co-solvent in several process for cellulose processing: hydrolysis and substitution of cellulose.

Part I. State of the art

Chapter 1. Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids*

Abstract

With depletion of the resources, biomass becomes a promising source of chemicals and fuels, currently obtained from petroleum. Cellulose is the most abundant material produced in the earth, but most of it is not processed due to the difficulty in dissolving it. Dissolution of cellulose requires severe temperature, non-conventional solvents and/or extreme acid or basic conditions, and its processing is very pollutant. Ionic liquids are presented as clean solvents for cellulose. These are substances composed entirely of ions that are liquid at room temperature. Among other interesting properties, ionic liquids are non-volatile and they are good solvents for a number of substances. Processes for cellulose processing in ionic liquids have been patented for several applications, being the most important: pre-treatment for biomass prior to fermentation for bio-ethanol production, hydrolysis for obtaining chemicals from biomass and substitution reaction for obtaining derivatives of cellulose and other natural polymers.

This chapter was published as: C. Jiménez de la Parra, A. Navarrete, M. D. Bermejo, M. J. Cocero, Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids, Recent Patents on Engineering, 2012, 6 (3) 159-181

1. INTRODUCTION

Nowadays, policies promoting the use of renewable energies and the rational use of raw materials are highly demanded. Thus, the development of new processes based on renewable raw materials and energy sources as biomass is necessary to support those requirements.

Lignocellulose is the most abundant vegetal biomass. It is mainly composed of three fractions: cellulose (30-60%), hemicellulose (20-40%) and lignin (10-30%), which are associated with each other.

- Lignin is a high molecular weight derivate of the amorphous heteropolymer phenylpropane. The main purpose of lignin is to give structural support to the plant. It is not soluble in water which makes the degradation of lignin very tough [1].
- Hemicellulose is a complex carbohydrate structure that consists of different polymers of pentoses, hexoses and sugar acids. Its main component is xylan [1].
- Cellulose is the most abundant polysaccharide in nature, with an annual production of 75 $\times 10^9$ tons/year [2]. It is constituted by β-D-glucose chains, consisting partially of crystalline and amorphous structures. Breaking or dissolving cellulose is relatively difficult in comparison with other polysaccharides because glucose molecules bind strongly together. It is not soluble in water or other conventional solvents at room temperatures. Thus, it is necessary to use strong acid or basis and/or high temperatures, what makes cellulose processing extremely polluting. For this reason, currently, only 0.2×10^9 tons/year are processed [3].

The main industrial application of cellulose is the production of paper usually from wood (ca. 150×10^6 tons/year). It is used after partial removal of the non-cellulosic (lignin, hemicelluloses) constituents from its original fiber form. Most of the long-haired cotton fibers (ca. 15×10^6 tons/year) are used in the manufacture of textiles. Only a minor portion of cellulose (ca. 5×10^6 tons/year) is used as starting material for the production of synthetic cellulosic fibers especially esters and other cellulose derivatives [3].

Basic chemicals (“building blocks”) such as glucose and lactic, glutaric or succinic acids etc., can also be obtained from cellulose and other polysaccharides such as starch. These molecules can be easily transformed into high added value compounds [4]. This is known as biorefining [5].

Recently, several studies and bibliographic reviews have been published where different chemicals are prepared from lignin [6] and cellulose [7] using methods, such as dissolution, hydrolysis, reaction, gasification or separation.

Traditional methods for the hydrolysis of cellulose are acid and enzymatic hydrolysis. Even when these processes have been remarkably improved in the last years, they present serious limitations. Enzymatic hydrolysis is expensive and time consuming, and sometimes requires biomass pretreatment. Acid hydrolysis, in turn, is limited by corrosion problems and it requires of high energetic pre-treatment and/or separation of the waste produced in the neutralization processes.

In 2002, Swatloski et al [8] proved that cellulose can be dissolved in high concentrations in a novel kind of solvents called ionic liquids. Ionic liquids as green solvents could be the basis on the development of cleaner processes to substitute highly polluting ones used currently in cellulose (or lignocellulosic compounds) transformation.

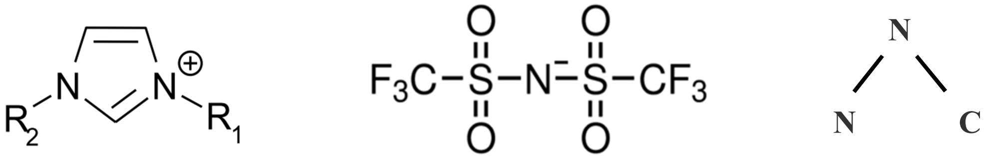
In this work, a brief introduction about ionic liquids is made, followed by an exposition of how the cellulose dissolution process works. The main part of the work is devoted to the new technologies that have been developed in the field of biomass processing using ionic liquids, paying special attention to the patents published and the companies involved in its development. These technologies have been divided into six main groups: dissolution and precipitation of cellulose; biomass fractionation; delignification or cellulose pretreatment for hydrolysis reactions or a fermentation process for the production of bioethanol; reactions to obtain bio-refining products and chemicals; preparation of cellulose composites and substitution reaction to obtain cellulose derivatives.

2. IONIC LIQUIDS

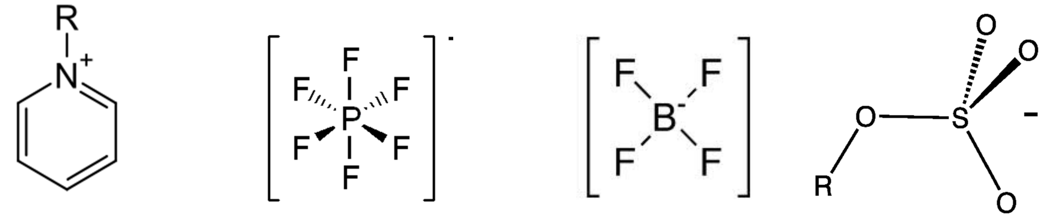
2.1. Definition and main properties

Ionic liquids (ILs) are substances composed entirely of ions that are liquid at room temperature, opposite to what happens to conventional inorganic molten salts that require much higher temperatures to be melted. The low melting points of ionic liquids are due to the high degree of asymmetry between cations and anions, which makes it difficult to form a solid crystal net [9].

Ionic liquids with different properties can be synthesized by combining different cation and anions. Thus, they are considered taylor-made solvents. Most widely used cations are those derived from pyridinium (py) or imidazolium (im) with alkyl substituents, and specially those with 1-alkyl-3-methyl imidazolium (amim). Among the most studied anions are bis(trifluoromethylsulfonylimide) (Tf_2N), triflate (TfO), hexafluorophosphate (PF_6), tetratfluoroborate (BF_4), alkylsulphates (RSO_4), nitrate (NO_3), acetate (Ac), as well as Cl^-, Br^- and I^- anions. The structures of these substances can be observed in figure 1.



imidazolium bis(trifluoromethylsulfonyl)imide dicyamide



pyridinium hexafluorophosphate tetrafluoroborate alkylsulphate

Figure 1. Most frequent cations and anions present in ionic liquids.

In recent times ionic liquids have become very popular due to some special properties. The most remarkable one is their negligible vapor pressure. In contrast to the volatile organic solvents normally used in industry, the evaporation of ILs into the atmosphere is low which decreases the contamination of the environment. Due to this property they are usually considered green solvents.

They present a high capacity to dissolve substances in a wide range of polarities at high concentrations (organics, inorganics, polymers including cellulose etc.). In addition their solvation properties can be also tuned by the appropriate modification of the cations, anions or both [9].

Other important properties of ionic liquids are: wide range of temperature in the liquid phase which can improve the control of kinetics in liquid phase reactions; high thermal and electrical conductivity; wide electrochemical window and high electrochemical stability against redox reactions [10]. Most ionic liquids are non-flammable and thermally and chemically stable and can be recovered and recycled.

As an inconvenient it can be mentioned that viscosities of ILs are relatively high compared to those of common organic solvents (one to three orders of magnitude). For a variety of ILs it has been reported to range from 66 to 1110 mPa at 20–25 ºC. The design of less viscous ILs is still a challenge for many applications [11].

2.2. Impurities in ionic liquids

It is known that physical and chemical properties of ILs and their catalytic activity can be significantly influenced by the presence of small amounts of impurities [12]. The most frequent impurities found in ionic liquids are water, halides, bases and metals. Most impurities come from ILs mode of preparation, thus it is extremely important to monitor the purity of ionic liquids.

Water, on the other hand, can be accumulated in ILs by absorption of moisture (in general, ILs are very hygroscopic). Depending on their structure, mainly in the anion, the IL can be miscible or immiscible with water [13, 14]. Even the water-immiscible ionic liquids are hygroscopic and are able to dissolve up to 1% of water [12]. The water content has a much stronger effect in the physical properties of the hydrophilic ILs than in those of the hydrophobic ones [13]. Contamination of ILs with a molecular solvent dramatically decrease viscosity and increase its electrical conductivity. Small amounts of impurities, such as water or chloride, increase slightly thermal conductivities.

2.3. Ionic liquids as reaction media

Ionic liquids present high potential as reaction media as well as catalysts for some processes [15-18]. They present advantages as high solvation power that makes it possible to reduce the size of reactors. As they constitute an ionic media, new reaction mechanisms, different from those found in molecular solvents, are presented. Catalysts soluble in ILs such as transition metals can be stabilized, which increases their useful life. Transition metal can also be supported in an IL, using a molecular solvent as a reaction media [19]. In fact, the most important contribution of ILs to catalysis is the enhancement of catalytic performance (activity, selectivity or new chemistry) and the possibility of catalyst separation and recycling by immobilization in the IL-phase. Some of these processes have already been scaled up to pilot or industrial scale [20, 21].

Enzymatic reactions can also be performed in IL media [22]. In general, an over-stabilizing effect on biocatalysts compared to traditional organic solvents without affecting the yield of the process has been observed [23].

3. CELLULOSE AND ITS SOLVATION PHENOMENA

3.1. Cellulose structure

Previous to its use most commercial applications require to dissolve the cellulose. To understand how this can be done, it is necessary to know the structure of the solid cellulose and how it changes when it is dissolved by an ionic liquid.

Cellulose is formed by an interconnected monomer unit (as every polymer) called cellobiose. Cellobiose is composed of two glucose molecules that are linked by an acetal function connecting C4 and C1 carbon atoms. Owing to the acetal bonds of the oxygen, every second molecule is rotated 180º [24]. The highly stable structure of cellulose has been explained by the hydrogen bonds that are formed in the molecules and between chains of molecules.

The degree of polymerization (DP) of cellulose is expressed in terms of glucose units and it is dependent on the source and treatment of the polymer. Several examples are shown in Table 1.

Table 1. Degree of polymerization of cellulose from different sources.

Source	DP
Cotton	800 – 10000
Wood	300- 1700
Bacterial	6500-10000
Microcrystalline	150 – 300
Regenerated	250 – 500

The crystal structure of cellulose in nature is cellulose I (native cellulose). This is a mixture of two crystalline phases named Ia and Ib and their proportions depend on the origin of cellulose [25, 26].

3.2. Main phenomena involved in cellulose dissolution

Currently, the study of the phenomena involved in cellulose dissolution is widely studied in scientific literature [27, 28]. First of all, it is necessary to understand the influence of thermodynamics, mass and energy transfer limitations as well as the influence of the structure of cellulose on its possible interaction with a given solvent.

- *Thermodynamic limitations*: Owing to the higher entropy generated, low molecular weight polymers are easy to dissolve. Conversely, the dissolution of cellulose will become more difficult as the DP is increased. Besides, the highly stable bonds present in cellulose makes it stiffer decreasing consequently the entropy generation for a change in the conformation of the molecule. Something different occurs when dealing with ionic polymers where an increased number of ions contribute to the entropy generation in the solution [28].
- *Mass and energy transfer*: The dissolution of a particle formed by a polymer has to include a step where the solvent first diffuses by contact inside the polymer and then takes the molecules out of the particle into the solvent. During this process, diffusion of the interacting substances, energy exchanged during mixing stages and mass transfer resistances are all involved. Therefore, it would be necessary to identify these effects during a solubility measurement [28].
- *Structural and molecular factors*: Crystallinity, structure of the solvent and polarity of the solute-solvent system are, at the same time, influencing the solvation process [27, 28].

3.3. Dissolution of cellulose

When the dissolution of cellulose occurs due to intermolecular interactions, the solvent is considered “non-derivatizing”. On the other hand, when these interactions are accompanied by the formation of unstable ether, ester, or acetal derivatives, the solvent system is considered “derivatizing” [29]. All the cellulose solvents considered so far have one thing in common: high polarity.

The following non-derivatizing solvents have been used with good results: aqueous solution of sodium hydroxide (NaOH), cuprammonium hydroxide (Cuam), cupriethylenediamine hydroxide (Cuen), N,N-dimethylacetamide/lithium chloride (DMA/LiCl), dimethylsulfoxide/tetrabutylammonium fluoride (DMSO/TBAF), N-methylmorpholine-N-oxide (NMMO) and ILs. Their main general effect is to form competitive hydrogen bonds with cellulose [30-33].

There are several proposals of the main phenomena influencing the dilution of cellulose in non derivatizing solvents which include: the capability of the solvent to form cyclic structures; the role of the chloride ion in breaking intermolecular hydrogen bonds in cellulose; the apparent coincidence of the amphiphilic nature of cellulose and that of its solvents [24].

Some derivatizing solvents used include: trifluoroacetic acid (TFA), NaOH/Carbon disulphide (CS_2), DMSO/paraformaldehyde and N,N-dimethylformamide/Dinitrogen tetroxide (DMF/N_2O_4). During the cellulose dilution they form unstable cellulose intermediates which render side reactions and undefined structures [29].

4. DISSOLUTION OF CELLULOSE IN IONIC LIQUIDS

Evidence on the dissolution of cellulose with ionic liquids is a “hot topic” in the scientific literature since 2002 when the solubility of cellulose in several ILs was proven [8]. It has been found that different ionic liquids can dissolve cellulose in concentrations around 20%.

While ILs with a weak coordinating anion, such as $BF_4^-$and PF_6^- do not dissolve cellulose, ILs derived from alkylimidazolium chloride [amim][Cl] could dissolve up to 25% in mass of cellulose [8]. There is evidence in the process of dissolution that bond formation between ILs and cellulose is catalyzed by bases [24]. NMR studies on the dissolution mechanism of cellulose in [C_4mim][Cl] indicate that the anion of ILs acts as a hydrogen bond acceptor which interacts with the hydroxyl group of cellulose [34, 35]. In fact, ionic liquids able to dissolve high concentration of cellulose have been found to present Kamlet–Taft parameters indicating a high polarity. Both β hydrogen bond basicity parameter and π^* dipolarity parameter with values near to one [36].

Only the ILs that have asymmetric cations dissolve cellulose [30]. The most important role in cellulose solubilization was played by the anion which was able to accept hydrogen bonds and which substituents were not bulky nor hydrophobic. The most frequently used anions are the following [15, 24]:

- Halide based-ILs, especially with the chloride anion. The higher the anion concentration, the better the solubilization. Thus, the small size and the strong electronegativity of the chloride are obvious advantages [37]. In addition, ILs with halide anion are cheap as they are used as starting materials for obtaining most ILs. On the other hand, the high melting point of chloride based ionic liquids (Tm>70ºC), the high viscosity and high hygroscopicity make their handling difficult [24]. The relatively high temperatures (T>80ºC) required for dissolving cellulose can result in cellulose modification by ILs themselves [38].

- Formate based ionic liquids present higher cellulose solubilities than chloride based under mild conditions. This result can be explained by the low viscosities of these types of salts [39]. However formate ILs generally exhibit low thermal stability, due to decarboxylation [40] and are known to be quite basic and unsuitable for enzymes [41].
- Acetate-based ILs constitute an interesting alternative due to the lower melting point, lower viscosity and their less toxic and corrosive character compared to chloride-based, and higher thermal stability compared to formate [41].
- Ionic liquids with alkyl-phosphate anions allow the preparation of a 10 wt% cellulose solutions (at 45 ºC for 30 min) with stirring, or to dissolve 2–4 wt% cellulose without heating. Also, phosphate-based ILs present high thermal stability in the 260–290 ºC range and low viscosities [40].

Even though little or weak interaction exists between cation of ILs and cellulose, their role in the dissolution mechanism should not be neglected [37]. Pinkert et al [42] proposed that, in order to dissolve cellulose, the cations of the ionic liquid should be aromatic heterocycles with a Sp2 nitrogen heteroatom; they should have ability to delocalize the positive charge and to participate in hydrogen bonding and dipolar ring character. The most successful cations for cellulose dissolution are based on the methylimidazolium (mim) and methylpyridinium (mpy) cores, with allyl-, ethyl-, or butyl- side chains [43]. Even numbers of carbon atoms in the alkyl side chain show high cellulose dissolution in the series C_2 to C_{20} compared with odd numbers [44]. The maximum dissolution power is reached with the C_4 side chain and increasing the alkyl chain leads to a decrease in cellulose solubilization. In addition, it is known that incorporating hydroxyl groups to the alkyl chains seem to enhance cellulose solubility [44]. This could be due to the additional polarity in the heteroatomic substituents on the imidazolium ring. Double bond containing side chain, reduce the viscosity of the IL [39] and increase its polarity [44].

This explains why, allyl functionalized imidazolium ILs present superior results in cellulose solubilization compared to conventional alkylimidazolium cation ionic liquids.

Apart from the structure and the properties of the ionic liquid itself, the ability of ILs to dissolve cellulose depends on the nature of the native cellulose (its DP and its crystallinity) on the operating conditions (temperature, reaction time, initial concentration of cellulose in the IL, activation with microwaves or ultrasounds) and presence of impurities, mostly water, that can significantly change the result [15, 42]. Indeed, the use of non-dried ILs can affect the solubility of cellulose and it was demonstrated that severely dried ILs are indispensable for an optimal dissolution [15].

The solution mechanism implies the formation of hydrogen bonds between the ionic liquids and the alcohol groups of cellulose, thus, if co-solvents able to form hydrogen bonds with the ionic liquids are added, the solubility of cellulose in ionic liquids decreases [42]. This is the reason why precipitation of the cellulose from the ionic liquid media is produced by mixing the solution with a dipolar solvent such as water, acetone or ethanol.

To dissolve cellulose in ionic liquids convective heating and stirring can be used but microwave energy and ultrasounds have been successfully applied. Microwave energy takes advantage of high conductivity of ionic liquid to produce a localized heat. Thus, it is possible to generate heat directly inside the ionic liquid without the restrictions imposed by conductive and convective heat transmission mechanism. On the other hand morphological changes in cellulose have been observed when applying microwave. These changes could increase reaction rate of cellulose in ionic liquids [28]. High-intensity ultrasound has also been explored as an intensification technology to reduce time of the solvation and processing of cellulose in ionic liquids [45]. Both technologies are worth to be explored.

5. PROCESSES BASED ON THE SOLUBILIZATION OF POLYMERS IN IONIC LIQUIDS

The process of dissolution of cellulose in ionic liquids was taken up by the research group of Robin Rogers in the University of Alabama (US) [46]. It was the starting point of the publication of a number of research articles and patents related to the dissolution of lignocellulosic materials in ionic liquids. From 2005 more than 70 patents has been published proposing different processes for biomass processing in ILs.

BASF Company showed an early interest in cellulose processing using ionic liquids acquiring the exclusive intellectual rights of the processes developed by the University of Alabama in the year 2005 [47]. Other companies such as Weyerhaeuser Company, Grasim Industries limited, Samsung electronics, Procter & Gamble, Se Tylose and Eastman Chemical Company have also patented processes based on ionic liquids.

In this section, first the dissolution and precipitation processes are presented. Then lignocellulosic materials fractionation processes to obtain mainly cellulose, or as a pretreatment to enzymatic or fermentation processes are summarized. Processes for obtaining chemicals and biofuels, or other composites are later presented. Finally, different patents for functionalization of cellulose are explained.

5.1. Dissolution and precipitation processes

In 1934, a method for the dissolution of cellulose in benzylpyridinium chloride was described in patent US 1,943,176. It can be considered the precursor of dissolution of cellulose in ionic liquids [48]. In recent times, 2003, the University of Alabama, through Swatloski et al, patented a process of dissolution and precipitation of cellulose in ionic liquids [46]. In the process the mixture of cellulose and ionic liquid is stirred until complete dissolution. Microwave radiation can be used to ease dissolution process. Cellulose can be regenerated from the ILs in a variety of structural forms including: flocks or powders (prepared by bulk quenching), tubes, fibers, extrudates, and films, by adding a protic substance, such as water, alcohols or ethers.

Different patents for the dissolution and precipitation of cellulose in ionic liquids have been developed. These processes are summarized in table 2.

Table 2. Patents of processes for cellulose dissolution and precipitation in ionic liquids.

Title / Company	**Conditions/ILs**	**Precipitation shape**
Dissolution and processing of cellulose using ionic liquids (2003) [46]	- Cellulose: 5-35%wt - H_2O< 1% wt - IL: quaternary ammonium cation	Flocks, powders tubes, fibers, extrudates, and films
Method for modifying the structure of a cellulose material by treatment with an ionic liquid (2008) [49] BASF	- Cellulose: 35-50%wt - T: 25-120ºC - IL: cations: quaternary ammonium, oxonium, sulfonium or phosphonium; anions: polyatomic anions	-
Cellulose solutions in Ionic Liquids (2008) [50] BASF	- Cellulose: < 35%wt - T <180ºC - IL: cations with protonated N, O, S or P	-
Solubility of cellulose in ionic liquids with addition of amino bases (2010) [51] BASF	- Cellulose: 1-25%wt - N-comprising base: 6-30% wt - T< 180ºC - IL: anions: Cl^-, CH_3COO^- or $CH_3SO_3^-$	-
Improved process for dissolving cellulose-containing biomass material in an ionic liquid medium (2011) [52]	- Demineralization: - T: 25-200ºC - IL: organic cation and inorganic (halogen) anion. Salt hydrates: $ZnCl_2 \cdot 4H_2O$. Inorganic molten salt hydrate	-

Novel compositions and methods useful for ionic liquid treatment of biomass (2011) [53]	- IL+aprotic solvent + biomass - Cellulose 15%wt - Molar ratio ketone: Alcohol: IL (X:Y:Z) X>3; 0.8<Y<1.2; Z=1 - IL:[C_2mim][Ac], cation: 1-alkyl-3-alkylimidazolium; anions: alkylsulfate, methylsulfate, hydrogensulfate, thiocyanate or halide	-
Cellulose matrix encapsulation and method (2004) [54]	- Cellulose:10-25%wt - Weight ratio cellulose : active substance 1000:1- 1:2 - Absence of water - Hydrophilic ionic liquid:cation: imi; anions: halogen, perchlorate, pseudohalogen or C_1-C_6 carboxylate	-
Polymer dissolution and blend formation in ionic liquids (2005) [55]	- T: 100° C microwave or ultrasonic. - IL: organic cation; anions: halogens, hexafluoroarsenate (AsF_6^-), hexafluoroantimonate (SbF_6^-), nitrite (NO_2^-), sulfate (SO_4^{2-})	Resins and blends: as molded or extruded plastic objects, fibers, beads, or films
Solvent system based on molten ionic liquid (2008) [56] BASF	- Cellulose: 1-35 %wt - H_2O > 5%wt - IL + protic solvent. Cation: imi; anions: halide, perchlorate, pseudohalide, sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), alkyl-phosphate or a C1-C6-carboxylate ion.	Non-fibrillated fibers fibers having a high degree of crystallinity (CI>0.5)
Method for processing cellulose in ionic liquids and fibers therefrom (2007) [57] Weyerhaeuser Co.	- Cellulose:1-35%wt - IL: cyclic or acyclic cation; anions: halogen, pseudohalogen or carboxylate.	Fibers and nonwoven web
A process of manufacturing low fibrillating cellulosic fibers (2011) [58] Grasim Industries limited	- Cellulose < 50%wt - Coagulation bath 40%> by weight of a protic solvent - T: 5- 60°C - IL: heterocyclic ring system with 1 or 2 N atoms cation	Fibers
Method for continuously preparing cellulose/ionic solution (2007) [59]		Fibers
Cellulose hollow fiber film prepared by ionic liquid method (2008) [60]	- IL: [Bmim]Cl, [Amim]Cl, [Hemim]Cl, [Bmim]OH, [Amim]OH, [Hemim]OH	-
Inflated fibers of regenerated cellulose formed from ionic liquid/cellulose dope and related products (2008) [61] Georgia-Pacific Consumer Products LP	- Effervescing agent: powdered carbonate salt - Activated with an acid - IL: imidazolium salt with Cl^- or Ac anion	Inflated fibers
Production of spherical particles from solutions containing a water-miscible solvent, according to the method of underwater granulation (2009) [62] BASF	- Pressure: 10-60 bar through the die plate - Cutting: a knife along the nozzle plate sweeps - IL: cations: quaternary ammonium (NR_4^+), oxonium, sulfonium or phosphonium (PR_4^+); anions: mono-,di-,tri-,or tetravalent anion	Spheres
Process for producing cellulose beads in ionic liquid (2010) [63] BASF	- Cellulose <50%wt - T: 50-150ºC - H_2O <20%wt - IL: Symmetrical imidazolium compounds	Spheres

Method for preparing cellulose microsphere by taking ionic liquid as solvent (2009) [64]		Microsphere

With the subsequent patents published [46]-[64], the original process was improved in different ways. Maase and co-workers [49] describe a process for modifying cellulosic material to obtain paper-like products by bringing it in contact with ionic liquid, but without completely dissolving it, reducing in this way the amount of ionic liquid required. In other patent owned by BASF, Maase and Stegmann [50] propose the use of ionic liquids that can be converted, by addition of a base, into a distillable form, which makes them easier to separate off. In a third patent [51], the same authors add to the cellulose –IL mixture a nitrogen-comprising base to increase the dissolution rate of the cellulose and to reduce the viscosity and the melting point of the ionic liquid mixture.

In his patent, O´Connor [52] describes a method that allows the use of biomass with a relatively high amount of minerals. Minerals are removed from biomass before the addition of the ionic liquid to prevent them to change the solvent properties of ionic liquids.

Dible and coworkers [53] proposed a method for recycling or recovering ionic liquids. The solution of IL and biomass or cellulose is mixed with a second solution comprising ketone and an alcohol solution to form a third solution, where biomass or cellulose precipitates or becomes solid and the third solution does not form a gel or have a viscous intermediate phase. The second phase is a precipitating solution, and the third solution is a precipitating mixture.

Holbrey et al [54] describe a method for encapsulating active substances such as dyes or magnetic particles in regenerated cellulose. To do so, a matrix of regenerated cellulose prepared from an ionic liquid/cellulose solution is mixed and homogeneously dispersed with an encapsulated active substance free of water. Matrices formed by this process are capable of release the encapsulated materials by diffusion through the shell to the surrounding medium at a slow rate.

In another patent, Holbrey and coworkers [55] propose blend formation from two or more polymers such as cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides or others. It consists of mixing at least one ionic liquid with at least two different polymeric materials to form a mixture. Then, a non-solvent such as water must be added to the mixture to remove the ionic liquid from the resin or blend. Resins or blends have predictable properties.

Many of the inventions are focussed on the precipitation of cellulose in different shapes such as fibers [56- 61] or spheres [62-64]:

- Fibers are obtained mainly by spinning the ionic liquid/cellulose [56-58] and mixing in some extension with protic solvents as water. Fibers can be continuously obtained by passing the ionic liquid muddy solution through a screw extruder for continuous dissolution [59]. Koko [61] proposed the production of inflated fibers of regenerated cellulose and other regenerated structures from ionic liquid/cellulose by encapsulating calcium carbonate or other effervescing agent in regenerated cellulose. The calcium carbonate is used to create carbon dioxide from within fibers that modifies the fiber structure.
- Spheres can be obtained by coagulation of cellulose. Cellulose dissolved in IL contacts with a second solvent which is miscible with the ionic liquid but in which cellulose does not dissolve. The coagulation of the cellulose starts when it interacts with the second solvent obtaining cellulose beads. Solution or dispersion is forced through a die plate, and it is cut on the opposite side of the nozzle plate in appropriate portions [62-63]. Lin et al [64] propose sphere formation by adding inert particles in a low speed stirred solution. An oil phase and a surface active agent are added and cellulose solution is condensed into spheres by reversed phase suspension and program temperature reduction.

5.2. Biomass fractionation

Before processing the different fractions of lignicellulosic, biomass must be separated. Normally lignin and hemicellulose are removed before cellulose utilization for paper or other cellulose derivatives production. Ionic liquids present new possibilities in lignocellulosic materials pretreatment for biomass fractionation. Lignin is insoluble in certain ILs and partially soluble in others. Some ILs that do not dissolve lignin, such as inorganic molten salt hydrates, are able to dissolve cellulose from the lignocellulosic composite material allowing a separation process [65].

Several patents that propose the fractionation of lignocellulose materials by ionic liquids are listed in table 3.

Table 3. Patents for the fractionation of lignocellulosic material by using ionic liquid.

Title/ Company	**Conditions/ ILs**
Solvents for use in the treatment of lignin-containing materials (2005) [66]	- Lignin material: 2-50%wt - T: 50-200ºC - Time: 1- 8 h - IL: cation: aryl organic acid; anions: inorganic or organic
Method of pretreating lignocellulose-based biomass (2008) [67] Samsung electronics	- Cellulose: 5-20% wt - T: 80- 150ºC - Time: 0.1 - 20 h - IL: 5-10 times higher than solid lignin - Hydrolase or hydrolysis catalyst - Saccharification: 24-65h - IL: large cation with N and small anion
Dissolution methods for lignocellulosic material (2008) [68]	- Lignocellulosic:0.1-30% wt - T: 20-200ºC microwave - H_2O < 1% wt - IL: five or six membered heterocyclic ring with 1 or more N, O, S atoms cations; anions: halogen, pseudohalogen or C_1-C_6 carboxylate.
Fractionation of a lignocellulosic material (2005) [69]	- T: 120-190ºC - Lignocellulosic material < 70%wt H_2O
Fractionation of lignocellulosic material using ionic liquids (2010) [70] Weyerhaeuser Co	- Lignocellulosic: 30%wt - T< 140ºC; - Time: 1-16 h; - Acid: H_2SO_4 - IL: imi cations; anion: C_1-C_6 carboxylate
Method for separating lignin and cellulose from lignocellulose by using ionic liquid solvent (2009) [71]	- H_2O + IL - IL: imi cation and halogenated alkane anions
Ionic liquid for solubilizing polymers (2008) [72] BASF	- Solubilized polymers > 35%wt - Tª< 180ºC, Microwave irradiation - Constituent of lignocellulosic: 50-90% - T: 20-200ºC - P: 0.1-100bar - Time: 1 minute-10 days - Base isolating - IL: polycyclic amidine catio; mono-,di-,tri-,or tetravalent anion
Ionic liquid systems for the processing of biomass, their components and/or derivates, and mixtures thereof (2010) [73]	- Biomass dissolved or suspended < 50%wt - T: <150ºC - H_2O< 1%wt - IL: alkyl-imi cation and halides or carboxylate anions

Upfal et al [66] proposed lignin-cellulose separation by dissolving biomass in IL and precipitating cellulose by adding water and/or by modifying pH or temperature. Then, an aqueous biphase is formed, and cellulose precipitates while lignin remains dissolved in the ionic liquid. Nevertheless, recycled IL contaminated with lignin decreases its capacity for dissolving cellulose.

To avoid contamination of the IL with lignin, Cho and co-workers [67] relate a method of fractionating lignocellulosic-based biomass by extraction of lignin with a basic solvent such as ammonia or sodium hydroxide or an organic solvent and extracting the cellulose and/or hemicellulose by adding an ionic liquid to the remaining biomass after extracting the lignin. According to the authors, the advantage of this method is that the use of the solvent is more economical because ionic liquids costs is about 2000 times more expensive than for example aqueous ammonia solution. Other advantage is to improve the recyclability of the IL, that it is not contaminated with lignin.

Myllymäki & Aksela [68] described a process for dissolving natural lignocellusic materials such as wood or straw in ionic liquids assisted by microwave irradiations and/or pressure and in absence of water. Cellulose and lignocellulosic material can be separated by precipitation of cellulose adding an anti-solvent.

Edye & Doherty [69] proposed dissolving the lignocellulosic material in an IL and adding a second liquid such as an aqueous hydroxide solution which is immiscible with the ionic liquid and is also a non-solvent for cellulose. A biphasic system is formed: an ionic liquid phase essentially free of lignocellulose and a second liquid phase comprising lignin in solution and cellulose as a precipitate. The two phases are separated and precipitated cellulose is recovered from the separated second liquid phase. The pH of the separated second liquid phase is decreased until lignin precipitates.

The process patented by Gifford and Severeid [70] consists on using the IL to dissolve cellulose and hemicellulose and partially dissolve lignin. Cellulose –enriched fraction is separated from the mixture and this fraction is characterized by a weight percentage of glucose solid about 10 percent points greater than the weight percent glucose attributable to cellulose and hemicellulose in the lignocellulosic material. On the contrary, Yingchong and coworkers [71] propose separating lignin and cellulose by dissolving lignin in an ionic liquid water solution, while cellulose is not dissolved and can be separated by filtering as a solid phase and lignin can be precipitated and recovered and the ionic liquid can be recycled.

D'Andola patented a process that includes: the solubilisation of polymers (cellulose and at least one synthetic polymer), the isolation of cellulose from cellulose containing sources, the obtaining of one constituent of lignocellulosic material and a method for obtaining a base [72]. The main point of this invention is that the cations of the ILs are derivated from polycyclic amine bases, which makes these ILs advantageously suitable for solubilizing polymers, specifically polysaccharides and polyurethanes. With this invention it is also possible to obtain at least one constituent of a lignocellulose material, wherein the constituent is solubilized selectively, or liberated selectively or solubilized and liberated selectively from a solubilized product of the lignocellulose material. This invention also claims a process for obtaining a base from the liquid medium, by the use of a solvent for the deprotonation of the ionic liquid, and by inducing a phase separation to give a phase enriched in the base that want to be obtained. That base is selected from the group consisting of alkali metal and alkaline earth metal hydroxides.

Rahman developed another method of fractionating biomass [73] by using a media consisting of biomass, ionic liquid, and a fractionation polymer. The mixture is monophasic at a temperature and adjusting the temperature a biphasic composition is provided. A portion of the biomass is fractionated between each phase of the biphasic mixture.

5.3. Ionic liquids for pre-treatment of biomass before sugar and fuel production.

Cellulose may be decomposed into sugars that are fermented to produce bio-ethanol in a second generation process, or other fermentation products such as lactic acid. Cellulose hydrolysis in aqueous media to produce sugars can be carried out both, in the presence of an acid catalyst (acid hydrolysis) or using hydrolyzing enzymes, cellulases. Cellulase hydrolysis [74] is preferred over acid hydrolysis in order to reduce the formation of undesirable degradation products of glucose that reduce glucose yield and inhibit fermentation and to avoid using of expensive corrosion-resistant materials.

For hydrolysis to take place both enzymes (cellulases) and water must penetrate in the cellulose crystalline fibrils. Pretreatment methods increase the surface area accessible to water and cellulases improving hydrolysis kinetics and conversion of cellulose to glucose. Pretreatment is one of the most expensive steps in the process of cellulosic biomass to fermentable sugar conversion, but an effective pre-treatment can reduce the use of expensive enzymes and can influence the cost downstream [75].

Pre-treatment methods usually consist of a mechanical pre-treatment of milling followed by a thermal and/or a chemical pretreatment such as steam explosion, liquid hot water pretreatments and/or acid or basic pretreatments. The main effects are dissolving hemicellulose and altering the lignin structure, providing an improved accessibility of the cellulose for hydrolytic enzymes [76].

There are several methods patented as pretreatments of lignocellulosic materials before a fermentation process. They are summarized in table 4. It is known that, when a pre-treatment with ionic liquids is carried out, any material that may inhibit the saccharification and fermentation process is minimized. The amount of hydrolase or hydrolysis catalyst necessary is reduced in a 50%, increasing reaction rate and thereby saccharification efficiency, while reaction time is decreased till 70% [67].

Some of the patents claim processes of pretreatment of the biomass previous to an enzymatic hydrolysis. Other methods propose to directly perform the hydrolysis of the biomass to sugars in the ionic liquids. In some of them, enzymatic process can take place in the presence of an ionic liquid [77].

Table 4. Summary of patents for pretreatment of biomass and further production of sugars or bio-fuels.

Title / Company	**Conditions /ILs**
Novel thermophilic cellobiohydrolase (2011) [77] Sandia Corporation	- IL >=5-20%wt - T >= 65 ºC - pH:4.7 - 5.5 - IL: Cation: imi; anions: alkanate, alkylsulfate, methylsulfonate ($MeOSO_3$), hydrogensulfate ($HOSO_3$, thiocyanate (SCN), halide
Pretreatment of solid biomass material comprising cellulose with ionic liquid medium (2011) [78]	- IL and solid biomass contacts under sub- solvating conditions. - Dry solid biomass dissolved in IL medium < 10%wt - Control water content and contact T - IL: organic cation. IL medium comprises a molten hydrated salts
Biomass pre-treatment (2008) [79]	- Lignocellulose, 30%wt, is not dissolved in the IL - T: 50-200ºC conventional heating or microwave - Time: 5 min-8 h - H_2O <10%wt - IL: cations: imi, pyrrolidinium (pyr) , py, phosphonium (P) or ammonium (NH_4); anions: halide, acetate, trifluoroacetate, dicyanamide or carboxylate
Saccharifying cellulose (2006) [80]	- Cellulose concentration: bellow or above the solubility limit. - Heating with agitation, microwave irradiation - IL: cations: imi, pyrroldinium (pyr), pyridinium (py), phosphonium (PR_4^+) or ammonium (NR_4^+); anions: halide, Ac, trifluoroacetate, dicyanamide or carboxylate
Use of lignocellulosic solvated in ionic liquids for production of biofuels (2008) [81]	- $T_{Disolution}$: 50-150ºC - H_2O and/or N-containing base < 1%wt - IL: cations: imi, py; anions: halogens, phosphates, alkylphosphates, alkenylphosphates and bis(tri-fluoromethylsulf-ony)imide.
Method for producing glucose by enzymatic hydrolysis of cellulose that is obtained from material containing lingo-cellulose using an ionic liquid that comprises a	- Cellulosic material - H_2O <15%wt - Precipitated cellulose is washed at 40ºC - 95ºC - IL: Polyatomic anions

polyatomic anion (2010) [82] BASF	
Enzymatic hydrolysis of a cellulose material treated with an ionic liquid (2010) [83] BASF	- Material containing ligno-cellulose - H_2O <15%wt - Enriched cellulose washed at T> 80ºC - IL: Polyatomic anions
Thermostable cellulases, and mutants thereof, capable of hydrolyzing cellulose in ionic liquid (2010) [84] Univ California	- IL<=0-20% v/v - $T_{Optimal}$ >= 65ºC - IL: cations: imi; anions: alkanate, alkylsulfate, methylsulfonate, hydrogensulfate, thiocyanate, halide
Method for producing useful substance from cellulose-containing material (2011) [85]	- IL: 1-ethyl-3-methylimidazolium salt
Method for the hydrolysis of cellulose raw material (2010) [86]	- $T_{Hydrolysis}$: 20-80ºC - Cellulases: 0.1-2% v/v - pH: 3.5 to 8 - IL: cations: alkylated imidazolium, pyridinium, ammonium, and phosponium; anions: halide, tetrafluoroborate, trifluoromethylsulfonylimide anion
Method for depolymerization of cellulose (2011) [87]	- Depolymerization: - Tº: 50-130ºC - Time reaction: 0.25-5h - Acid groups of catalyst: $-SO_3H$, $-OSO_3H$, $-PO_2H$, $-PO(OH)_2$, $-PO(OH)_3$ - Ion exchange resin: - Surface area: 1-500mm^2 g^{-1} - Pore volume:0.002-2 cm^3 g^{-1} - Average pore diameter:1-100 nm - Ion exchange capacity:1-10 mol g^{-1} - IL: cations: alkylated imidazolium, pyridinium, ammonium, and phosponium; anions: organic, inorganic anions.
Method for controlling rate of lowering molecular weight of polysaccharides contained in cellulosic biomass, and method for producing sugar, alcohol, or organic acid (2011) [88]	- IL: Hydrophilic ionic liquid: [Emim][OAc], [Emim][Cl], [Emim][DEP]
Conversion Method (2009) [89]	- Cellulose: 5-35%wt - T<150ºC; - Acid:0.1 -10 wt%, pKa=2 - Weight ratio water:cellulose 1:1 to 1:15 - IL: cations: py, pyrr, pyrazinium, imi, pyrazolium, oxazolium, triazolium, thiazolium, piperidinium, pyrroldinium, quinolinium and isoquinolium; anions: halide or cyanate anion
Method for breaking down cellulose (2009) [90] BASF	- $T_{Disolution}$: 0 -150ºC - $T_{Degradation}$:0-200ºC, if ILs have acid functions → T:0-150ºC - Acid: 0.1-50% - H_2O: 5-10 % - IL: anions: halides and halogen, carboxylic, SO_4^{2-}, SO_3^{2-}, $RaOSO_3^-$, $RaSO_3^-$, PO_4^{3-}, $RaRbPO_4$
Method for breaking down cellulose in solution (2009) [91] BASF	- Polysaccharide: 0.1-50% wt - $T_{Disolution}$: 0 -200ºC - $T_{Hydrolysis}$: Room T-200ºC - Acid: 0.1 - 50%

	- H_2O: 5-10 % - Degradation with inorganic or organic acids - IL: Anions: HSO_4^-, HPO_4^{2-}, $H_2OPO_4^-$, and $HRaPO_4^-$
Biomass hydrolysis (2011) [92]	- Polysaccharide: 0.1-50% wt - $T_{Disolution}$: 100-110ºC - $T_{Hydrolysis}$: 70-140ºC - Acid: 5- 40% - H_2O: 20% - IL: cations: imi or py; anions: Cl^-, trifluoroacetate, tribromoacetate or thiocyanate (SCN)

Among the patents that propose the utilization of ionic liquid for cellulose pre-treatment previous to an enzymatic hydrolysis there are the ones proposed by Cho et al [67], O'Connor [78], Varanasi and co-workers [79, 80], and Argyropoulus [81]. They propose mixing lignocellulosic material with the ionic liquid in different ways: not dissolved in the ionic liquids [78, 79], partially dissolved [80] or totally dissolved [81]. The contact is reduced to a short but sufficient time to disrupt lignin and swell the biomass structure. Balanslefer et al patented two pretreatment processes for BASF company: for the hydrolysis of cellulosic materials [82] and lignocellulosic [83]. In both inventions the material is pre-treated by dissolving in an ionic liquid containing a polyatomic anion. These ILs allow treating cellulose with certain water content without precipitation of cellulose. In addition, corrosion problems due to monoatomic anions such as Cl^- are avoided. After the pretreatment cellulose enriched material is precipitated, washed and separated from the solution of IL. The enzymatic hydrolysis is improved with respect to the untreated cellulose.

Sapra et al proposed two patents. In patent US20110207182 [77] biomass, previously pretreated with the ionic liquid, is contacting with a specific polypeptide, that hydrolizes the cellulose. It is also possible to add one or more thermostable or thermophilic endoglucanase enzymes. In patent WO2010124266 [84], biomass is pretreated with the ionic liquid [emim][Ac] and then cellulose is hydrolyzed by adding a thermostable cellulase unaffected even in the presence of 4% IL in the reaction solution, increasing the yield of the process

Jo et al [85] described a method where cellulose-containing material is contacted with an ionic liquid to permeate the cellulose-containing material. The solution cellulose-containing material and IL is contacted with a cellulase-producing microorganism, such as recombinant yeast, to simultaneously saccharify and ferment a carbon source.

Schüth et al [86] proposed the contact of cellulose with an ionic liquid and with a solid acid catalyst such as an acidic ion exchange resins, metal oxides, or zeolitic materials.

DP of depolymerized cellulose ranges from 20 to 100, and then this cellulose is subjected to an enzymatic hydrolysis. In patent US2011/0015387 [87] Schüth and coworkers described the type of solid catalyst used in the process.

Tabata and coworkers [88] also proposed a method for lowering the molecular weight of polysaccharides contained in a cellulosic biomass, and a method for producing sugars, alcohols or organic acids. Cellulosic biomass is mixed with ionic liquid under an atmosphere with a partial pressure ratio differing from air. They propose that when the process is carried out in an atmosphere with oxygen partial pressure higher than the air, the rate of lowering MW can be increased. Solid and liquid component are separated and the solid component is subjected to a glycosylation step by enzyme treatment.

Among the processes proposing the pretreatment and hydrolysis of the lignocellulosic materials to water soluble sugars in the ionic liquid is the one developed by Fanselow et al [89] that propose adding one mol of water for each monomer of cellulose and a certain amount of acids. The process uses ILs with halide or cyanate anions instead of carboxylates because these last ones do not lead to satisfactory hydrolysis, although they dissolve cellulose. Massonne and co-workers developed two patents, one proposing a thermal degradation [90] and other proposing an acid hydrolysis [91]. A variety of anions can be selected for the thermal degradation but it is important the use of anions selected from the group consisting of $HSO_4^{-,}$ HPO_4^{2-}, $H_2OPO_4^-$, and $HRaPO_4^-$, because the use of acid ionic liquids decrease the temperature.

In the case of thermal treatment [90], it is possible the formation of dehydrocelluloses. Different energy sources can be applied as X-rays, UV/visible light, microwave energy or ultrasonic energy. In both inventions the addition of water may be necessary if the water content of cellulose used is insufficient to reach the desired degree of degradation. The lower average degradation of cellulose under identical reaction condition is getting when the larger is the ratio n_{AGU}/n_{acid} or n_{AGU}/n_{water}, where n_{AGU} is the mol of anhydroglucose units of the cellulose. When the degradation occurs with an acid [91], it is also possible to stop the hydrolysis reaction when the desired degree of degradation has been reached by scavenging the acid with a base.

Raines and Binder in patent US 2011/0065159 [92] proposed a similar process in which the biomass hydrolysis is carried out in an ionic liquid in the presence of catalytic acid at a temperature sufficiently high to initiate hydrolysis. Water is added to the reaction mixture after initiation of hydrolysis at a controlled rate in order to avoid precipitation and undesired sugar dehydration products as 5- hydroxymethylfurfural (5-HMF). Glucose yield from cellulose hydrolysis using this process can be as high as 85%.

5.4. Cellulose processing in ionic liquid media for obtaining bio-refining products or chemicals

Cellulose can be further subjected to chemical reactions (hydrolysis, oxidation, hydrogenation or gasification) to obtain basic chemicals (“building blocks”) that can be intermediates in the synthesis of more complex substances such as 5-HMF, levulinic or lactic acids [75].

IL has been proposed as reaction media for obtaining different valuable chemicals and fuels from cellulose. Table 5 shows the main points of the different patents.

Table 5. Summary of patents for the production of bio-refining products or chemicals.

Title/ Company	Conditions/ ILs	Products
Simultaneous catalytic conversion of cellulose and lignin to a liquid fuel in an ionic liquid (2011) [65]	- Addition of acid catalyst - $T > 70$ºC - IL: inorganic molten salt hydrated	Liquid fuel
Method for conversion of carbohydrate polymers to value-added chemical products (2009) [93]	- Carbohydrate polymer < 30% wt - Time:0.01-8 h - $T < 120$ºC - H_2O:2-20 wt% - Catalyst: at least two metal halides or metal salts, and at least one more metal halides. - IL:[emim][Cl], [bmim][Cl], [emim][Br]	Glucose and 5-hydroxylmethylfurfural (HMF)
Biocell – three step process for obtaining a liquid fuel from cellulose consisting mainly of isomers of methyl pyran and methyl tetrahydropyran using N alkyl imidazol chloride as solvent and catalyst (2010) [94] Inventus Productos quimicos LDA	- $T_{\text{Dissolution}}$:40-120ºC - $P_{\text{Hydrogenation}}$: 2-100 bar - $T_{\text{Hydrogenation}}$: 50-180ºC. - IL: Alkyl-imidazolium chloride	Isomers of methylpyran and methyl tetrahydropyran
Biomass fuel synthesis methods for increased energy efficiency (2007) [95]	- Working fluid contains a gas: NH_4^+, CO_2 or CH_4. - $T_{\text{Hydrolysis}}$: 15ºC < $T_{\text{Pretreatment}}$ - IL: contain phosphates, polyammonium sulfonamides	Biomass fuel
Chemical transformation of lignocellusic biomass into fuels and chemicals (2009) [96]	- Polar protic solvent, DMA or N-methylpyrrolidone +Salt: 0.5 - 15wt% - Catalyst: mineral acid or a metal halide - IL < 40%wt - T_{Reaction}: 50-200ºC - IL: cation: Alkylimidazolium or alkylpyridinium anion: halide	Furfural, and more than 30% HMF

Product preparation and recovery from thermolysis of lignocellulosics in ionic liquids (2008) [97]	- Pyrolytic conditions: - T: 150-300° C - Anaerobically - IL: cation imi and py, anion: halogens, phosphates, alkylphosphates, alkenylphosphates, and bis(trifluoromethylsulfonyl)imide	Commodity chemicals
Production process of furfural from cellulose using a solvent and catalyst an imidazolium sulphate chloride in a reaction with simultaneous extraction with dibutyl ether (2012) [98]	- T: 80-200ºC - Time:30min-4h - Ratio N-alkylumidazolium sulphate: N-alkylimidazolium chloride: 1:0.5 - Water: 1-20% mole ionic reaction phase - Sulphuric acid:1-30% mole ionic reaction phase - Dibutyl ether: 10-100% mole ionic reaction phase	Furfural
Method for the production of fuels from biomass (2009) [99]	- Polysaccharide <50% wt - Acidic heterogeneous catalyst: - Comprises at least one metal component of: Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, Os, Cu, Zn, Mo, W. - Ratio catalyst-biomass: 1:1000 to 1:10% wt - T: 180-450ºC - IL: quaternary ammonium, oxonium, sulfonium or phosphonium cation; mono-,di-,tri- or tetravalent anion	Biofuels

Mostly the processes patented consist of dissolving the biomass in an IL, and a subsequent heating for a certain time in the presence of catalyst, reagents or additives. Heinerman [65] proposes a process to produce liquid fuel by hydrogenation in the presence of an acid catalyst and/or by increasing the temperature to a range from 200ºC to 600ºC. In this process, undissolved and dissolved lignins are not separated from the solution and are partially converted into hydrocarbons compounds. Zhang et al [93] describe the process and the catalyst or a selective conversion of cellulose and other carbohydrate polymers to value added intermediate and end-use chemicals such as glucose and 5-HMF. By the appropriate selection of mixed halide catalysts and adjusting time and temperature, desired product and yield can be selectively tuned achieving yields up to 56% in a single step process. Additional acids to effect dehydration are not required.

The process Biocell [94] propose obtaining liquid biofuel from cellulose in three steps: (1) cellulose dilution in N-alkyl imidazolium chloride containing an excess of hydrochloric acid, (2) cellulose hydrolysis into glucose and dehydrating glucose to isomers of hydroxymethyl pyranone, adding to the reaction mixture a water solution containing 10% sodium chloride, (3) extracting them with n-butanol, concentrating the butanol extract by distillation. Residues of N-alkylimidazolium chloride are extracted from the butanol phase by using again a water solution containing 10% NaCl. The almost chloride free butanol concentrate is hydrogenated with gaseous hydrogen using Pd or Pt catalysts and isolating the biofuel by distilling out the butanol.

Gurin [95] developed a high efficiency method for synthesizing biomass fuels that uses ILs in the pretreatment of the biomass and for energy generation by using a combination of ILs and carbon dioxide under supercritical conditions. The process uses an integrated CO_2 absorption heat pump and power generation cycle that utilizes the IL- biomass solution as the working fluid of a thermodynamic cycle.

Binder and Ralner developed a method [96] for converting a carbohydrate to a furan, in a polar aprotic solvent in the presence of halide salts and optionally in the presence of an acid catalyst and/or an ionic liquid.

Argyropoulos described a method for pyrolysis of a lignocellulosic material to form a recoverable product [97]. The method comprises the combination of lignocellulosic material with an ionic liquid where lignocellulosic material is at least partially dissolved. The mixture is heated anaerobically, and several fractions are formed: distillate fraction, a tar fraction, and a char fraction. Sometimes other recoverable products are also possible, such as levoglucosenone, levulonic acid, levulinic acid, 5-HMF, 2-furaldehyde (furfural), 2-methylfurfural, alcohols, phenols, aldehydes, organic acids, furans or catechols.

Recently Correia proposed a method for the production of furfural from biomass [98]. It consists on a reaction with simultaneous extraction; the reaction medium contains, as a first solvent and catalyst a mixture of N-alkylumidazolium sulphate, N-alkylimidazolium chloride, sulphuric acid and cellulose, and as a second solvent dibutylether. Furfural is separated from the ether phase by distillation.

Grosse et al [99] described a process for the production of fuels from biomass in a heterogeneously catalyzed reaction using ionic liquids. Solution containing the dissolved starting material in the IL has at least one hydrogen source and is contacted with, at least, one heterogeneous catalyst. Reaction product is separated by distillation / rectification, a membrane process, an extraction method or by displacement of the reaction product with a suitable anti-solvent.

5.5. Cellulose and ionic liquids for the formation of composites and biopolymers.

There are many patents for the production of composites and/or biopolymers through the use of cellulose and ionic liquids. Table 6 shows a list of these patents.

Table 6. Patents for the production of composites and/or biopolymers.

Title/ Company	Conditions/ ILs	Composites
Ionic liquid reconstituted cellulose composites as solid support matrices (2007) [100] University of Alabama	- Weight ratio regenerated cellulose: First active substance or Second active substance 1000:1 to about 1:2. - IL: hydrophilic ILs, free of water, organic solvent and nitrogen containing bases	Reconstituted cellulose composites as solid support matrices
Polymer derivates and composites from the dissolution of lignocellulosic in ionic liquids (2008) [101]	- Lignocellulosic: 2-20%wt - $T_{Dissolution}$: 50-150ºC - Complete dissolution < 48h - IL: capable to dissolve and/or disperse lignocellulosics	Membranes, fibers, nanofibers and other nanocomposites
Method for producing regenerated biopolymers and regenerated products obtained by said method (2010) [102] BASF	- Biopolymer: 1-35 wt%, - $T_{Dissolution}$: 30-150ºC. - H_2O< 5%wt - Precipitation in a coagulation medium: protic coagulant + additive for adjusting specific properties - IL: cations: quaternary ammonium, oxonium, sulfonium, phosphonium, anions: mono-,di-,tri-,or tetravalent	Regenerated biopolymers in the form of carbohydrates, in the form of fiber, filament or film,
Method for producing solid materials on the basis of synthetic polymers and/or biopolymers and use thereof (2009) [103] BASF	- Chaotropic liquids: -100 to 150ºC - $T_{Solubilization}$: 0-100ºC - Polymer:0.1-10% wt - Cations: noncyclic or heterocyclic onium compounds - IL: inorganic anions: halides, pseudohalide, sulphide, halometallate, cyanometallate, carbonylmetallate, haloborate, halophosphate	Regenerated gels
Synthesis of Au, Pd, Pt or Ag nano-or microcrystals via reduction of metal salt by cellulose in the ionic liquid 1-butyl-methyl imidazolium chloride (2009) [104]	- Cellulose+IL+salt - Metal salt: $M(NO_3)_x$, MCl_x, MBr_x, Mi_x, $M(OAc)_x$, $M(TfO)_x$, $M(aca)_x$, $HAuCl_4 \cdot 3H_2O$ - Molar ratio cellulose to metal salt: 1:1 to 20:1 - 2 methods: (i) thermally: reduction of the metal salt with cellulose by heating, T^a:50-250ºC; (ii) photoreduction of the metal salt by irradiation with light, 200-800nm - IL: bmimCl	Nano-or microcrystal of Au, Pd, Pt or Ag
Extraction biopolymers from a biomass using ionic liquids (2006) [105] The Procter & Gamble	- Dissolution step: - Biopolymer: 5-50%wt - Time: 1min-5h - Mixing step: - Weight ratio IL:biomass 20:1 to 200:1. - T: 20-130ºC - Time:10min-24 h - IL:_cations: mi, py, oxazolium, pyridazinium, pyramidinium, pyrazinium, ammonium,	Biopolymer

	phosponium, pyridinium, 1,2,3-triazolium; 1,2,4-triazolium;Thiazolium, Quinolinium, isoquinolinium, piperdinium, pyrrolidinium; anions: halides, C1-C6 carboxylates, C1-C6 alkyl sulfates, mono- or di- C1-C10- alkyl sulfosuccinate.	

Most of the processes described in these patents [100-103[103] consist mainly on the dilution or dispersion of cellulose [100], wood [101] or other lignocellulosic materials or biopolymers [102-103], together with an additive or active substance. The precipitation of the dissolved biopolymer is achieved by addition of an anti-solvent and it is separated by decantation, centrifugation and/or filtration, obtaining a matrix of regenerated polymer in which the additive is homogeneously distributed, being possible to bond to this matrix other polymers or active substances. Lignocellulosic materials can be shaped to form fibers, membranes, films or filaments [101-102]. Additive can be a variety of substances such as a pore-forming agent, a plasticizer, a bactericide, a cross linking agent, a hydrophobizing agent, and antistatic and/or a coloring agent [102] or organometallic compounds, nanoparticles, biomolecules, cell compartments and cell aggregates [103].

Among the applications for the product obtained, BASF Chemicals, through Champ [103], proposes producing solid materials based on synthetic polymers and/or biopolymers that are used as support particles and support materials used in liquids fracturing media for borehole stimulation in natural gas and mineral oil extraction technology.

Taubert et al [104] patented a preparation method for nano-or microcrystal of Au, Pd, Pt or Ag by mixture of cellulose and at least one metal salt in the IL [bmim][Cl] and thermally inducing a reduction of the metal salt with cellulose at temperatures between 50 to 250ºC. It is followed by a photoreduction of the metal salt by irradiation of the mixture with light in the visible range. They have studied the preparation of gold microcrystals having a plate-like shape. In this reaction cellulose has a double function: it is the reducing agent and is a template for the formation of the metal particles. Thanks to the high thermal stability of the IL, the reaction can be conducted at various temperatures, which enables tuning of the reaction in terms of particle size, shapes and connectivity. The change of the particle shapes can be attributed to the role of the cellulose as a template in conjunction with an effect provided by the ionic liquid. Metal particle morphologies and sizes mainly depend on the reaction temperature or irradiation parameters.

The company P&G through Hecht et al [105] developed a method for extracting and separating biopolymers from a biomass comprising the biopolymer and additional materials that are insoluble in certain ionic liquids and a method for dissolving biopolymers such as chitin, chitosan, elastin, collagen, keratin or polyhydroxyalkanoate, in an ionic liquid. The amount of biopolymer recovered by this process ranged from 0.1% to 50% by weight of biomass.

5.6. Functionalization of cellulose

Polymers derived from the functionalization of cellulose are obtained by reacting totally or partially the hydroxyl groups (-OH) of cellulose with various reagents. The anhydroglucose unit (AGU), which is the fundamental repeating structure of cellulose, has three hydroxyl groups that can react to form esters, ethers, etc, so the maximum degree of substitution is 3.

These derivatives can be acetates, carboxymethylates, benzoylates, urethanes (carbamates), (meth)acrylates, carbonates, sulfates, sulfonates, phthalates, tritylates, furorates, maleated esters, or ester resins [42] Cellulose esters and ethers are the cellulose derivatives more used. They are used in coatings, membranes, binders, fillers, composites, drilling fluids, explosives, optical films, or separation media, as well as in medical applications (dialysis, tissue and bone engineering, wound dressing, joint replacement), in the food industry, or for the sorption of heavy metals [42].

Due to the fact that cellulose is insoluble in all common solvents, reactions to form derivatives are usually carried out in heterogeneous systems [3]. Nevertheless, cellulose can be dissolved in ionic liquids and the homogeneous reaction of cellulose improves the reaction rate, and the degree of substitution of derivates and the distributions of functional groups may be controlled [2].

5.6.1. Inventions for cellulose esters production using ionic liquids

The conventional processes for the synthesis of cellulose esters use dissolved pulp or cellulose obtained from the sulfite or the Kraft process with an acid pre-hydrolysis step to remove hemicelluloses. Common raw materials are wood pulp or cotton fiber.

Cellulose is reacted with acetic acid and anhydride in the presence of sulfuric acid. Then it is put through a controlled, partial hydrolysis to remove the sulfate and a sufficient number of acetate groups to give the product the desired properties.

Different processes for the production of esters from cellulose or other polysaccharides using ionic liquids have been patented [106-114]. Most of these patents were developed by Buchanan and coworkers [107-113] and belong to Eastman Chemical Company, but the processes have not been taken yet to industrial scale. These patents are summarized in table 7*Table*.

Table7. Summary of different inventions for cellulose ester production

Title/Company	**Conditions/IL**	**Agent**
Method for acylating cellulose with a specific degree of polymerization (2009) [106] BASF	- Poly-oligosaccharides: 0.1-50%wt - T< 200ºC - IL: cations: quaternary ammonium, oxonium, sulfonium or phosphonium; anions: mono, bi- tri- tetravalent: halides, halogen-comprising compounds, sulfates, sulfites, sulfonates, phosphates, phosphonates, phosphonites, phosphinites, carboxylic acids, boronates, silicates	- Acylating reagent: carboxylic acid
Reformation of ILs (2008) [107]	- Cellulose:1- 40wt% - Catalyst:0.01-30 mole % per AGU - <u>Interconversion:</u> - T: 0 to 200ºC - P: 100 to 21000 kPa - time:1 min -24h, - <u>Esterification:</u> - T: 100-180ºC - P: 10-1000psi - time: 10-1000 min	- Molar ratio carboxylate anion donor:intermediate IL anion content 1:1 to 20:1 - Intermediate IL carboxylate anion donor 1 to 20 molar equivalents per alkyl amine formate.
Cellulose esters and their production in carboxylated ionic liquids (2008) 0194807. [108] Eastman Chemical Company	- Water-wet cellulose < 5% water - Cellulose: 1-40%wt - T: 0-120ºC - Time: 1min-48h - IL: [emim]Ac, cations: alkyl substituted imi, py, pyrazolium, oxazolium, triazolium, thiazolium; anions: C1 to C20 carboxylate or substituted carboxylate.	- Acylating reagent (carboxylic anhydre...)< 4 molar equivalents/ AGU - Catalyst: AGU < 30% mol - Cellulose:acylating reagent 90:10-10:90 wt ratio - Catatalyst: protic acids, weak Lewis acids: <30 mol % per AGU
Cellulose esters and their production in halogenated ionic liquids (2009) [109] Eastman Chemical Company	- Cellulose: 5%wt - Binary component: 0.01 to 100 mol% per AGU - IL: anions: halide: chloride, bromide, iodide, fluoride and mixtures of two of more thereof	- Carboxylic acid:0.1-25% wt - Acylating reagent (1 or more C1 to C20 straight-or branched- chain alkyl or aryl carboxylic anhydres, carboxylic acid halides, diketene, or acetoacetic acid esters): 0.01-20 molar equivalents based on the total amount of cellulose in the reaction medium. - DS at least 1.5

Production of cellulose esters in presence of a co solvent (2009) [110] Eastman Chemical Company	- IL: Halogenated and/or carboxylated	- Co-solvents: 0.01-25% wt
Cellulose solutions comprising tetraalkylammonium alkylphosphate and products produced therefrom (2010) [111] Eastman Chemical Company	- Cellulose: 1-40 wt% - Contact: - T: 25-150ºC - time: 5min-24h; - Esterification: - T:20-140ºC - time:1min-48h - IL:Tetraalkylammonium alkylphosphate, halogenated and/or carboxylated	- Acylating reagent: (C1-C20 straight- or branched-chain alkyl or aryl carboxylic anhydrides, carboxylic acid halides, diketene or acetoacetic acid esters): 0.5-20 equivalents - DS:0.1-3 - DP > 250.
Regioselectively substituted cellulose esters produced in a Carboxylated ionic liquids process and products produced therefrom (2010) [112] Eastman Chemical Company	- T:20-150ºC - IL: cations: Tetraalkylammonium, alkylphosphate. - Ratio catión:anion 1:1 to 1:10	- Acylating reagent + cosolvent: 1-40%wt
Treatment of cellulose esters (2009) [113] Eastman Chemical Company	- Cellulose: 1-40%wt - Esterification: - T:0-120C - Time: 1min-48h - IL: halide or carboxylated ILs	- Bleaching agent: 0.1- 5 wt%
Starch esterification method (2007) [114]	- Starch:1- 35% wt - $T_{disolution:}$ 0-250ºC >=$T_{esterification}$ - Water <1%wt - IL: cations: five or six-membered heterocyclic ring, aromatic or saturated, with heteroatoms: one or more nitrogen, oxygen or sulphur atoms, anions: halogen, pseudohalogen or C1-C6 carboxylate	- Organic esterifying reagent: C1-C11 or C1-C6 carboxylic acid - DS of 1-3.

In general, these processes include the four steps shown in figure 2.

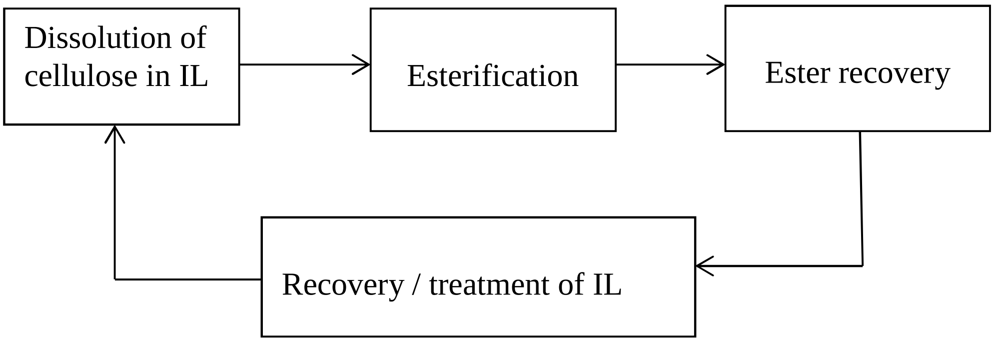


Figure 2. Scheme of the esterification process in ionic liquid media

1) Dissolution of the polysaccharide in the ionic liquid. Different ILs have been proposed to carry out the process: carboxylated [108], halogenated [109] and tetraalkylammonium alkylphosphate ILs [111] among others, or even using co-solvents [110]. Some authors mentioned the possibility of adding a certain amount of water to the mixture or using non-dried cellulose, normally up to a water content of 5% [106], [108]. Buchanan and coworkers [108] point a certain water content enhances the properties of the reaction media, mainly decreasing its viscosity, nevertheless cellulose esters, prepared using water-wet cellulose, have less molecular weight compared to esters prepared in a dry media. In 2009, Buchanan & Buchanan [110] proposed the addition of co-solvent that does not cause precipitation of the cellulose but able to change the viscosity of the highly viscous cellulose – ionic liquid solutions at lower contact temperatures.

2) Esterification is produced by an acylating reagent such as carboxylic acid and derivates. When using carboxylated ILs, substituents can be the anions of the IL, in which case the IL would be modified containing more than one kind of ionic liquid. Buchanan [106] proposes the contact of cellulose with the carboxylated IL used as reaction media, and then with, at least, one acylating reagent in the presence of a catalyst. In this way, it is possible to produce a mixed cellulose ester, with a first and second pendant acyl groups that are different from one another. First pendant acyl group originates from the ionic liquid and the second one originates from acylating reagent. If one or more ILs with halide anions are used [109], the esterification is carried out in the presence of a binary compound that acts changing the network structure of the ionic liquid containing the dissolved cellulose ester. This change in network structure may lead to the observed surprising and unpredicted advantages of using the binary component: it can accelerate the rate of esterification, can serve to improve solution and product colour, prevents gelation of the esterification mixture, provides increased DS values in relation to the amount of acylating reagent employed, and/or help to decrease the molecular weight of the cellulose ester product.

Acylating agents can be added consecutively in different stages [111]. One benefit of the invention is that the initial addition of acylating reagent leads to a reduction in solution viscosity of the contact mixture, what can allow a reduction of contact temperature during subsequent acylating reagent additions. Another benefit is that when one or more acylating reagents are added in a staged addition, one acylating reagent can be added and allowed to react during the first stage then a second acylating reagent can be added during the second stage, thereby leading to novel cellulose esters with unique substitution patterns.

When one or more acylating reagents are added the C6 of the cellulose was acylated faster than C2 and C3. The type of ionic liquid affects the regioselectivity of the cellulose ester: when carboxylated ionic liquids are utilized the regiselectively substituted ester is produced where, C6>C2>C3 [112]. When a tetraalkylammonium dialkylphosphates is used, the RSD is C6>C3>C2 [111]. Those cellulose esters have different physical properties relative to conventional esters.

3) Ester recovery. The produced ester is separated by adding an excess of a protic solvent such as water, low alcohol or ketone, in which the acylated cellulose is not soluble [106]. Acylated cellulose is separated by filtration and/or centrifugation [106].

4) Ionic liquid recovery/treatment. If the ionic liquid is not modified it can be recovered and cleaned by distillation [106]. Buchanan and coworkers [107] developed a patent for reforming carboxilated ionic liquids modified during the process, consisting of putting in contact a portion of the carboxylic ionic liquid with an alkyl amine formate ionic liquid, and all of the anions of the separated carboxylated ionic liquid can be converted substantially to a single type of anion providing a reformed ionic liquid. A portion of this reformed ionic liquid can be contacted with one or more carboxylate anion donor such as carboxylic acids, anhydrides or alkyl carboxylates under conditions sufficient to produce an ion exchange and thereby produce a recycled IL that can be used for dissolving more cellulose. The anion exchange can be accomplished in the presence of at least one alcohol.

Buchanan and Buchanan also invented a method for producing cellulose ester that can be contacted with at least one bleaching agent to produce bleached cellulose esters [113].

These patents are in relation to the one from Myllymaki and Aksela [116]. They proposed a method for preparing an organic starch ester assisted by microwave irradiation or pressure. The starch is mixed with the ionic liquid as solvent to dissolve the starch. The presence of auxiliary solvents or co-solvents is not necessary, and it is preferably to carry out the process in absence of water. The solution is then mixed with an organic esterifying reagent and finally the organic starch ester is separated from the solution by the addition of a non- solvent, as various alcohols, to the reaction medium.

The main advantages of the present invention are: 1) it is possible to achieve a complete and fast dissolution of starch at temperatures below 100ºC and in shorter reaction times by the use of microwave irradiation or pressure than in conventional methods; 2) native starch can be employed. The reaction is carried out in a non-aqueous media, therefore a fast separation is possible. The risk of chain degradation decreases due to the soft reaction conditions and it is easy to control the DS.

5.6.2. Inventions for cellulose ether producing using ionic liquids

The conventional industrial preparation of cellulose ethers is carried out under heterogeneous reaction conditions. It takes place in two steps. In the first step cellulose is initially activated with concentrated alkali liquor. Cellulose must be activated to lose its partially crystalline structure increasing in this way the accessibility of the hydroxyl groups [115]. In a second step, activated cellulose is reacted with alkyl halides or epoxy alkyl compounds at elevated temperature. The main drawback of this process is that the cellulose as well as its reaction intermediates and products never leave their solid form therefore the product quality strongly depends on the quality of the stirring system and on the geometry of the reaction vessel [116].

As ionic liquids are able to dissolve cellulose, they allow the etherification reaction to be developed in homogeneous phase, being an important advantage of the process. A summary of the patents about ether production is presented in Table 7.

Table 7. Patents of processes of cellulose ether production.

Title/ Company	**Conditions/Ionic Liquid**	**Agent**
Method for preparing a cellulose ether (2007) [116]	- Cellulose: 1 to 35% wt - T: 0-250ºC Absence of water and organic bases - IL: bmimCl	- Etherifying agent: chloroacetic acid/alkali metal chloroacetate + inorganic base (Li, Na or K hydroxide)
Homogeneous synthesis of Cellulose ethers in ionic liquids (2009) [117] Se Tylose GMBH & Co Kg	- Cellulose dissolved:1-35%wt - <u>Etherification</u>: - T:0-250ºC - Time: 0.5-96 hours; - Water: 0-25%wt - Pressure: 0.1- 2 bar - Melting point:-100 to 200ºC - IL: Organic cation and organic or inorganic anion. (emimAc, edmimAc,edmimCl)	- Co-solvent or organic solvents: DMSO, DMF, dimethoxythane and chloroform

Patent WO 2005/054298 [116] proposed preparing cellulose ether by dissolving cellulose in the ionic liquid together with an etherifying agent in the presence of an inorganic base, without the addition of organic solvent or co-solvent. Nevertheless, according to Moellmann et al [117], when a base is added it must be neutralized after the reaction is completed, which produces a considerable amount of salt that must be removed. In their patent, owned by SE TYLOSE GMBH & CO, they avoid using organic or inorganic bases by treating the dissolved cellulose with an etherification agent using an organic co-solvent to adjust the viscosity of the cellulose solution, the polarity of the ionic liquids and the miscibility of etherification agent in ionic liquids. Catalyst, acids or a moderate amount of water can be added but it is not necessary. With both methods it is possible to prepare existing and new cellulose ethers controlling the DS via molar ratio of etherification reagent per anydroglucose unit, reaction time and temperature.

5.6.3. Inventions for cellulose sulphates and sulfonates production and other cellulose derivates using ionic liquids.

Another type of functionalization is the modification of biopolymers with sulphate or sulfonate moieties. Sulfonation and sulfation products can be used as water–soluble detergents, emulsifiers and demulsifiers, penetrating and solubilizing agents, lubricating additives and rust inhibitors. These materials are used in household and commercial detergent applications, food processing, dyes, cosmetics manufacturing, and metal treating compounds and lubrication agents.

The synthetic sulphated or sulfonated polymers are typically produced from petro-chemical sources via well-known chemical process. For being produced from cellulose first the cellulose pulp, for example Kraft pulp, must be oxidized with sodium periodate for example and then reacted with a sulfonated reagent, as sodium bisulphite ($NaHSO_3$) to produce sulfonated cellulose. Sulfonation of the cellulose fiber significantly increases the dry and wet tensile strength as well as the wet strength-dry strength ratio, making this modified cellulose fiber extremely useful in a wide variety of paper products [118].

Table 8 shows different methods for the production of cellulose sulphates and sulfonates by using ionic liquids.

Table 8. Patents about cellulose sulphates and sulfonates production by using ILs.

Title/Company	Conditions/ILs	Agent
Methods for modifying biopolymer in ionic liquids (2007) [119] Procter & Gamble	- Biopolymer: starch, citosin, dextran, gums - Room temperature – 130ºC - Time: 1 min-5h, - IL:Biopolymers 1:2 -100:1. - Reaction mixture: - T: <=130ºC - Time:1 min-12 h with stirring - IL:Quaternary ammonium salt	- Chlorosulfonic acid, SO_3.pyridine complex, sulphuric acid, sulfamic acid, SO_3, and mixtures thereof - Modifying agent: 1-6 moles/ moles of monomer unit of the biopolymer.
Methods for modifying cellulosic polymers in ionic liquids (2007) [120] Procter & Gamble	- Starting material: cellulose o cellulose ethers - IL: Quaternary ammonium salt	- Sulfation or sulfonation agent: chlorosulfonic acid, SO_3.pyridine complex, sulphuric acid, sulfamic acid, SO3, and mixtures thereof
Preparing low substituted water-soluble cellulose sulfate used in biomedical application for spherical simplex membrane, by dissolving cellulose in ionic liquid and adding sulfurizing reagent to the medium (2007) [121]	- Reaction - T:25-80C - Timet: 0.5-3h - IL:bmimCl	- Trimethylsilylether of the cellulose (TMS cellulose) is dissolved in DMF. - Sulphating agent: sulfur trioxide, chlorosulfonic acid or Sulforylchlorid
Process for silylating cellulose (2009) [122] BASF	- Cellulose: 0.1-50% wt. - $T_{disolution}$:Room T – 200ºC - $T_{reaction}$:20-200ºC	- Silylating agent: RxRyRz–Si-X
Method for manufacturing cellulose derivatives containing amino groups in ionic liquid (2009) [123] Dow Wolff Cellulosics GMBH	- Reaction - T:10-80ºC - IL: cation: imi	- Lactam: N-methyl-2-pyrrolidone, [epsilon]-caprolactam, N-methyl-[epsilon]-caprolactam or N-methyl-2-piperidone. - Lactam is activated by an organic Lewis acid. - Molar ratio lactam:Lewis acid 1:0.4-1:2
Method for producing cellulose acetals (2009). [124] BASF	- The cross linking: - T<= 200C. - IL: cations: quaternary ammonium, oxonium, sulfonium or phosphonium; anions: mono, bi- tri-tetravalent	- Reacting with a vinyl ether

The Company Procter and Gamble has patented two processes that describe methods for sulfation or sulfonation of a cellulose or cellulose ether [119] or another biopolymer such as starch, citosin, dextran, gums [120] in ionic liquid media. In both processes, first, biopolymer is partially or totally dissolved in the ionic liquid and then a sulfation or sulfonation agent is added, converting biopolymer into a sulphated or sulfonated biopolymer. The modified biopolymers are separated of the mixture by adding a recovery solvent, such as water, alcohols, ethers, acetone and mixtures thereof. The recovery solvent and the ionic liquid are then separated by evaporation, distillation or drying over an absorbent. The ionic liquid recover can be re-used or recycled. The degree of substitution (DS) in the resulting modified biopolymer typically ranges from about 1 to about 6 moles of sulfate or sulfonate (or both) substituents per mole of monomer unit of the biopolymer.

Gericke et al [121] related a novel method for preparing low substituted water-soluble cellulose sulfate (NaCS) for biomedical applications (DS<0.7). For the preparation cellulose is dissolved in the ionic liquid and viscosity is adjusted by addition of an organic solvent such as DMF, DMSO or DMA. Then cellulose reacts homogeneously with the sulphating agent. NaCS is isolated in a precipitation medium consisting of an alcohol/a water mixture by adding a solution of sodium hydroxide in order to additionally neutralize the product. This invention also relates that acylation and sulfation of cellulose can be carried out parallel by using as both sulphating and acylating reagents for example acetic anhydride and sulfuric acid.

Other similar processes taking advantage of the homogenous media provided by IL for obtaining substituted derivatives of cellulose have been patented.

· Massonne et al proposed a process for silylating cellulose and derivates [122].

· Meinolf et al [123] developed a process for producing cellulose polymers substituted with amino groups by reacting cellulose with a lactan.

· Massonne et al [124] patented the production of cellulose derivatives such as esters, ethers, or nitrates from acetylated cellulose that can be used in the textile, the food, building and lacquer industry. In a first step the cellulose or polysaccharide is reacting in a homogeneous solution in IL media with vinyl ether. The acetylated cellulose can be cross linking by treating it with acid. The cross linked cellulose obtained by this process is novel and can lead to the formation intermolecular and intramolecular acetal bondings.

6. CURRENT & FUTURE DEVELOPMENTS

In the last years the use of lignocellulosic materials and other biopolymers to obtain different products has increased. It is expected that in the future most of the products currently obtained from oil are obtained from renewable substances.

ILs have generated a lot of interest as a clean alternative to the traditional polluting processes, both in industry and academia, owing to their capacity for dissolving biopolymers . The processes proposed are simple and relatively easy to implement being somehow limited by the high viscosity of the mixture biopolymer/IL and in some cases with the recoverability and recyclability of the IL.

Since 2005 to the present more than 70 patents related to the processing of biomaterials to form different chemicals and fuels as well as composite materials and substituted polymers, have been published. A great number of these patents are owned by companies such as BASF and Eastman Chemical Companies. Nevertheless, none of these processes is yet implemented at industrial scale.

7. LIST OF ABBREVIATION

Abbreviation	**Name**
Ac	Acetate
[amim][Cl]	Alkylimidazolium chloride
RSO_4	Alkylsulphates
Tf_2N	Bis(trifluoromethylsulfonylimide)
CS_2	Carbon disulphide
CI	Crystallinity Index
DP	Degree of polymerization
DS	Degree of substitution
DMA	N,N-dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
N_2O_4	Dinitrogen tetroxide
SbF_6^-	Hexafluoroantimonate
AsF_6^-	Hexafluoroarsenate
PF_6	Hexafluorophosphate
HMF	Hydroxymethylfurfural
Im	Imidazolium
IL	Ionic Liquid
mim	Methylimidazolium
NMMO	N-methylmorpholine-N-oxide
Mpy	Methylpyridinium
NO_2^-	Nitrite

pyrr	Pyrroldinium
SO_4^{2-}	Sulfate
TRS	Total reducing sugar
[C2mim][Ac]	1-ethyl-3-methylimidazolium acetate
[Amim][OH],	1-alkyl-3-methylimidazolium hydroxide
[bmim][OH],	1-butyl-3-methylimidazolium hidroxide
[emim] $HOSO_3$]	1-ethyl-3-methylimidazolium hydrogensulfate
[emim][$MeOSO_3$]	1-ethyl-3-methylimidazolium methylsulfate
[emim][SCN]	1-ethyl-3-methylimidazolium thiocyanate
[Hemim][Cl],	1-(2'-hydroxylethyl)-3-methylimidazolium chloride
[Hemim][OH]	1-(2'-hydroxylethyl)-3-methylimidazolium hydroxide

8. REFERENCES

[1] D. Fengel, G. Wegener, Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin, New York, 1983
[2] BASF, Processing Cellulose with Ionic Liquids. Available at: http://www.intermediates.basf.com/chemicals/web/en/content/products-andindustries/ionic-liquids/applications/cellulose_processing (Accessed: 17 June 2012)
[3] Ullmann´s Encyclopedia of industrial chemistry
[4] T. Jenkins, “Toward a biobased economy: examples from UK,” Biofuels, Bioprod. Bioref. 2 (2008). 133-143.
[5] Chemical Industry Vision 2020 Alternative, renewable, and novel feedstocks for producting chemicals, [online] 2007, www.chemicalindustryvision2020.org (Accesed 17 June 2012)
[6] J. Bozell, J.E. Holladay, D. Johnson, J.F. White, Top Value Added Chemicals from Biomass, Volume II - Results of Screening for Potential Candidates from Biorefinery Lignin, (U. S. Department of Energy), [online] 2007, http://www1.eere.energy.gov/biomass/pdfs/pnnl-16983.pdf (Accesed: 17 June 2012).
[7] T. Werpy , G. Petersen, Top Value Added Chemicals from Biomass, Volume I - Results of Screening for Potential Candidates from Sugars and Synthesis Gas, (U. S. Department of Energy, Energy Efficiency and Renewable Energy), (2004), www1.eere.energy.gov/biomass/pdfs/35523.pdf (Accesed: 17 June 2012).
[8] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, Dissolution of Cellulose with Ionic Liquids,” Journal of American Chemical Society, 12 (2002) 4974-4975.
[9] K. N. Marsh, J. A. Boxall, R. Lichtenthaler, Room temperature ionic liquids and their mixtures - a review, Fluid Phase Equilibria, 21 (2004) 93-98.
[10] A. Jarosik, S. R. Krajewski, A. Lewandowski, P. Radzimski, Conductivity of ionic liquids in mixtures, J. Mol. Liq., 123 (2006) 43-50.

[11] A. P. Froba, H. Kremer, A. Leipertz, Density, refractive index, interfacial tension, and viscosity of ionic liquids [EMIM][EtSO4], [EMIM][NTf2], [EMIM][N(CN)2], and [OMA][NTf2] in dependence on temperature at atmospheric pressure, J. Phys. Chem. B, 112 (2008) 12420-30.

[12] K. R. Seddon, A. Stark, M. J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem., 72 (2000) 2275-2287.

[13] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, Green Chem., 3 (2001). 156-164.

[14] A. E. Visser, W. M. Reichert, R. P. Swatloski, H. D. Willauer, J. G. Huddleston, R. D. Rogers, "Characterization of hydrophilic and hydrophobic ionic liquids: Alternatives to volatile organic compounds for liquid-liquid separations, ACS Symp. 880 (2002) 289-308.

[15] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: Recent progress from knowledge to applications, Applied Catalysis A: General, 373 (2010) 1–56.

[16] R. Sheldon, Catalytic reactions in ionic liquids, Chem. Commun., 23 (2001) 2399-2407.

[17] C. M. Gordon, New developments in catalysis using ionic liquids, Applied Catalysis A: General, 222 (2001) 101-117.

[18] T. Welton, Ionic liquids in catalysis, Coordination Chemistry Reviews, 248 (2004) 2459-2477.

[19] A. Riisager, R. Fehrmann, M.Haumann, P. Wasserscheid, Supported Ionic Liquid Phase (SILP) systems – novel fixed bed reactor concepts for homogeneous catálisis in continuous fixed-bed reactors, Eur. J. Inorg. Chem, (2006) 695-706.

[20] A. Forestière, H. Olivier-Bourbigou, L. Saussine, Oligomerization of Monoolefins by Homogeneous Catalysts," Oil Gas Sci. Technol., 64 (2009) 649-667.

[21] M. Maase, P. Wasserscheid, T. Welton, Industrial Applications of Ionic Liquids, Ionic Liquids in Synthesis, Wiley-Vch Verlags GmbH & Co. KGaA, 2d. , (2008) 663–687.

[22] F. Van Rantwijk, R. A. Sheldon, Biocatalysis in ionic liquids, Chem. Rev, 107 (2007) 2757-2785.

[23] P. Lozano, T. De Diego, S. Gmouh, M. Vaultier, J. L. Iborra, Dynamic structure-function relationships in enzyme stabilization by ionic liquids, Biocatal. Biotransf, 23 (2005) 169-176.

[24] J. Vitz, T. Erdmenger, C. Haensch, U. S. Schubert, Extended dissolution studies of cellulose in imidazolium based ionic liquids, Green Chem, 11 (2009) 417-424.

[25] D. Klemm, B. Heublein, H. P. Fink, A. Bohn, Cellulose: Fascinating Biopolymer and Sustainable Raw Material, Angewandte Chemie International Edition, 44 (2005) 3358-3393.

[26] D. L. VanderHart, R. H. Atall, Further Carbon-13 NMR Evidence for the coexistence of Two Crystalline Forms in Native Celluloses in The Structures of

Cellulose, R. D. Rogers and K. R. Seddon, Vol. 340, ACS Symposium Series, (1987) 88-118.

[27] A. Pinkert, K. N. Marsh, S. Pang, Reflections on the Solubility of Cellulose, Industrial & Engineering Chemistry Research, 49 (2010) 11121-1113.

[28] B. Lindman, G. Karlström, L. Stigsson, On the mechanism of dissolution of cellulose, Journal of Molecular Liquids, 156 (2010) 76-81.

[29] T. Heinze, A. Koschella, Solvents applied in the field of cellulose chemistry: a mini review, Polímers: Ciência e Tecnologia. 15(2005) 84-90.

[30] T. F. Liebert, T. Heinze, Exploitation of Reactivity and Selectivity in Cellulose Functionalization Using Unconventional Media for the Design of Products Showing New Superstructures, Biomacromolecules, 2 (2001) 1124-1132.

[31] J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren, M. Guo, Homogeneous Acetylation of Cellulose in a New Ionic Liquid, Biomacromolecules, 5 (2004) 266-268.

[32] G. T. Ciacco, T. F. Liebert, E. Frollini, T. Heinze, Application of the solvent dimethyl sulfoxide/tetrabutyl-ammonium fluoride trihydrate as reaction medium for the homogeneous acylation of Sisal cellulose, Cellulose, 10 (2002) 125-132.

[33] T. Heinze, T. Liebert, P. Klüfers, F. Meister, Carboxymethylation of cellulose in unconventional media, Cellulose, 6 (1999) 153-165.

[34] R. C. Remsing, R. P. Swatloski, R. D. Rogers, G. Moyna, Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a 13C and 35/37Cl NMR relaxation study on model systems, Chem Commun (2006) 1271–1273.

[35] J. S. Moulthrop, R. P. Swatloski, G. Moyna, R. D. Rogers, High-resolution 13C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions, Chem. Commun, (2005) 1557–1559.

[36] Y. Fukaya, K. Hayashi K, M. Wada, H. Ohno, Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions, Green Chem, 10 (2007).

[37] A. P. Dadi, S. Varanasi, C. A. Schall, Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step, Biotechnol. Bioeng, 95 (2006) 904-10.

[38] G. Ebner, S. Schiehser, A. Potthast, T. Rosenau, Side reaction of cellulose with common 1-alkyl-3-methylimidazolium-based ionic liquids, Tetrahedron Lett, 49 (2008) 7322-7324.

[39] Y. Fukaya, A. Sugimoto, H. Ohno, Superior Solubility of Polysaccharides in Low Viscosity, Polar, and Halogen-Free 1,3-Dialkylimidazolium Formates, Biomacromolecules, 7 (2006) 12, 3295-3297

[40] Y. Fukaya, K. Hayashi, M. Wada, H. Ohno, Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions, Green Chem, 10 (2007) 44-46.

[41] H. Zhao, G. A. Baker, Z. Song, O. Olubajo, T. Crittle, D. Peters, Designing enzyme-compatible ionic liquids that can dissolve carbohydrates, Green Chem, 10 (2008) 696-705

[42] A. Pinkert, K. N. Marsh, S. Pang, M. P. Staiger, Ionic Liquids and their interaction with Cellulose, Chem. Rev, 109 (2009) 6712–6728.

[43] T. Erdmenger, C. Haensch, R. Hoogenboom, U. S. Schubert, Homogeneous Tritylation of Cellulose in 1-Butyl-3-methylimidazolium Chloride, Macromol. Biosci., 7 (2007) 440-445.

[44] L. Feng and Z. I. Chen, Research progress on dissolution and functional modification of cellulose in ionic liquids, J. Mol. Liq., 142 (2008) 1-5.

[45] S. Possidonio, L. C. Fidale, O. A. El Seoud, Microwave-assisted derivatization of cellulose in an ionic liquid: An efficient, expedient synthesis of simple and mixed carboxylic esters, J. Polymer Science Part A: Polymer Chemistry, 48 (2009) 134-143.

[46] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, Dissolution and processing of cellulose using ionic liquids, (2003) W. O Patent WO2003029329

[47] BASF, Cellulose Processing, Available at: http://www.basionics.com/en/ionic-liquids/applications/biopolymer/cellulose-processing.htm (Accessed on June 3,2011)

[48] C. Graenacher, Cellulose solutions, (1934) U. S. Patent 1,943,176.

[49] M. Maase, U. Vagt, W. Gaschler, O. Koch, H. Kröner, Method for modifying the structure of a cellulose material by treatment with an ionic liquid, (2008) W. O. Patent WO2008119770.

[50] M. Maase, M. Stegmann, Cellulose solutions in Ionic Liquids, (2008) U. S Patent US20080190321.

[51] M. Maase, M. Stegmann, Solubility of cellulose in ionic liquids with addition of amino base, (2010) U. S. Patent, US20107754002.

[52] P. O´Connor, Improved process for dissolving cellulose-containing biomass material in an ionic liquid medium, (2011) W. O. Patent WO2011027220.

[53] D. C. Dibble, A. Cheng, A. George, Novel compositions and methods useful for ionic liquid treatment of biomass, (2011) U. S Patent US20110073805.

[54] J. D. Holbrey, S. K. Spear, M. B. Turner, R. P. Swatloski, R. D. Rogers, Cellulose matrix encapsulation and method, (2004) U. S. Patent US20040038031.

[55] J. D. Holbrey, R. P. Swatloski, J. Chen, D. Daly, R. D. Rogers, Polymer dissolution and blend formation in ionic liquid, (2005) U. S. Patent US20050288484.

[56] V. Stegmann, K. Massonne, M. Maase, E. Uerdingen, M. Lutz, F. Hermanutz, F. Gaeh, Solvent system based on molten ionic liquids, its production and use for producing regenerated carbohydrates, (2008) U. S. Patent US20080269477.

[57] A. N. Neogi, M. Luo, H. West, Method for processing cellulose in ionic liquids and fibers therefrom, (2008) U.S. Patent US20080241536.

[58] B. Kapoor, P. Lodha, P. Patil, A. Shrivastava, K. Shouche, E. Uerdingen, M. Siemer, T. Wisniewski, U. Vagt, K. Massonne, A process of manufacturing low fibrillating cellulosic fibers, (2011) W. O. Patent WO2011048608.

[59] J. Wu, S. Wang, Z. Jun, G. Wei, J. He, Method for continuously preparing cellulose/ionic solution, C. N. Patent CN101085838, July 3 2007

[60] B. Cheng, W. Zheng, H. Zang, Cellulose hollow fiber film prepared by ionic liquid method, (2008) C. N. Patent CN 101234297

[61] B. J. Koko, Inflated fibers of regenerated cellulose formed from ionic liquid/cellulose dope and related products, (2008) U. S. Patent US20080135193.

[62] N. Güntherberg, K. P. Farwerck, A. Kurps, D. Barrera-Medrano, E. Uerdingen, V. Stegmann, M. Lutz, Production of spherical particles from solutions containing a water-

miscible solvent, according to the method of underwater granulation, (2009) W.O. patent WO2009065891.

[63] M. Braun, N. Guentherberg, M. Lutz, A. Magin, M. Siemer, S. Narayanan, B. Linner, F. Ruslim, G. A. Fernández Ramírez, Process for producing cellulose beads in ionic liquid, (2010) U. S. Patent US20100331222.

[64] D. Lin, D. Fei Shi, S. Yao, Y. Du, Method for preparing cellulose microsphere by taking ionic liquid as solvent, (2009) C. N. Patent CN 101612540.

[65] J. J. Heinerman, J. A. Moulijn, P. O´ Connor, J. C. Rasser, A. E. Rosheuvel, Simultaneous catalytic conversion of cellulose and lignin to a liquid fuel in an ionic liquid, (2011) W. O. Patent WO2011028776.

[66] J. Upfal, D. R. Macfarlane, Solvents for use in the treatment of lignin-containing materials, (2005) W. O. Patent WO2005017252.

[67] H. Y. Cho, S. J. Sim, J. W. Kim, S. J. Han, J. C. Park, S. M. Park, Method of pretreating lignocellulose- based biomass, (2010) U. S. Patent US20100279372.

[68] V. Myllymäki and R. Aksela, Dissolution methods for lignocellulosic material, (2005) W. O. Patent WO2005017001.

[69] L. A. Edye and W. O. S. Doherty, Fractionation of a lignocellulosic material, (2008) W. O. Patent WO2008095252.

[70] A. P. Gifford and D. E. Severeid, Fractionation of lignocellulosic material using ionic liquids, (2010) U. S. Patent US20100163018.

[71] M. Yingchong, W. Ligang, L. Kunlan, W. Shaojun, Y. Jiayou, L. Yinling, Method for separating lignin and cellulose from lignocellulose by using ionic liquid solvent, (2009) C. N. Patent CN 101580522.

[72] G. D`Andola, L. Svarzas, K. Massone, V. Stegman, Ionic liquid for solubilizing polymers, (2008) W. O. Patent WO2008043837.

[73] M. Rahman, N. Sun, Y. Qin, M. Maxim, R. D. Rogers, Ionic liquid system for the processing of biomass, their components and/or derivates, and mixtures thereof, (2010) W. O. Patent WO2010056790.

[74] A. P. Dadi, S. Varanasi, C. A. Schall, Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step, BiotechnolBioeng., 95 (2006) 904-10.

[75] O. J. Olusola, M. Sudip, A. U. Lamidi, O. A. Kolawole,O. A. Olayinka, O. S. Tolu, S. Satanand, C. Rashmi, Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxylmethylfurfural," Energy Environ. Sc., 3 (2010) 1833-1850.

[76] A. T. W. M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, Bioresource Technology, 10 (2009) 10–18.

[77] R. Sapra, J. I. Park, S. Datta, B. A. Simmons, Novel thermophilic cellobiohydrolase, (2011) U. S. Patent US20110207182.

[78] P. O´Connor, Pretreatment of solid biomass material comprising cellulose with ionic liquid medium, (2011) W. O. Patent WO2011027223.

[79] S. Varanasi, C. A. Schall, A. P. Dadli, J. Anderson, K. Rao, Biomass pretreatment, (2008) U. S. Patent US20080227162.

[80] S. Varanasi, C. A. Schall, A. P. Dadli, Saccharifying cellulose, (2010) U. S. Patent US20100233773.

[81] D. Argyropoulus, Use of lignocellulosic solvated in ionic liquids for production of biofuels, (2008) U. S. Patent US20080190013.

[82] T. Balensiefer, H. Schroeder, S Freyer,G. D´Andola, K. Massonne, Method for producing Glucose by enzymatic hydrolysis of cellulose that is obtained from material containing lingo-cellulose using an inonic liquid that comprises a polyatomic anion, (2010) U. S. Patent US201000817998.

[83] T. Balensiefer, J. Brodersen, S. Freyer, G. D´Andola, W. Stegmann, Enzymatic hydrolysis of a cellulose material treated with an ionic liquid, (2010) U. S. Patent US20100112646.

[84] R. Sapra, S. Datta, Z. Chen, B. M. Holmes, B. A. Simmons, H. W. Blanch, Thermostable cellulases, and mutants thereof, capable of hydrolyzing cellulose in ionic liquid, (2010) W. O. Patent WO2010124266.

[85] S.J. Jo, R. Nakamura, S. Katahira, N. Ishida, H. Takahashi, K. Tabata, K. Nakashima, C. Ogino, A. Kondo, N. Takahashi, Method for producing useful substance from cellulose-containing material, (2011) US Patent US 20110033906.

[86] F. Schüth, R. Rinald, P. Engel, A. Spiess, J. Büchs. Method for the hydrolysis of cellulose raw material, (2010) W.O. Patent WO2010111995.

[87] F. Schüth, R. Rinaldi, R. Palkovitz. Method for depolymerization of cellulose, (2011) U. S. Patent US20110015387.

[88] K. Tabata, H. Takahashi, H. Miyafuji. Method for controlling rate of lowering molecular weight of polysaccharides contained in cellulosic biomass, and method for producing sugar, alcohol, or organic acid, (2011) US patent US20110053230.

[89] M. Fanselow, J. Holbrey, K. R. Seddon, Conversion Method, (2009) U. S. Patent US20090198046.

[90] K. Massonne, G. D´Andola, V. Stegmann, W. Mormann, M. Wezstein, W. Leng, S. Frever, Method for breaking down cellulose, (2009) U. S. Patent US20090020112.

[91] K. Massonne, G. D´Andola, V. Stegmann, W. Mormann, M. Wezstein, W. Leng, Method for breaking down cellulose in solution, (2009) U. S. Patent US20090062524.

[92] R. T. Raines and J. B. Binder, Biomass hydrolysis, (2011) U. S. Patent US20110065159.

[93] Z. C. Zhang, H. M. Brown, Y. Su, Method for conversion of carbohydrate polymers to value-added chemical products, (2009) U. S. Patent US20090270608.

[94] P. B. Da Silva Correia, Biocell – three step process for obtaining a liquid fuel from cellulose consisting mainly of isomers of methyl pyran and methyl tetrahydropyran using N alkyl imidazol chloride as solvent and catalyst, (2010) U. S. Patent US20100305340.

[95] M. Gurin, Biomass fuel synthesis methods for increased energy efficiency, (2007) U. S. Patent US20070161095.

[96] J. B. Binder and R. T. Ralners, Chemical transformation of lignocellusic biomass into fuels and chemicals, (2009) W. O. Patent WO 2009155297.

[97] D. Argyropoulo, Product preparation and recovery from thermolysis of lignocellulosics in ionic liquids, (2008) U. S. Patent US20080185112.

[98] P. B. Correia, Production process of furfural from cellulose using a solvent and catalyst an imidazolium sulphate chloride in a reaction with simultaneous extraction with dibutyl ether, (2012) U S Patent US20120184756.

[99] B. A. Grosse, L. Mleczko, A. Wolf, W. Dietrich, Method for the production of fuels from biomass, (2009) W.O. Patent WO2009071181.

[100] R. Rogers, D. Daly, M. Turner, S. Spear, J. Holbrey, Ionic liquid reconstituted cellulose composites as solid support matrices, (2007) W. O. Patent WO2007005388.

[101] D. Argyropoulo, H. Xie, Polymer derivates and composites from the dissolution of lignocellulosic in ionic liquids, (2008) U. S. Patent US20080188636.

[102] E. Uerdingen, M. Siemer, M. Lutz, T. Wisniewski, F. Hermanutz, F. Gachr, Method for producing regenerated biopolymers and regenerated products obtained by said method, (2010) U. S. Patent US20100256352.

[103] S.Champ and R.Chapman, Method for producing solid materials on the basis of synthetic polymers and/or biopolymers and use thereof, (2009) W. O. Patent WO2009103681.

[104] A. Taubert and L. Zhonghao, Synthesis of Au, Pd, Pt or Ag nano-or microcrystals via reduction of metal salt by cellulose in the ionic liquid 1-butyl-methyl imidazolium chloride, (2009) W. O. Patent WO2009080522.

[105] S. H. Hecht, R. L. Niehoff, K. Narasimhan, C. W. Neal, P. A. Forshey, D. V. Phan, A. D. M. Brooker, K. H. Combs, Extraction biopolymers from a biomass using ionic liquids, (2006) U. S. Patent US20060241287.

[106] K. Massonne, V. Stegmann, G. D´Andola, M. Werner, M. Wezstein, L. Wei, Method for acylating cellulose with a specific degree of polimerization, (2009) U. S. Patent US20090182138.

[107] C. M. Buchanan and N. L. Buchanan, Reformation of ionic liquids, (2008) U. S. Patent US20080194807.

[108] C. M. Buchanan, N. L. Buchanan, R. T. Hembre, J. L. Lambert, Cellulose Esters and their production in carboxylated ionic liquids, (2008) U. S. Patent US20080194808.

[109] C. M. Buchanan and N. L. Buchanan, Cellulose esters and their production in halogenated ionic liquids, (2009) U. S. Patent US20090203898.

[110] C. M. Buchanan and N. L. Buchanan, Production of cellulose esters in presence of a cosolvent, (2009) U. S. Patent US20090203900.

[111] C. M. Buchanan, N. L. Buchanan, E. Guzman-Morales, Cellulose solutions comprising tetraalkylammonium alkylphosphate and products produced therefrom, (2010) W. O. Patent WO2010120269.

[112] C. M. Buchanan, N. L. Buchanan, R. T. Hembre, J. L. Lambert, M. E. Donelson, M. G. Gorbunova, T. Kuo, B. Wang, Regioselectively substituted cellulose esters produced in a Carboxylated ionic liquids process and products produced therefrom, (2010) U. S. Patent US20100029927.

[113] C. M. Buchanan and N. L. Buchanan, Treatment of cellulose esters, (2009) U. S. Patent US20090203899.

[114] V. Myllymaki and R. Aksela, Starch esterification method, (2007) U. S. Patent US20070073051.

[115] E. A. Klohr, J. Neubauer, W. Koch, K. Szablikowski, D. Redeker, W. Wagenknecht, F. Loth, Novel cellulose ethers and methods for producing the same, (1999) W. O. Patent WO003891.

[116] V. Myllymaki and R. Aksela, Method for preparing a cellulose ether, (2007) U. S. Patent US20070112185.

[117] E. Moellmann, T. Heinze, T. Liebert, S. Koehler, Homogeneous synthesis of cellulose ethers in ionic liquids, (2009) U. S. Patent US20090221813.

[118] D. Rajalaxmi, N. Jiang, G. Leslie, A. J. Ragauskas, Synthesis of novel water-soluble sulfonated cellulose, Carbohydr Res., 345 (2010) 284-90.

[119] J. J. Scheibel, J. A. Menkaus, K. N. Price, Methods for modifying biopolymer in ionic liquids, (2007) W O Patent WO2007112304.

[120] P. Chwala, C. J. Kenneally, J. A. Menkaus, J. J. Scheibel, K. R. Seddon, Methods for modifying cellulosic polymers in ionic liquids, (2007) W. O. Patent WO2007112382.

[121] M. Gericke, T. Liebert, T. Heinze, Preparing low substituted water-soluble cellulose sulfate used in biomedical application for spherical simplex membrane, by dissolving cellulose in ionic liquid and adding sulfurizing reagent to the medium, (2007) D. E. Patent DE2007035322.

[122] K. Massonne, V. Stegmann, G. D´Andola, W. Mormann, W. Lenmg, Process for silylating cellulose, (2009) U. S. Patent 20090281303.

[123] B. Meinolf, T. Heinze, D. Susann, K. Andreas, “Method for manufacturing cellulose derivatives containing amino groups in ionic liquid,” (2010) European Patent EP2072530.

[124] K. Massonne, V. Stegmann, G. D´Andola, M. Werner, M. Wezstein, L. Wei, Method for producing cellulose acetals, (2009) U. S. Patent US20090187016.

Part II. Physical Properties

Chapter 2. Influence of Water Concentration in the Viscosities and Densities of Cellulose Dissolving Ionic Liquids. Correlation of viscosity data*

Abstract

The densities and viscosities of aqueous mixtures of two cellulose dissolving ionic liquids: 1-allyl-3-methylimidazolium chloride [amim][Cl] and 1-ethyl-3-methyl imidazolium acetate [emim][Ac] have been experimentally determined for water concentration up to approx. 35% water at atmospheric pressure and temperature range from 298.15 to 373.15 K. Molar excess volumes were calculated, resulting in negative values. Literature viscosity correlations were modified in order to describe the viscosity as a function of temperature and water concentration for water concentrations lower than x_{H2O}=0.4 and for all the water concentration range. These modified equations were applied to correlate viscosity of water + ionic liquid viscosity data for other 1-alkyl-3-methylimidazolium chloride ionic liquids as well as for ethanol + 1-ethyl-3-methyl imidazolium acetate from literature obtaining a good reproducibility of the data.

This Chapter was published as: C. Jiménez de la Parra, J. R. Zambrano, M. Dolores Bermejo, Á. Martín, J. J. Segovia, M. J. Cocero, Influence of water concentration in the viscosities and densities of cellulose dissolving ionic liquids. Correlation of viscosity data, The Journal of Chemical Thermodynamics, 91, 2015, 8-16.

1. INTRODUCTION

It is well known 1-alkyl-3-methylimidazolium (-mim) ionic liquids (ILs) with chloride (Cl) and acetate (Ac) anions are susceptible to dissolve cellulose and other natural polymers allowing their green processing [1]. Nevertheless the high viscosity of ionic liquids in general and of those with a chloride anion in particular is a limitation for these processes, and, what it is more, their viscosity is increased when cellulose or other polymer is dissolved in the IL presenting even non-newtonian behaviour [2]. Nevertheless, for many of these processes other molecular solvents are added to the mixture: i.e. water and sometimes acids for hydrolysis process are added in amounts low enough to prevent cellulose precipitation [3], or in higher amounts to finally precipitate the cellulose or cellulose derived polymers [1]. And it is known that viscosity of ionic liquids is in general decreased with increasing concentrations of molecular solvents such as water or organic solvents [4].

In literature there are several density and viscosity data of imidazolium chloride ionic liquids mixtures with water and other molecular solvents such as: densities of ethanediol + 1-butyl-3-methylimidazolium chloride (C_4mimCl) from 298 to 318 K [5]. In the case of water: densities of binary systems water + 1-butyl, 1-hexyl and 1-octyl-3methylimidazolium chloride (C_4mimCl, C_6mimCl, C_8mimCl) were determined in the temperature range from 298 to 308 K using the vibrating tube densimeter [6]. Rebelo and co-workers [7] measured the densities and speed of sound of C_8, C_{10} and C_{12}-mimCl ILs in diluted aqueous solutions at temperature range from 283.15 to 313.15 K to prove the self-aggregation phenomena of long chained alkylimidazolium chloride ILs. Gómez et al [8] determined densities and viscosities of mixtures water + C_4, C_6 and C_8 -mimCl ILs at temperatures from 298.15 to 343.15 K. Liu et al [9] studied densities and viscosities of binary mixtures water + 1-butyl-3-methylimidazolium chloride (C_4mimCl) at 298 K. Sing & Kumar [10] determined densities and viscosities of diluted aqueous solutions C_4mimCl and C_8mimCl in water. Calvar et al [11] studied the physical properties of the ternary mixture ehanol+ water + C_4mimCl. To the best of our knowledge densities mixtures water + 1-allyl-3-methylimidazolium chloride (AmimCl) have only been determined at 298 K, viscosities were also determined at this temperature, decreasing both, densities and viscosities with water concentration [12]. Viscosities of binary mixtures water + AmimCl and ethanol + AmimCl were determined by Xu et al, observing as well the decrease of viscosities with temperature and water molecular solvent concentration [13].

In literature several density and viscosity sets of data of binary systems involving ILs of the 1-alkyl-3-methylimidazolium acetate (-mimAc) family can be found. Qian et al [14] determined densities and viscosities of 1-methylimidazolium acetate IL and its binary mixtures with alcohols. Araujo et al [15] determined viscosities of C_2mimAc with nucleic acid bases. Quijada et al [16] determined the viscosities and densities of mixtures of water and ethanol with C_2mimAc at temperatures from 298 to 343 K. Romich et al [17] determined viscosities and densities of mixtures water + C_2mimAc at temperatures from 293 to 353 K at water molar fractions higher than 0.34. Fendt et al [18] determined the viscosities of mixtures of C_2mimAc, C_4mimAc and other acetate ILs with water and other solvents such as 1,2-ethanediol, acetonitrile, dimethylformamide at 298 K using a concentric cylinders viscometer. Hall et al [19] determined the densities and viscosities of pure C_2mimAc and water + C_2mimAc mixtures with high water compositions.

In this work, the density and dynamic viscosity of different binary mixtures of water and the ionic liquids 1-ethyl-3-methylimidazolium acetate (C_2mimAc) and 1-allyl-3-methylimidazolium chloride (AmimCl) at wide temperature and water molar fractions lower than 0.35 were experimentally determined. From these data, excess molar volumes were determined. Literature correlations were modified to calculate viscosity of the mixtures water + IL as a function of temperature and water concentration for water molar fractions lower than 0.4 and for all the water concentration range. These modified correlations were used to describe the viscosity of binary mixtures of ionic liquids of the same families with water and with ethanol.

2. EXPERIMENTAL

2.1. Materials

The ionic liquids used, 1-ethyl-3-methylimidazolium acetate (C_2mimAc) 95% purity and 1-allyl-3-methylimidazolium chloride (AmimCl) 98% purity were purchased by Iolitec. Water ACS reagent was supplied by Sigma Aldrich. Ionic liquids were treated by vacuum evaporation to dry them and to remove the residual volatile impurities at 95 ºC for at least 48 h. Characteristic of the ionic liquids are shown in table 1.

Table 1. Characteristic of the ionic liquids used in this work.

IL	Source	Purity (ww%)	Initial water content (wt%)
AmimCl	Iolitec GmbH	>98	0.52
C_2mimAc	Iolitec GmbH	>95	0.39

2.2. *Methods and Procedures*

Mixture of IL and water were prepared by mass using a high-precision analytical balance Sartorius CP 224S with a reproducibility of ± $1 \cdot 10^{-4}$g. The binary mixture was completely mixed by using magnetic stirrer and a Branson 3210 ultrasonic bath at room temperature for at least 3h. Karl Fisher titration was used for verify water content in triplicate using KF Mettler Toledo C20 immediately before and after density and viscosity measurements finding significant changes in the water composition. Thus, the average water concentration between the three measured was used. For samples with lower than 10% mol in water the results presented are the average of the measures obtained with several samples. An Anton Paar (model SVM 3000) automated rotational Stabinger viscometer and vibrating tube densimeter was used to carry out the measurements of viscosity and density of IL + water binary mixtures in a wide range at atmospheric pressure. With this apparatus, measurements can be done from 233.15 to 373.15 K in a viscosity range from 0.2 mPa·s to 20,000 mPa·s and in a density range from 0.65 $g \cdot cm^{-3}$ to 2 $g \cdot cm^{-3}$. The standard uncertainty of the temperature is ± 0.02 K (k=1) from (278.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.5 % (k=1), and the standard uncertainty of the density is ± 0.0005 $g \cdot cm^{-3}$ (k=1). The SVM 3000 Stabinger viscometer has a cylindrical geometry, and it is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob that rotates more slowly. The SVM 3000 apparatus also has a density measuring cell that employs the oscillating U-tube principle. Both density and viscosity cells are filled in one cycle, and the measurements are carried out simultaneously.

3. RESULTS

Results of the viscosity and density of C_2minAc and AmimCl are presented in tables from 2 to 5.

Table 2. Viscosities of the binary mixtures water + 1-ethyl-3-methylimidazolium acetate

x_{H2O}	0.072	0.102	0.132	0.188	0.266	0.355
St Dev.	0.007	0.010	0.009	0.002	0.009	0.002
T/K	**μ/mPa·s**					
298.15	124±3	119±3	112±3	100±2	85±5	75±2
303.15	92±2	89±2	84±2	76±2	66±2	58±1
313.15	55.4±0.2	53.6±0.2	51.1±0.2	46.7±0.2	41.8±0.2	36.9±0.1
323.15	35.4±0.5	34.5±0.4	33.1±0.4	30.6±0.3	27.7±0.4	24.8±0.3
333.15	24.3±0.2	23.8±0.2	22.9±0.2	21.4±0.2	19.5±0.2	17.7±0.1
343.15	17.63±0.06	17.23±0.06	16.73±0.06	15.69±0.05	14.44±0.05	13.19±0.05
353.15	13.21±0.08	12.96±0.06	12.58±0.07	11.89±0.07	11.00±0.07	10.11±0.06
363.15	10.28±0.04	10.09±0.04	9.82±0.03	9.32±0.03	8.67±0.03	8.00±0.03
373.15	8.19±0.03	8.07±0.03	7.86±0.03	7.48±0.03	6.98±0.02	6.47±0.02

The standard uncertainty of the temperature is ± 0.02 K

Table 3. Densities of the binary mixtures water + 1-ethyl-3-methylimidazolium acetate

x_{H2O}	0.072	0.102	0.132	0.188	0.266	0.355
St Dev.	0.007	0.010	0.009	0.002	0.009	0.002
T/K	**ρ/g·cm^{-3}**					
298.15	1.0983±0.0007	1.0983±0.0009	1.0988±0.0005	1.0997±0.0006	1.1005±0.0006	1.1018±0.0005
303.15	1.0953±0.0007	1.0953±0.0009	1.0958±0.0005	1.0966±0.0005	1.0975±0.0006	1.0989±0.0006
313.15	1.0892±0.0006	1.0892±0.0006	1.0897±0.0005	1.0905±0.0005	1.0914±0.0005	1.0928±0.0005
323.15	1.0832±0.0006	1.0832±0.0010	1.0837±0.0005	1.0845±0.0005	1.0855±0.0006	1.0868±0.0005
333.15	1.0772±0.0006	1.0772±0.0010	1.0777±0.0005	1.0785±0.0005	1.0795±0.0005	1.0808±0.0006
343.15	1.0712±0.0006	1.0713±0.0008	1.0717±0.0005	1.0726±0.0005	1.0735±0.0005	1.0748±0.0005
353.15	1.0654±0.0006	1.0654±0.0011	1.0659±0.0005	1.0667±0.0005	1.0677±0.0006	1.0689±0.0006
363.15	1.0595±0.0006	1.0596±0.0008	1.0600±0.0005	1.0608±0.0005	1.0618±0.0005	1.0629±0.0005
373.15	1.0538±0.0006	1.0539±0.0008	1.0543±0.0005	1.0551±0.0005	1.0560±0.0005	1.0571±0.0005

The standard uncertainty of the temperature is ± 0.02 K

Table 4. Viscosities of the binary mixtures water + 1-allyl-3-methylimidazolium chloride

x_{H2O}	0.045	0.091	0.126	0.152	0.193	0.267	0.335
St Dev.	0.006	0.008	0.001	0.008	0.001	0.001	0.008
T/K	**μ/mPa·s**						
298.15	1884±7	1416±5	1090±4	887±3	697±2	427±2	258.7±0.9
303.15	1137±4	891±3	691±2	580±2	459±2	293±1	184.2±0.6
313.15	473±2	392±1	312±1	270±1	221±1	151±1	101.0±0.4
323.15	232±8	196±3	164±7	147±7	121±3	86±1	61±1
328.15	167±5	144±2	123±6	108±3	91±3	67.1±0.8	48.6±0.8
333.15	124±3	108±1	92±3	84±3	71±1	53.1±0.5	39.3±0.5
343.15	73±1	64.9±0.5	56.3±1.0	51.7±1.0	45.0±0.5	35.0±0.3	26.8±0.2
353.15	46.2±0.4	41.8±0.3	36.9±0.4	34.3±0.4	30.4±0.3	24.3±0.2	19.2±0.1
363.15	31.2±0.2	28.6±0.1	25.6±0.2	24.0±0.2	21.6±0.1	17.70±0.09	14.26±0.07
373.15	22.21±0.08	20.53±0.07	18.58±0.07	17.60±0.06	15.98±0.06	13.37±0.05	10.98±0.04

The standard uncertainty of the temperature is ± 0.02 K

Table 5. Densities of the binary mixtures water + 1-allyl-3-methylimidazolium chloride

x_{H2O} **St Dev.**	0.045 0.006	0.091 0.008	0.126 0.001	0.152 0.008	0.193 0.001	0.267 0.001	0.335 0.008
T/K				**ρ/g·cm^{-3}**			
298.15	1.1459±0.0005	1.1457±0.0005	1.1454±0.0005	1.1453±0.0005	1.1449±0.0005	1.1439±0.0005	1.1430±0.0005
303.15	1.1430±0.0005	1.1427±0.0005	1.1424±0.0005	1.1423±0.0005	1.1418±0.0005	1.1409±0.0005	1.1401±0.0005
313.15	1.1369±0.0005	1.1367±0.0005	1.1366±0.0005	1.1364±0.0005	1.1360±0.0005	1.1351±0.0005	1.1344±0.0005
323.15	1.1310±0.0006	1.1310±0.0005	1.1307±0.0006	1.1306±0.0006	1.1302±0.0006	1.1295±0.0005	1.1286±0.0006
328.15	1.1282±0.0006	1.1281±0.0005	1.1281±0.0006	1.1279±0.0006	1.1275±0.0006	1.1267±0.0005	1.1258±0.0006
333.15	1.1254±0.0006	1.1254±0.0006	1.1252±0.0006	1.1250±0.0006	1.1247±0.0006	1.1240±0.0006	1.1230±0.0006
343.15	1.1199±0.0005	1.1198±0.0005	1.1197±0.0006	1.1195±0.0006	1.1191±0.0006	1.1183±0.0005	1.1174±0.0006
353.15	1.1144±0.0005	1.1143±0.0005	1.1142±0.0006	1.1139±0.0005	1.1136±0.0006	1.1128±0.0006	1.1118±0.0005
363.15	1.1088±0.0007	1.1089±0.0006	1.1087±0.0005	1.1084±0.0005	1.1080±0.0005	1.1073±0.0006	1.1063±0.0005
373.15	1.1036±0.0005	1.1035±0.0005	1.1033±0.0005	1.1030±0.0005	1.1027±0.0005	1.1018±0.0005	1.1009±0.0005

The standard uncertainty of the temperature is ± 0.02 K

It is observed that AmimCl presents viscosities almost one order of magnitude higher than C_2mimAc. For both ILs viscosities decrease when increasing temperature and water concentration as described in literature ([4], [8], [9], [13], [14] [16], [18]).

Densities of AmimCl and C_2mimAc are of the same order of magnitude. In both ionic liquids densities decrease with temperature, but in the case of AmimCl density slightly decrease with the molar fraction of water while in the C_2mimAc density slightly increase with water molar fraction.

Comparison of the measured magnitudes with literature data are presented in figures from 1 to 4. In figure 1, experimental and literature viscosities of the system water + C_2mimAc are compared. In general measurements are in good agreement with literature data [16]-[20]. At lower temperatures and water concentration discrepancies in viscosity are higher probably due to the high hygroscopicity of the ILs used and the difficulty in keeping the water content constant across the measurement procedure. In figure 2, comparison of measured densities of the binary mixture water + C_2mimAc with those of literature are shown. Our data are consistent with those of Quijada et al [16]. Even when literature data were determined at different water concentration ranges, the data exhibit the same tendency than the data of Romich et al [17]. Nevertheless density data of the pure C_2mimAc measured by Froba [20] seems slightly higher value than the other data.

In figure 3, experimental viscosities of the system water + AmimCl are compared to literature data showing important discrepancies. To better compare the data logarithmic scale has been used. At 298 K the data presented in this work are slightly higher than the tendency of the data presented by Wu and co-workers [12]. For other temperatures, the data presented in this work present values one order of magnitude higher than the data measured by Xu et al [13]. In figure 4, densities presented here for water + AmimCl mixtures are compared to the data of Wu and co-workers [12] at 298 K. Both datasets present similar trends, with the exception of Wu's data at x_{H2O}=0 which present a value slightly higher [12].

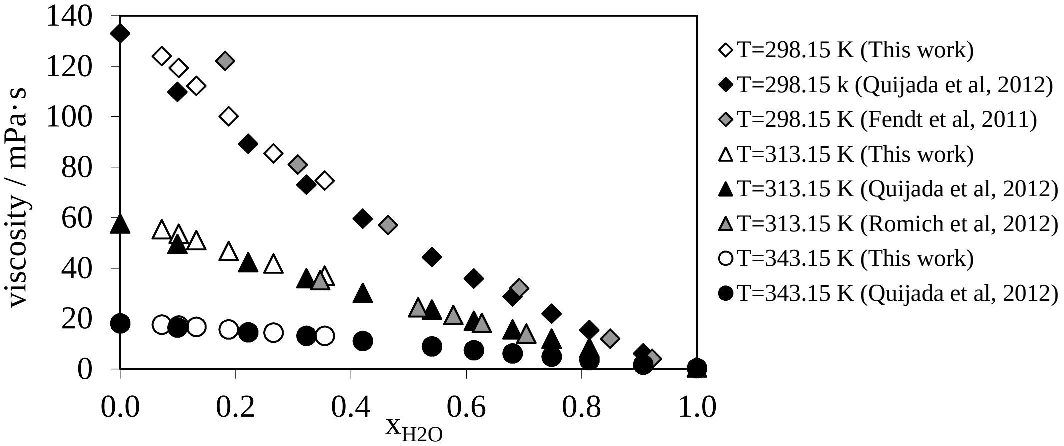


Figure 1. Viscosity of binary mixtures Water + C_2mimAc. Comparison to literature data [16], [17] and [18]

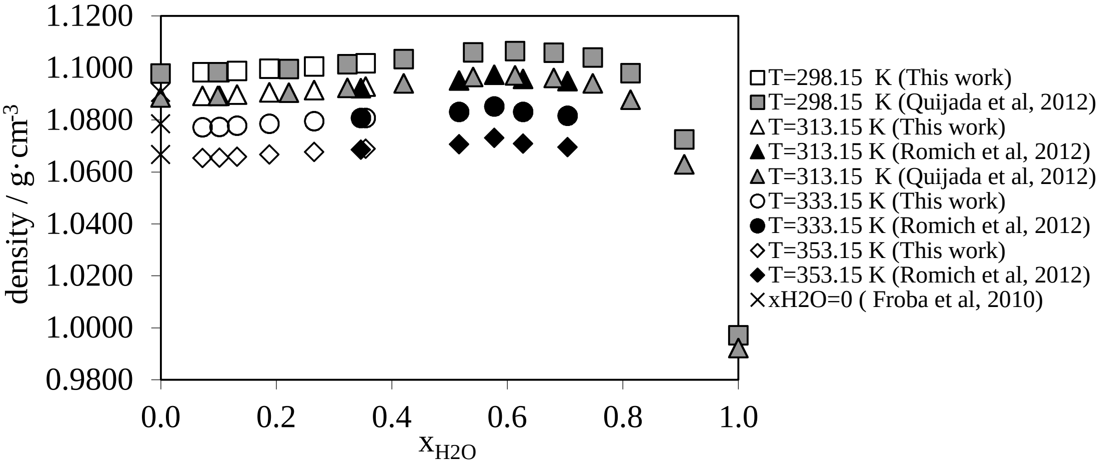


Figure 2. Density of binary mixtures Water + C_2mimAc. Comparison to literature data [16], [17], [20]

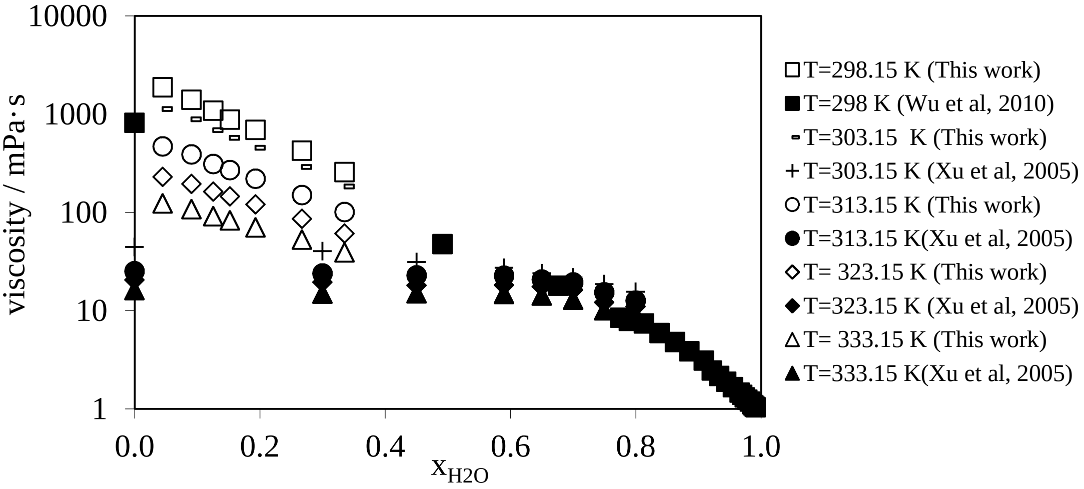


Figure 3. Viscosity of binary mixtures Water + AmimCl. Comparison to literature data [12], [13]

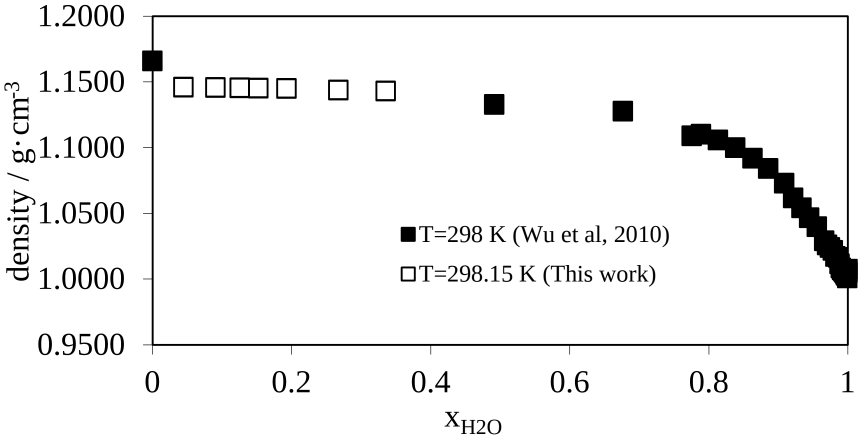


Figure 4. Density of binary mixtures Water + AmimCl. Comparison to literature data [12]

3.1. Excess molar volumes

Excess molar volumes of both water + IL systems were calculated considering the density of the pure ionic liquid as the density measured at the lower water concentration. To cover all the composition range, literature data were used in this calculation [12], [17]. Results are shown in figure 5. It is observed that excess molar volume is decreasing with increasing water concentration for both ILs reaching a minimum for molar fractions of around 0.6-0.7. Excess molar volumes are more negative for C_2mimAc. The influence of the temperature in the excess molar volumes is negligible. Negative molar volumes indicates that when adding water to the ionic liquid the molar volumes of both liquids are not additives, and the components of the mixture are more closely “packed”, and thus the density is higher than the one expected by simple addition of molar volumes. The minimum can be due to hydrogen bonds between water molecules and ionic liquids. At higher concentrations of water excess, molar volumes increase again because of the dissociation of the ions forming the ionic liquids [8].

The results for the AmimCl are consistent with the results obtained by Gomez et al [8] with other alkylimidazolium chloride ILs, C_6 and C_8mimCl, that presents minimum of around -0.6 $cm^3\ mol^{-1}$ at water concentrations of 0.6 but present values slightly positives at high water concentration. For these ionic liquids, influence of the temperature is more important than for the ILs considered in this work.

In the case of C_2mimAc, more negative excess molar volumes were obtained using the data of Romich et al [17] (-1.6 cm^3mol^{-1} at x_{H2O}=0.58) than those obtained by Hall et al [19] (approx -1 cm^3mol^{-1} at x_{H2O}=0.8) for C_2mimAc. Nevertheless, this last work only performs experimental measurements for the pure IL and in the range of water concentrations higher than 0.7. In literature, positive and negative molar volumes have been described. Mokhtarani et al [21] found positive molar volumes for pyridinium based ILs. Rodríguez & Brennecke [22] found negative deviation for C_2mim Ethylsulphate, except at T> 338 K and high water content that were slightly positive and C_2mim Trifluoroacetate and for C_2mim Triflate positive deviations except for T< 288.15 K at high water concentrations that were negative. Qian et al [14] found negative excess volumes up to -1 cm^3mol^{-1} for methanol in mixtures alcohols + mimAc, for methanol, ethanol and 1-propanol and slightly positive for 1-butanol at very low IL concentration. Thus excess molar volumes are larger for alcohols able to form stronger hydrogen bonds with the IL, forming a better packing. Larger excess volumes of H_2O+ C_2mimAc than those of H_2O + AmimCl indicate better packing of water with C_2mimAc. Less negative and positive molar volumes are typical of less hydrophilic or hydrophobic ILs.

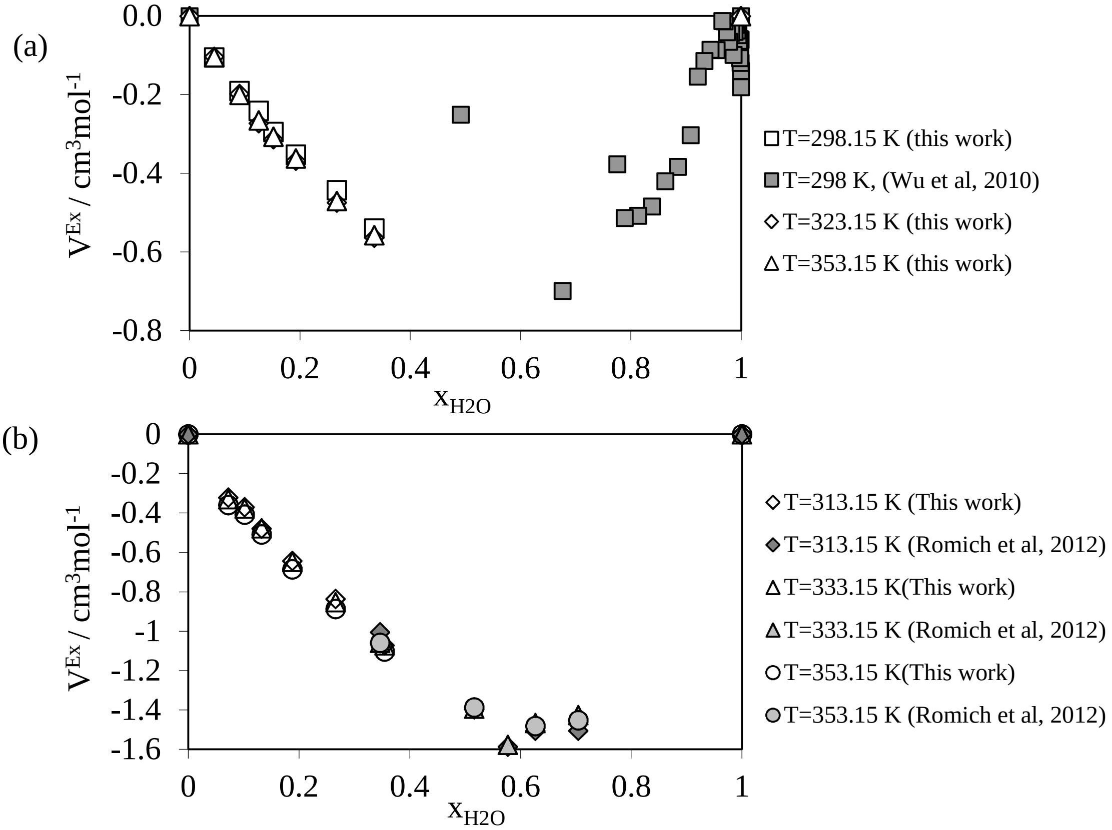


Figure 5. Excess molar volumes of the systems (a) H_2O + AmimCl; (b) H_2O + C_2mimAc calculated using experimental and literature data [12], [17]

3.2. Viscosity correlation

Several equations have been considered in this work to correlate viscosities of the water + ILs mixtures as a function of temperature and water composition. In first place the expression proposed by Seddon et al [4] for a number of molecular solvents + ILs mixtures (presented in eq. 1) was used.

$$\mu = \mu_S \cdot \exp(-x_{CS} / a) \tag{1}$$

Where μ_s is the viscosity of the pure IL, x_{CS} is the molar fraction of the molecular solvent and α is a constant with different values for each IL. This expression was proposed for a constant temperature of 293 K. In this work, the first term was substituted by the well known exponential type equation typical for describing the viscosity dependence with temperature.

$$\mu = \exp(\frac{A}{T(K)} + B) \tag{2}$$

Where μ is the viscosity of the pure IL, T is the temperature in K, and *A* and *B* are constant dependent on the IL. Thus, substituting the eq. 2 into eq. 1, eq. 3 is obtained.

$$\mu = \exp\left(\frac{A}{T(K)} + B\right)\cdot \exp(-x_{H2O}/C) \qquad (3)$$

An addition temperature dependent parameter has been introduced in the equation (3) in order to improve the description of the experimental value, obtaining eq.4:

$$\mu = \exp\left(\frac{A}{T(K)} + B\right)\cdot \exp\left(\frac{x_{H2O}}{C + D\cdot T(K)}\right) \qquad (4)$$

Where *A*, *B*, *C* and *D* are empirical parameters depending on the IL. These parameters have been adjusted by minimization of the objective function presented in eq.4.

$$Obj = \Sigma\left(\frac{\left|\mu_{\exp} - \mu_{calc}\right|}{\mu_{\exp}}\right) \qquad (5)$$

Parameters, as well as values of the objective function are presented in table 6.

Table 6. Parameters fitted to the correlations for calculating the viscosities of the aqueous mixtures of AmimCl and C$_2$mimAc

<table>
<tr><td colspan="5">$\mu = \exp\left(\frac{E}{T^2} + \frac{A}{T} + B\right)\cdot \exp\left(\frac{x_{H2O}}{C + D\cdot T}\right)$</td></tr>
<tr><td colspan="5">Range $x_{H2O}<0.4$</td></tr>
<tr><td>IL</td><td colspan="2">C$_2$mimAc</td><td colspan="2">AmimCl</td></tr>
<tr><td>A</td><td>4192</td><td>-8280</td><td>-15113</td><td>6844</td></tr>
<tr><td>B</td><td>-9.192</td><td>9.540</td><td>17.64</td><td>-15.357</td></tr>
<tr><td>C</td><td>0.973</td><td>2.53</td><td>0.784</td><td>0.367</td></tr>
<tr><td>D</td><td>$-5.22\cdot 10^{-3}$</td><td>$-1.01\cdot 10^{-2}$</td><td>$-3.10\cdot 10^{-3}$</td><td>$-1.76\cdot 10^{-3}$</td></tr>
<tr><td>E</td><td>0</td><td>2063000</td><td>3636000</td><td>0</td></tr>
<tr><td>Av. Dev.</td><td>6.7%</td><td>1.6%</td><td>2.6%</td><td>13%</td></tr>
<tr><td>Max. Dev.</td><td>17%</td><td>7.0%</td><td>10.2%</td><td>33%</td></tr>
<tr><td colspan="5">$\ln\ \mu = x_{IL}\cdot\left(\frac{E}{T^2} + \frac{A}{T} + B\right) + x_{H2O}\cdot \ln\ \mu_{H2O} + \frac{x_{IL}\cdot x_{H2O}}{(x_{IL} + F)}\cdot (B\cdot T + C)$</td></tr>
<tr><td colspan="5">Valid for all the concentration range</td></tr>
<tr><td>IL</td><td colspan="2">C$_2$mimAc</td><td colspan="2">AmimCl</td></tr>
<tr><td>A</td><td colspan="2">-8280</td><td colspan="2">-15113</td></tr>
<tr><td>B</td><td colspan="2">-0.0119</td><td colspan="2">0.0174</td></tr>
<tr><td>C</td><td colspan="2">7.3</td><td colspan="2">-3.51</td></tr>
<tr><td>D</td><td colspan="2">$-1.01\cdot 10^{-2}$</td><td colspan="2">$-3.103\cdot 10^{-3}$</td></tr>
<tr><td>E</td><td colspan="2">2063000</td><td colspan="2">3636000</td></tr>
<tr><td>F</td><td colspan="2">0.1382</td><td colspan="2">0.221</td></tr>
<tr><td>Av. Dev.</td><td colspan="2">3.9%</td><td colspan="2">2.3%</td></tr>
<tr><td>Max. Dev.</td><td colspan="2">33%</td><td colspan="2">7.3%</td></tr>
</table>

With this equation a good description of the viscosity for water concentration up to 40% mol (the range studied in this work) is achieved, nevertheless at higher water concentrations the behaviour is not lineal with water concentration and a more complex equation must be used. For the C_2mimAc the average relative deviation is of viscosity prediction in the range studied were of 6.7%, being the maximum deviation of 17% for T=373.15 K and 35.5% mol H_2O compared to the experimental data presented in this work.

In the case of AmimCl, the better fitting achieved using eq. 4 gives an average relative deviation of 13% and a maximum relative deviation of 33% at T=373.15 K and 33.5% H_2O compared to the experimental data presented in this work. It is observed that large deviations are presented at low and high water concentrations. The predictions obtained are not good. It is due to the deviation from straight line from the ln μ vs 1/T at low water concentrations. To solve this problem a modification was proposed in eq. 4, in such a way that the term describing the ln μ of the “pure” ionic liquid” will consist of a cuadratic expression and not a linear one, obtaining eq. 6, in which an additional parameter E is introduced.

$$\mu = \exp(\frac{E}{T^2} + \frac{A}{T} + B) \cdot \exp\left(\frac{x_{H2O}}{C + D \cdot T}\right) \qquad (6)$$

The equation was fitted to the experimental data presented in this work using the expression presented in eq.5 as objective function. The optimized parameters are presented also in table 6 for both water + IL systems. With the modified equation, prediction of the viscosity could be done with an average relative deviation of 2.6% and a maximum relative deviation of 10.2% corresponding to a T=298.15 K and 26.7% mol H_2O for the system H_2O + AmimCl. For the system H_2O + C_2mimAc the average relative deviation was of 1.6% and a maximum deviation was of 7.0% for 35.4% mol H_2O and 298 K. The predictions together with the experimental data are presented in figures 6 and 7.

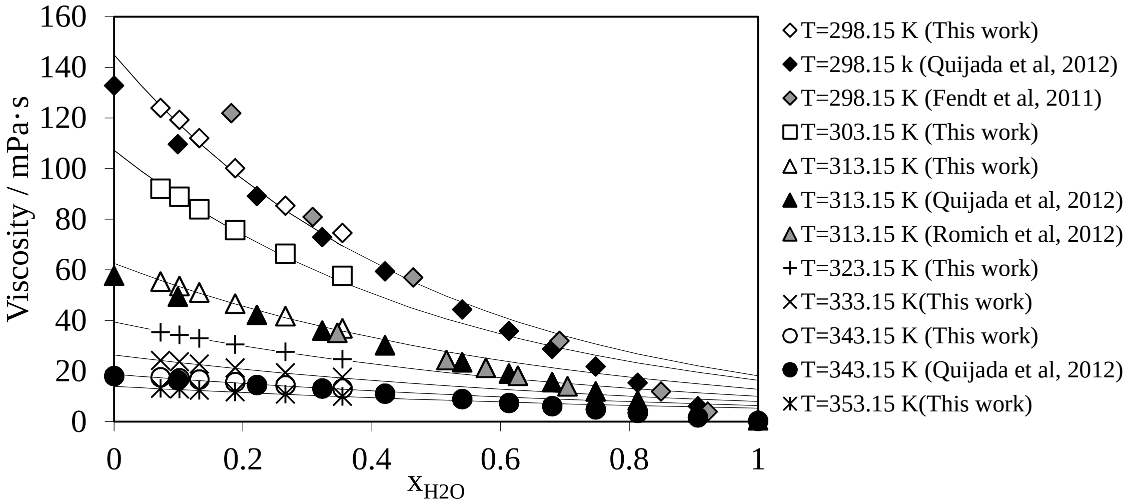


Figure 6. Experimental viscosities of the system H_2O + C_2mimAc (data from this work, Quijada et al [16], Romich et al [17] and Fendt et al [18]) and those calculated with equation 6.

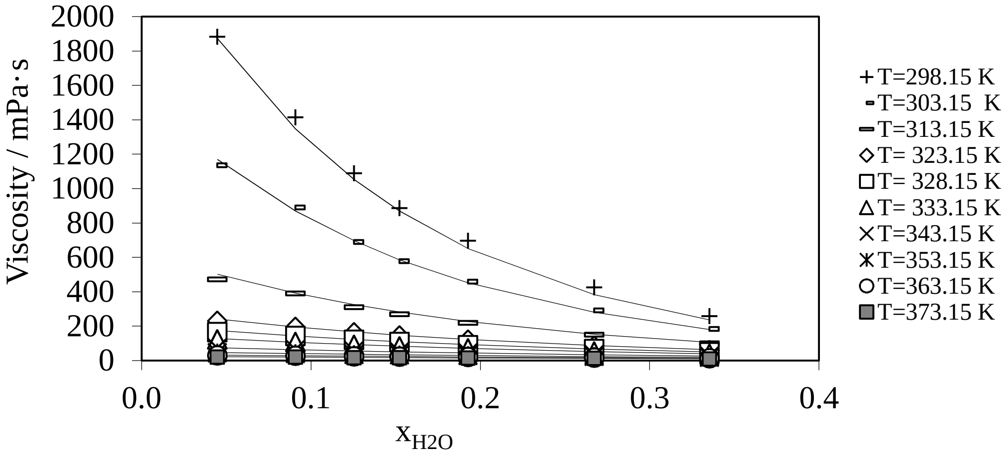


Figure 7. Experimental viscosities of the system H_2O + AmimCl and those calculated with equation 6.

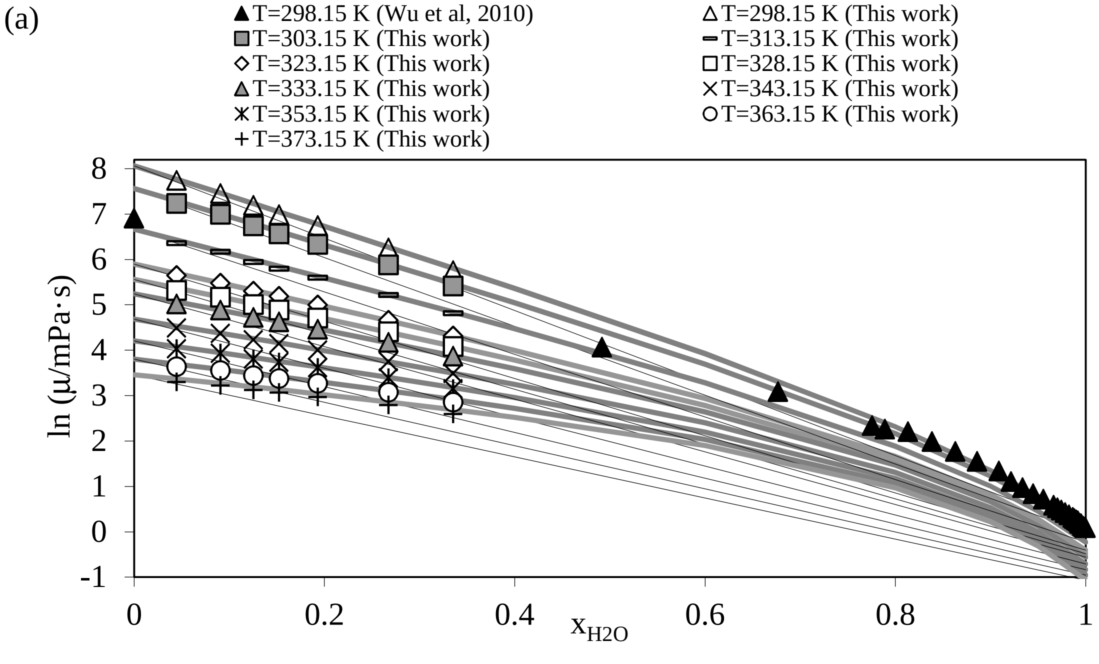
The correlation presented is only valid for water molar fractions lower than 0.4. In figure 6 the whole water concentration range has been represented in order to show that at water molar fractions higher than 0.4 the shape of the predicted curve is very different from the tendency of the experimental data. In an attempt to find an expression to calculate viscosity of the mixture H_2O + IL in the whole range of concentrations, the well known method of Grunberg and Nissan [23], [24] presented for binary mixtures in eq. 7 has been used.

$$\ln \mu = x_{IL} \cdot \ln \mu_{IL} + x_{H2O} \cdot \ln \mu_{H2O} + x_{IL} \cdot x_{H2O} \cdot G_{12} \qquad (7)$$

Where x_{IL} and x_{H2O} are the molar fraction of water and IL, μ_{H2O} and μ_{IL} are the viscosities of the pure compounds and G_{12} a constant parameter. The first part of this equation (shown in eq. 8) is considered as a kind of ideal viscosity by Hall et al [19] for mixtures ILs + water.

$$\ln\ \mu = x_{IL} \cdot \ln\ \mu_{IL} + x_{H2O} \cdot \ln\ \mu_{H2O} \qquad (8)$$

The comparison of ideal viscosities with experimental viscosities in all the concentration range is shown in figure 8 (a) and (b) for aqueous mixtures of AmimCl and C_2mimAc respectively in thin straight lines. Viscosity of the pure ILs C_2mimAc and AmimCl, was calculated with eq. 6 using the parameters from table 6. For the system H_2O + AmimCl, it is observed that at low water concentrations there is a linear relation between ln μ and x_{H2O}, the shape of the curve is curving at high water concentrations. What it is more, the slopes of the experimental data are more different from the ideal ones when the temperature is increasing. In the case of the system H_2O + C_2mimAc, the system is highly non-ideal as it can be observed in figure 8 (b), lnμ vs x_{H2O} is only lineal up x_{H2O} around 0.5, and the slopes are much lower than the ideal ones even at low temperatures.



(b)

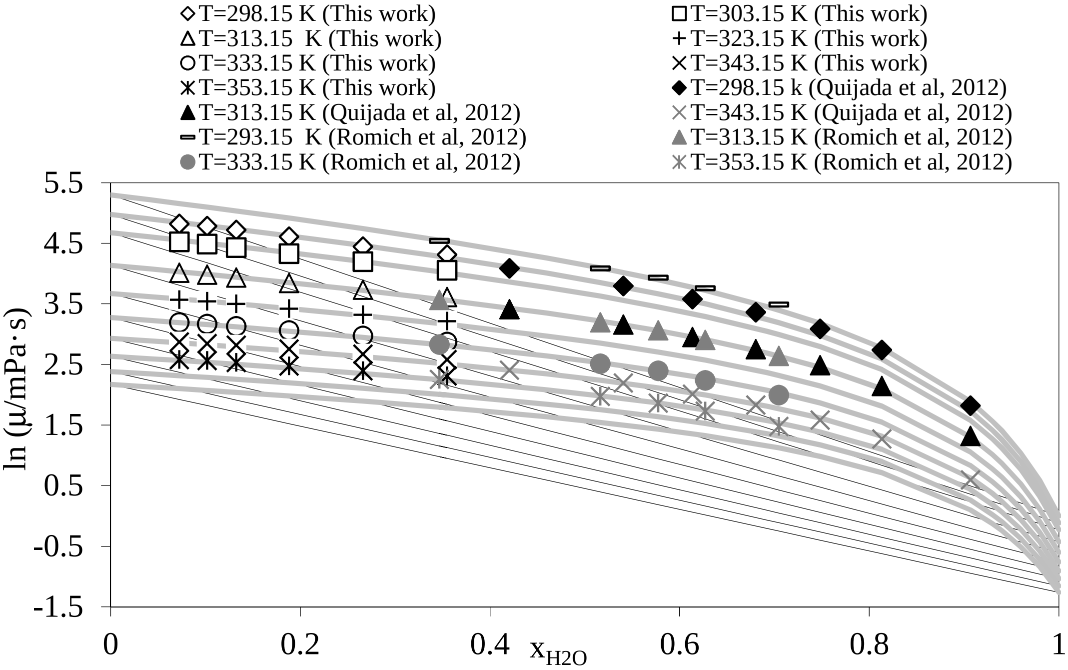


Figure 8. Comparison of the experimental data presented in this work and taken from literature (symbols) [12], [16], [17] with the ideal viscosity for the binary systems (thin straight lines), and the viscosity calculated by the Grunberg and Nissan modified equation (thick grey line): a) H_2O + AmimCl; b) H_2O + C_2mimAc.

Following equation 7, the non-idealities can be described by using a term exclusively dependant of the product of molar fractions of both components, but a good description was not achieved in this way. The deviation from the ideality was highly dependent on water molar fraction and on temperature. Thus, an expression of the type shown in eq. 9 was used to fit the viscosities of water + IL mixture in all the concentration range.

$$\ln \mu = x_{IL} \cdot \left(\frac{E}{T^2} + \frac{A}{T} + B\right) + x_{H2O} \cdot \ln \mu_{H2O} + \frac{x_{IL} \cdot x_{H2O}}{(x_{IL} + F)} \cdot (C \cdot T + D) \qquad (9)$$

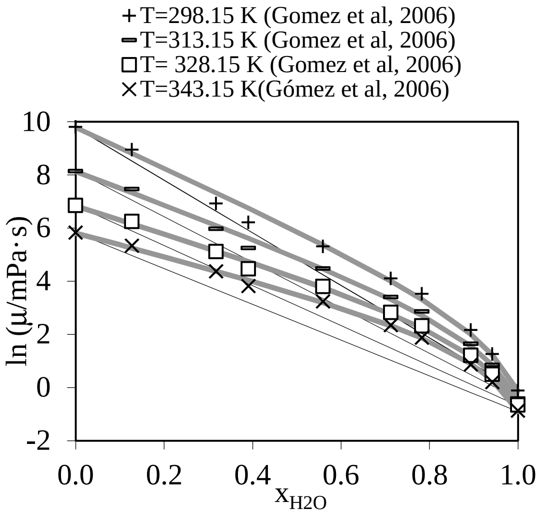
Where *A, B, C, D, E* and *F* are empirical parameters which optimized values are listed in table 7 for both water + IL systems. With this equation a good description of the viscosity as a function of temperature and water molar fraction was achieved for all the water concentration range as it can be observed in figure 8. Equation was calculating with an average relative deviation of 2.3% for the system H_2O + AmimCl being the maximum deviation of 7.3% for 33.5% water at 363 K, while for the system H_2O + C_2mimAc, the average relative deviation with respect the experimental data was of 3.9% and the maximum deviation was of 33% for 74.8% mol H_2O at 333.15 K. For the system H_2O + C_2mimAc, data presented in this work as well as literature data [16], [17] has been used to fit the parameters, while for the system H_2O + AmimCl, only the experimental data presented here have been used to fit the parameters because the other data set were not consistent with our data. Nevertheless in the figure 8 data for the system H_2O + AmimCl, the data of Wu et al [12] were plotted in order to check that the equation is able to follow the tendency of the data at higher water concentrations.

Eq. 6 and 9 were used to correlate the viscosity of aqueous mixtures of alkylimidazolium chloride ILs (C_4mimCl, C_6mimCl and C_8mimCl) and of the system Ethanol + C_2mimAc using literature data [8], [16], [25]. For the ionic liquid C_4mimCl parameters for water concentration lower than 40% mol was not performed because of the lack of consistent data of the system in literature. Viscosities for the pure C_4mimCl were correlated using data from Seddon et al [25]. Optimized parameters as well as maximum and average deviations of these binary systems are shown in table 7.

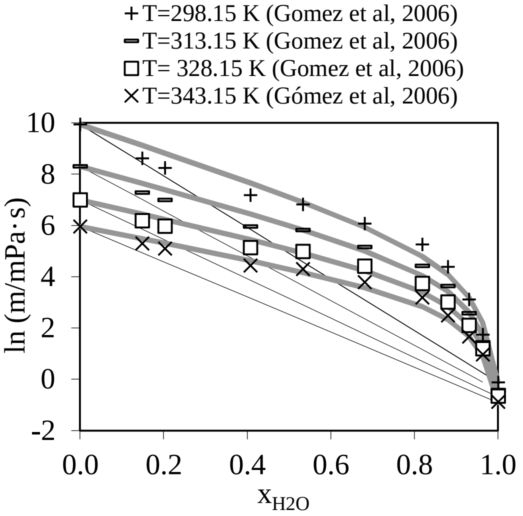
Table 7. Parameters fitted to the correlations for calculating the viscosities of the aqueous mixtures of H_2O + C_4, C_6 and C_8mimCl and Ethanol + C_2mimAc using literature data [8], [16], [25]

<table>
<tr><td colspan="5">$\mu = \exp(\frac{E}{T^2} + \frac{A}{T} + B)\cdot \exp\left(\frac{x_{H2O}}{C + D\cdot T}\right)$</td></tr>
<tr><td></td><td colspan="4">Range $x_{H2O}<0.4$</td></tr>
<tr><td>IL</td><td>H_2O + C_4mimCl</td><td>H_2O + C_6mimCl</td><td>H_2O + C_8mimCl</td><td>Ethanol + C_2mimAc</td></tr>
<tr><td>A</td><td></td><td>-19875</td><td>-16573</td><td>-8277</td></tr>
<tr><td>B</td><td></td><td>24.58</td><td>19.51</td><td>9.54</td></tr>
<tr><td>C</td><td></td><td>0.489</td><td>0.542</td><td>1.053</td></tr>
<tr><td>D</td><td></td><td>$-2.005\cdot 10^{-3}$</td><td>$-2.29\cdot 10^{-3}$</td><td>$-4.35\cdot 10^{-3}$</td></tr>
<tr><td>E</td><td></td><td>4612000</td><td>4091000</td><td>2063000</td></tr>
<tr><td>Av. Dev</td><td></td><td>8.8%</td><td>10%</td><td>2.6%</td></tr>
<tr><td>Max</td><td></td><td>26%</td><td>30%</td><td>10%</td></tr>
<tr><td colspan="5">$\ln\ \mu = x_{IL}\cdot(\frac{E}{T^2} + \frac{A}{T} + B) + x_{H2O}\cdot \ln\ \mu_{H2O} + \frac{x_{IL}\cdot x_{H2O}}{(x_{IL} + F)}\cdot(B\cdot T + C)$</td></tr>
<tr><td colspan="5">Valid for all the concentration range</td></tr>
<tr><td>A</td><td>-11070</td><td>-19875</td><td>-16570</td><td>-8277</td></tr>
<tr><td>B</td><td>10.51</td><td>24.58</td><td>19.51</td><td>9.54</td></tr>
<tr><td>C</td><td>0.00525</td><td>0.001234</td><td>-0.0208</td><td>0.01177</td></tr>
<tr><td>D</td><td>-0.2343</td><td>2.16</td><td>11.02</td><td>-2.06</td></tr>
<tr><td>E</td><td>3246000</td><td>4612000</td><td>4090000</td><td>2063000</td></tr>
<tr><td>F</td><td>0.111</td><td>0.121</td><td>0.0499</td><td>0.372</td></tr>
<tr><td>Av. Dev.</td><td>4.9%</td><td>13%</td><td>23%</td><td>3.4%</td></tr>
<tr><td>Max</td><td>22%</td><td>70%</td><td>76%</td><td>9.4%</td></tr>
</table>

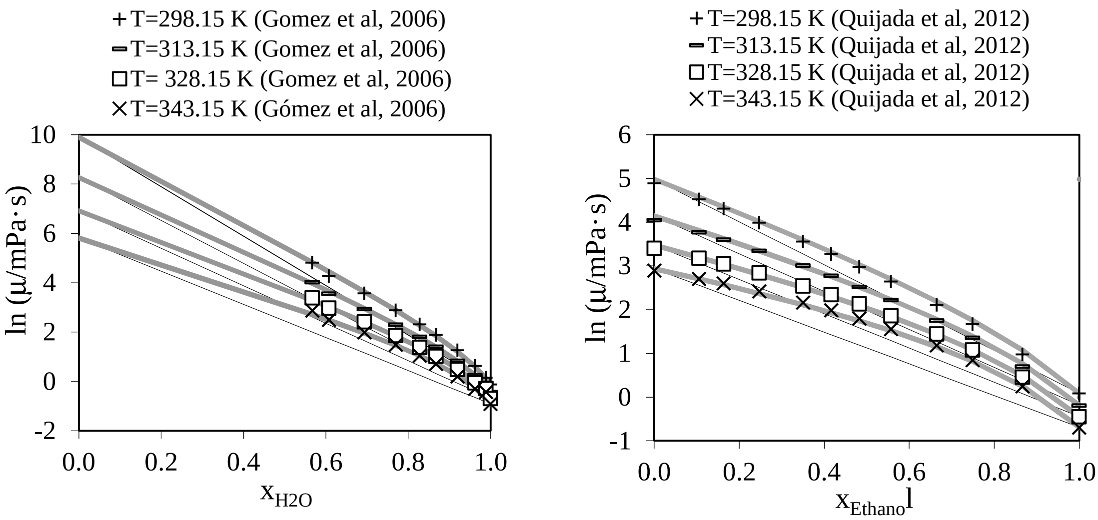
Good description of the viscosity of the mixtures are achieved with average deviations lower than 15% except in the case of the system H_2O + C_8mimCl, where average deviations were as high as 23 %. Thus, the modified equations can satisfactorily represent the viscosities of aqueous systems involving ionic liquids of the 1-alkyl-3-methylimidazolium chloride families and acetate as well as when the co-solvent used is a polar organic solvent such as ethanol. In figure 9 the ideal viscosities as well as the prediction of the modified Grunberg and Nissan equation together with literature data are shown for the above mentioned systems. It is observed that the non-ideality in the viscosity of the mixtures H_2O + $C_n$mim is increasing with higher number of carbon in the alkyl chain (n), as the viscosity of the real system is becoming more different than those indicated by ideal viscosity. In the case of the system Ethanol + C_2mimAc, it can be observed in figure 9 (c) that when ethanol is used as a co-solvent a behaviour more similar to the ideal is obtained and a larger decrease in viscosity for the same molar fraction of co-solvent, compared to the system H_2O + C_2mimAc shown in figure 8 (b).



(a) Viscosity H_2O + C_6mimCl



(b) Viscosity H_2O + C_8mimCl



(c) Viscosity H_2O + C_4mimCl

(d) Viscosity Ethanol + C_2mimAc

Figure 9. Comparison of the literature data [8], [16] (symbols) with the ideal viscosity for the binary systems (thin straight lines), and the viscosity calculated by the Grunberg and Nissan modified equation (thick grey line): a) H_2O + C_6mimCl; b) H_2O + C_8mimCl; c) H_2O + C_4mimCl; d) Ethanol + C_2mimAc.

4. CONCLUSIONS

Densities and viscosities of the systems H_2O + 1-allyl-3-methyilimidazolium chloride and H_2O +1-ethyl-3-methylimidazolium acetate were experimentally determined in the temperature range from 298.15 to 373.15 K and for water molar fractions lower than 0.35.

Viscosities and densities of the system H_2O +1-ethyl-3-methylimidazolium acetate were consistent with existent literature data. Data of the system H_2O + 1-allyl-3-methyilimidazolium chloride, present inconsistencies with the scarce literature data existent.

Excess molar volumes of the mixtures were calculating obtaining negative values, being more negative for the system H_2O +1-ethyl-3-methylimidazolium acetate, what indicates a strongly packed structure attributed to the formation of hydrogen bonds.

Literature equations has been modified in order to correlate the viscosity data a function of temperature and water molar fraction, for both water molar fractions lower than 0.4 and for all the water concentration ranges. Napierian logarithm of viscosities of pure ionic liquids has been correlated as a cuadratic equation instead of the traditional lineal equations. Seddon and Grunberg and Nissan equations were modified to describe the highly no ideal viscosity behaviour as well as the temperature dependence, obtaining an average deviations lower than 15% in the viscosity in most systems considered. The equation has been extended successfully to describe the viscosity of other aqueous imidazolium chloride binary systems as well as to the system ethanol + 1-ethyl-3-methylimidazolium acetate using literature data.

5. REFERENCES

[1] A. Pinkert, K.N. Marsh, S. Pang, M.P. Staiger, Ionic liquids and their interaction with cellulose, Chem. Rev. 109 (2009) 6712–6728.

[2] Y. Lv, J. Wu, J. Zhang, Y. Niu, C. Liu, J. He, J. Zhang, Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions. Polymer, 53 (2012) 2524–2531.

[3] S. Morales-de la Rosa, J. M. Campos-Martín, J. L.G. Fierro, High glucose yields from the hydrolysis of cellulose dissolved in ionic liquids, Chem. Eng. J. 181– 182 (2012) 538– 541.

[4] K.R. Seddon, A. Stark, M.J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem. 72 (2000) 2275–2287.

[5] B. Kumar, T. Singh, K.S. Rao, A. Pal, A. Kumar. Thermodynamic and spectroscopic studies on binary mixtures of imidazolium ionic liquids in ethylene glycol, J. Chem. Thermodyn. 44 (2012) 121-127.

[6] N.V. Sastry, N.M. Vaghela, P.M. Macwan, Densities, excess molar and partial molar volumes for water+ 1-butyl- or, 1-hexyl- or, 1-octyl-3-methylimidazolium halide room temperature ionic liquids at T= (298.15 and 308.15) K , J. Mol. Liq. 180 (2013) 12-18.

[7] M. Tariq, F. Moscoso, F.J. Deive, A. Rodriguez, M.A. Sanromán, J.M.S.S. Esperança, J.N. Canongia Lopes, L.P.N. Rebelo, Probing the self-aggregation of ionic liquids in aqueous solutions using density and speed of sound data. J. Chem. Thermodynamics 59 (2013) 43–48.

[8] E. Gómez, B. González, Á. Domínguez, Emilia Tojo, José Tojo, Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and

Their Binary Mixtures with Water at Several Temperatures, J. Chem. Eng. Data 51 (2006) 696-701.

[9] W. Liu, L. Cheng, Y. Zhang, H. Wang, M. Yu, The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation, J. Mol. Liquids 140 (2008) 68–72.

[10] T. Singh, A. Kumar, Thermodynamics of dilute aqueous solutions of imidazolium based ionic liquids, J. Chem. Thermodynamics 43 (2011) 958–965,

[11] N. Calvar, B.Gonzalez, A.Dominguez, J. Tojo, The physical properties of the ternary mixture ethanol+water+1-butyl-3-methylimidazolium chloride at 298.15 K, J. Solution Chem. 35 (2006) 1217–1225.

[12] D. Wu, B. Wu, Y. M. Zhang, H. P. Wang, Density, Viscosity, Refractive Index and Conductivity of 1-Allyl-3-methylimidazolium Chloride + Water Mixture, J. Chem. Eng. Data, 55 (2010) 621–624.

[13] H. Xu, D. Zhao, P. Xu, Conductivity and viscosity of 1-allyl-3-methylimidazolium chloride+water and+ethanol from 293.15 K to 333.15 K, J. Chem. Eng. Data 50 (2005) 133–135.

[14] W. Qian, Y.J. Xu, H. Zhu, C. Yu, Properties of pure 1-methylimidazolium acetate ionic liquid and its binary mixtures with alcohols, J. Chem. Thermodyn. 49 (2012) 87-94.

[15] J.M.M. Araujo, A.B. Pereiro, F. Alves, I. M. Marrucho, L.P.N. Rebelo, Nucleic acid bases in 1-alkyl-3-methylimidazolium acetate ionic liquids: A thermophysical and ionic conductivity analysis, J. Chem. Thermodyn. 57 (2013) 1-8.

[16] E. Quijada, S.v.d. Boogaart, J.H. Lijbers, G.W. Meindersma, A.B.d. Haan, Experimental densities, dynamic viscosities and surface tensions of the ionic liquids series 1-ethyl-3-methylimizazolium acetate and dicyanamide and their binary and ternary mixtures with water and ethanol at T = (298.15 K to 343.15 K) J. Chem. Thermodyn. 51 (2012) 51-58.

[17] C. Romich, N.C. Merkel, A. Valbonesi, K. Schaber, S. Sauer, T.J.S. Schubert, Thermodynamic Properties of Binary Mixtures of Water and Room-Temperature Ionic Liquids: Vapor Pressures, Heat Capacities, Densities, and Viscosities of Water + 1-Ethyl-3-methylimidazolium Acetate and Water + Diethylmethylammonium Methane Sulfonate, J. Chem. Eng. Data 57 (2012) 2258-2264.

[18] S. Fendt, S. Padmanabhan, H.W. Blanch, J.M. Prausnitz, Viscosities of Acetate or Chloride-Based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents, J. Chem. Eng. Data 56 (2011), 31-34.

[19] C.A. Hall, K. A. Le, C. Rudaz, A. Radhi, C. S. Lovell, R. A. Damion, T. Budtova, M. E. Ries, Macroscopic and Microscopic Study of 1-Ethyl-3-methyl-imidazolium Acetate−Water Mixtures, J. Phys. Chem. B 116 (2012) 12810−12818.

[20] A. P. Fröba, M. H. Rausch, K. Krzeminski, D. Assenbaum, P. Wasserscheid, A. Leipertz, Thermal Conductivity of Ionic Liquids: Measurement, Int J Thermophys 31 (2010) 2059–2077.

[21] B. Mokhtarani, A. Sharifi, H. Reza Mortaheb, M. Mirzaei, M. Mafi, F. Sadeghian, Density and viscosity of pyridinium-based ionic liquids and their binary mixtures with water at several temperatures, J. Chem. Thermodynamics 41 (2009) 323–329.

[21] H. Rodríguez, J.F. Brennecke, Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid, J. Chem. Eng. Data 51 (2006) 2145-2155.

[22] L. Grunberg, A.H. Nissan, Mixture Law for Viscosity, Nature, 164 (1949) 799 - 800.

[23] B.E. Poling, J. M. Prausnitz, J. P. O’Connell, The Properties of Gases and Liquids, 5th Edition, McGraw-Hill, New York, 2004.

[24] K.R. Seddon, A. Stark, M.J. Torres, Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids, ACS Symp. Ser. 819 (2002) 34-49.

Part III. Use of Protic Ionic Liquids for Biomass Processing

Chapter 3.New Protic Ionic Liquid for Cellulose Dissolution under Mild Conditions*

Abstract

A new protic ionic liquid effective for dissolution of cellulose under mild conditions has been developed. This ionic liquid was obtained as room temperature ionic liquid in one-pot procedure by mixing the strong base 1,4-diazabicyclo[4.3.0]non-5-ene and methoxyacetic acid. Itis able to dissolve up to 10 wt% of cellulose at just 40 ºC in 3h with stirring. Degradation neither of the ionic liquid nor cellulose was detected after the dissolution process. Besides this kind of Ionic Liquids can be recovered with a high purity and in a high yield easily by distillation.

** This chapter was done in collaboration with N. Plechkova, H. Q. N. Guaratnate, and K. Seddon from The QUILL Research Centre from The Queen's University of Belfast, Northern Ireland (UK)*

1. INTRODUCTION

Lignocellulosic biomass is a promising source of chemicals and biofuels. Cellulose is the most abundant organic biopolymer on the Earth [1]. It consists of β-(1→4)-linked anhydroglucose units. In addition, cellulose has a highly crystalline structure due to there is many intermolecular hydrogen bond between adjacent cellulose chains. These bonds and the crystalline structure make it insoluble in water and difficult to dissolve in other conventional solvents. Thus, for the processing of lignocellulosic biomass for producing materials, fuels and chemicals highly pollutant or energy intensive processes are currently used. Therefore it is necessary to investigate new solvents for biomass dissolution with some specific characteristics such as good solvation power, low viscosity for promoting the dissolution process due to the higher mobility of the ions and able to reduce the crystallinity of the cellulose during the dissolution process and to be regenerated without neither degradation nor derivation of the biopolymer and involving less energy costs [2].

Ionic liquids are organic salts composed entirely of ions that are liquid at room temperature. They are presented as clean solventsmainly due to their negligible vapour pressure. It is possible to tune their physic-chemical properties such as polarity, viscosity, density and melting point by choosing different cations and anions. In 2002 the use of ionic liquids for the dissolution and regeneration of polysaccharides was re-published [3]. They have produced a lot of interest because they can offer new possibilities for the treatment and functionalization of cellulose in a homogeneous media [4]. Thus, more than 70 process for cellulose processing has been patented from 2005 [5] and more than 60 different ionic liquids have been proved to be able to dissolve cellulose [6], [7].

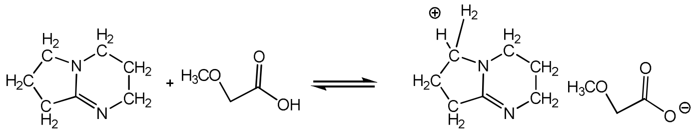
In the dissolution process the influence of the cation in the cellulose solubility is less important than the anion but it cannot be neglected [2]. Chloride, acetate or alkyphosphate anions are the most common in these ionic liquids. Most of the used ionic liquids are based on the extensively used imidazolium and pyridinium cations. 1-alkyl-3-methylimidazolium salts are suggested to be so far the most promising ILs for the modification of cellulose. 1-butyl-3methylimidazolium chloride [bmim][Cl] was able to dissolve up to 25 wt% of cellulose under microwave irradiation [3], but this ionic liquid has some drawbacks such as its high toxicity, non-biodegradability and the necessity of high temperature because of its high melting temperature (80ºC) and viscosity [7]. 1-Ethyl-3-methylimidazolium acetate[emim][Ac], is considered one of the most efficient solvent for cellulose dissolution, it can be defined as non-toxic, non-corrosive and even biodegradable [8] but it is not possible to recover them with a yield higher than 95% [9]. Zhao et al found that the ionic liquid 1-ethyl-3-methylimidazolium propionate has a higher solvation power than acetate, and was able to dissolve up to 18 wt% of cellulose at 100 ºC while [emim][Ac] dissolved 16 wt% [10]. The dissolution of cellulose under mild conditions was already carried out with the ionic liquid N-ethyl-N´-methylimidazoliumdimethylphosphonate ($[C_2mim][(MeO)_2PO_2]$), that is able to dissolve up to 10 wt% of cellulose at 45 ºC in 30 min with stirring [11].

Other not imidazolium not pyridinium based ionic liquids investigated for lignocellulosic biomass treatment were summarized by Wang et al [6]. Quaternary ammonium based ionic liquids such as N,N-dimethylammonium acetate was able to dissolve up to 2 wt% of cellulose at temperatures up to 100 ºC [10].N,N,Ntriethyl-3,6,9-trioxadecylammonium acetate $[Me(OEt)_3Et_3N][Ac]$ and N,N,N-triethyl-3,6-dioxaheptylammonium $[Me(OEt)_2Et_3N][Ac]$ were able to dissolve up to 10 wt% of cellulose at 110 ºC, [12]. The ionic liquid synthetized by Bicak [13], 2-hydroxy ethylammoniumformate, also shows some dissolution ability, and dispersions up to 30% of cellulose content can be prepared but no clear solutions are obtained even when stirred for 24 h. Phosphonium salts like tetrabutylphosphoniumformate $[Bu_4P][Fm]$ were able to dissolve 6 wt% cellulose at 110 ºC.

The purity of the ionic liquid is very important for the dissolution process due to the presence of impurities, such as water or halides affect cellulose solubility. Water has a negative influence in the aggregation of the polymer chains, decreasing the accessibility of the polymer and therefore itsreactivity. If a commercial process for cellulose treatment with ionic liquids wants to be implement it is necessary to make it environmental and economically sustainable. A solvent with a high solvation power, able to dissolve cellulose at low temperatures and with the capacity to be recycled with a high yield and purity needs to be developed.

In this chapter, the processing of biomass in a new kind of ionic liquid is presented. The work of Alistair King et al [9] has been taken as reference. They developed the concept of distillable Acid-Base Conjugate Ionic liquids. These ionic liquids were reported to totally dissolve up to 10 wt% cellulose at 105 ºC during 20 h with recyclability up to 99 % by distillation afterwards. Achinivu et al [14] also demonstrated that some protic ionic liquids, prepare by a facile procedure and that can be recycled easily, were able to extract large amounts of lignin from biomass and later to be recovered as pure PILs with a yield close to 100%.

The new ionic liquid prepared by the conjugation of the strong base 1,5-diazabyciclo[4.3.0]-non-5ene, $C_7H_{12}N_2$, (DBN), with the acid methoxyacetic acid, (MeOAc), with a molar ratio of acid:base 1:1 was studied. It was able to dissolve cellulose under milder conditions, at only 40 ºC in 3h without degradation. The reversible formation of this ionic liquid [dbnH][MeOAc] is presented in scheme 1.



Scheme 1. Reversible formation of [dbnH][MeOAc]

2. EXPERIMENTAL

2.1. Materials

1,4-diazabicyclo[4.3.0]non-5-ene (DBN) (98 % purity), methoxyacetic acid (98 % purity), cellulose acetate, acetic anhydride (>99% purity), phenyl isocyanate (>98% purity) and THF HPLC grade (>99.9 %) were purchased by Sigma Aldrich, methanol (>99.8% purity) was purchased by Panreac and DMSO-d6 was purchased by VWR. All of them were used as received. Powder cellulose with a size of 20 µm was purchased from Sigma Aldrich and it was dried overnight at 70 °C before used.

2.2. Characterization methods

NMR spectra were carried out on a Bruker 400MHz spectrometer at 60 ºC with 16 scans for ^1H NMR and up to 1024 scans for ^{13}C NMR using as external reference, for lock purpose, a capillary with a mixture of DMSO-d6:DMSO (0.9:0.1). The thermogravimetric analysis (TGA) was made with a TGA equipment Q5000 V3.10 Build 258 increasing 10.00 K/min from 273.15 to 773.15K. Differential scanning calorimetry (DSC) was performed in a DSC Q2000 V24.4 Build 116 with scanning rate for both heating and cooling of 10.00 K/min in the temperature range 183.15K to 343.15 K. IR data were recorded in the liquid state on a Perking- Elmer Spectrum 100 FT-IR using 10 scans and a wave number from 450 to 4500 cm

The viscosity of the pure ionic liquid and the solutions of cellulose were measured with Rheological Viscosimeter Bohlin Gemini from 298 K to 385 K at interval of 5 K and the density of the ionic liquid was with a densimeter Metler Toledo DM40 from 293 K to 303 K at interval of 5 K and from 303 K to 363 K at interval of 10 K. Water content of the ionic liquid was determined with Karl Fisher.

GPC analysis were performed in a Waters HPLC IR detector 2414 was used. A Shodex KF – 802.5 column and Shodex KF-G pre-column were used. Pure THF at 1 mL/min was used as mobile phase. The column oven temperature was 30 ºC. Low molecular weight polystyrene 250 to 70000 Da was used as external standard.

2.3. Preparation of the Ionic Liquid

This ionic liquid [dbnH][MeOAc] was easily synthesized by the transfer proton from the acid to the base. The purity of the [dbnH][MeOAc] was determined via NMR analysis. Figure 1 shows the ^{1}H NMR spectra of the neat acid and base and the ionic liquid synthetized.

A big batch of [dbnH][MeOAc] was prepared in a 100 mL round flask by adding 1 equivalent of methoxyacetic acid to neat DBN in two portions. The flask was cool down in ice while the acid was added. The mole ratio acid: base (1:1) was confirmed by analyzing the integrated areas of each peak in the chemical shift. The same batch was used for doing all the dissolution experiments.

2.4. Cellulose Dissolution and Precipitation experiments

All the samples were prepared by adding a known amount of cellulose to 1 g of ionic liquid as shown in table 2. The cellulose dissolved in the ionic liquid was precipitated in a 5-fold amount of MilliQ-water. The solution was centrifuged at 4400 rpm for 10 minutes, the supernatant was recovered and the precipitated cellulose was filtered under vacuum and washed with 200 mL of water. The recovered solid was dried at 70 ºC overnight.

2.5. Cellulose molecular weight determination

Original crystralline powder cellulose, and cellulose recovered from the ionic liquid dbn:methoxyethanoic acid (1:1 and 1:2), [emim][Ac] and [bmim][Cl] were derived into cellulose tricarbanilate using phenyl isocyanate as reagent [18]. 0.005 g of cellulose were swollen by 1 mL DMSO for 10 minutes. Then 0.1 mL of phenyl isocyanate was added to the solution. The reaction was carried out for 24h at 70ºC with stirring. Reaction was stopped and 0.1 mL of dry methanol was added in order to react with the excess of reagent. Cellulose tricarbanilate was precipitated by adding 10-fold amount of a solution of methanol: water of 70 %. Solution was washed 3 times with the methanol solution and 3 times with water. Solid was dried and analysed by GPC. Samples were dissolved in THF in a concentration of 1% wt.

2.6. Cellulose functionalization to obtain cellulose acetate

Functionalization of cellulose with acetate was carried out following Fidale et al procedure [17]. 5 wt% of cellulose was dissolved in [dbnH][MeOAc] at 40 ºC for 3 h at high speed stirring and 4 mol acetic anhydride/mol AGU were added and let react for 24 h at 40ºC. Afterwards cellulose acetate was precipitated by adding 1:5 ml of water and the solid was washed with 200 mL of MilliQ-water, filtered under vacuum and dried at 70 ºC overnight. The DS was determined comparing the IR spectra of pure cellulose triacetate purchases by Sigma and used as standard with the cellulose acetate obtained by first dissolving cellulose in [dbnH][MeOAc]. The DS was obtained by comparing the size of the area of the new peak, at 1737 cm^{-1} corresponding to the group C=O of the acetate group, with the area of the peak of the cellulose acetate provided by Sigma Aldrich with a DS=2.46 (X=0.82) and used as standard , as shown in eq. (1):

$$X = \frac{A_P - A_C}{A_{A.C.} - A_C} \cdot 0.82 \tag{1}$$

$$DS=3 \cdot X \tag{2}$$

Where, A_i is the Area of the FT-IR spectra at 1737 cm-1. The subindex P is referred to the solid product of reaction, C to the cellulose and A.C. to the pure cellulose acetate. X is the reaction conversion. As in each AGU unit there are three OH positions that can be substituted by and Acetyl group the maximum degree of substitution is 3.

3. RESULTS AND DISCUSSION

3.1. Other protic Ionic Liquids synthetized

In order to carry out this research different protic ionic liquids were synthetized. To do so strong and not big bases (although some bases weaker were also tested) were mixed with different acids in a ratio 1:1. Once they were prepared only those that were liquids were taken into account and ^1H NMR was run in order to establish what could be its dissolution capacity. If the proton was shiftedthe dissolution of cellulose was tested, and in some cases also cellobiose and glucose dissolution. Table 1 showed a list with all ionic liquids that were synthetized even when not all of them were successful for our proposal.

Table 1.Description of different protic ionic liquids synthetized. Acidic OH^- proton shift was obtained by ^1H NMR.

BASE (pK_a)	**ACID (pK_a)**	**Acidic OH^- Proton shift**	**Biomass dissolution**
Dimethylethylamine (pK_a=10.16)	Methanoic Acid (pK_a=3.8)	10.9 to 12.7	Cellobiose, Glucose, NOT Cellulose
	Methoxyethanoic acid (pK_a=3.54)	10.6 to 13.4	Cellobiose, Glucose
	Ethanoic Acid (pK_a=4.7)	11.8 to 14.1	Cellobiose, Glucose
	Tartaric acid (pK_a=2.95)	SOLID	Will check in the future
	Citric acid (pK_a=3.14)	SOLID	Will check in the future
Diethylamine (pK_a=11.02)	Methanoic Acid (pK_a=3.8)	10.9 to 10.26	Will check in the future
	Methoxyethanoic acid (pK_a=3.54)	10.6 to 9.4	Will check in the future
	Ethanoic Acid (pK_a=4.7)	SOLID	Will check in the future
Dipropylamine (pK_a=11)	Methanoic Acid (pK_a=3.8)	10.9 to 9.8	Will check in the future
	Methoxyethanoic acid (pK_a=3.54)	SOLID	Will check in the future
	Ethanoic Acid (pK_a=4.7)	SOLID	Will check in the future

Dimethylethanolamine (pK_a=9.23)	Methanoic Acid (pK_a=3.8)	SOLID	Will check in the future
	Methoxyacetic acid (pK_a=3.54)	10.6 to 8.8	NOT cellulose
Imidazole (pK_a=7)	Methanoic Acid (pK_a=3.8)	10.9 to 15.16	Will check in the future
	Methoxyethanoic acid (pK_a=3.54)	SOLID	Will check in the future
	Ethanoic Acid (pK_a=4.7)	11.8 to 14.85	NOT cellulose
1-Methylimidazole (pK_a=6.95)	Methanoic Acid (pK_a=3.8)	10.9 to 15.96	NOT cellulose
	Methoxyethanoic acid (pK_a=3.54)	10.6 to 15.90	Cellobiose
	Ethanoic Acid (pK_a=4.7)	11.8 to 14.92	NOT cellulose
1-Butylimidazole (pK_a=7.09)	Methanoic Acid (pK_a=3.8)	10.9 to 15.96	NOT cellulose
	Methoxyethanoic acid (pK_a=3.54)	10.6 to 14.18	NOT cellulose
	Ethanoic Acid (pK_a=4.7)	11.8 to 14.62	NOT cellulose
Pyridine (pK_a=5.7)	Methanoic Acid (pK_a=3.8)	10.9 to 15.13	NOT cellulose
	Methoxyethanoic acid (pK_a=3.54)	10.6 to 14.03	NOT cellulose
	Ethanoic Acid (pK_a=4.7)	11.8 to 13.35	NOT cellulose
Triethylamine (pK_a=9.99)	Methoxyethanoic acid (pK_a=3.54)	10.6 to 12.76	Cellobiose
Tripropylamine (pK_a=10.65)	Methoxyethanoic acid (pK_a=3.54)	2 phases	Not cellulose
Tributylamine (pK_a=10.89)	Methoxyethanoic acid (pK_a=3.54)	2 phases	Not cellulose

Many experiments were run without success and it was decided to come back and try to improve the distillable acid base of Alistair King [9]. The use of strong bases such as 1,1,3,3-tetramethylguaninide (TMG), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabyciclo[4.3.0]-non-5ene (DBN) was described in two patents, WO2011161326 [15] and WO2008043837 [16], but none of them claimed the dissolution of cellulose at temperatures below 50 ºC. In this work [tmgH][MeOAc] and [dbuH][MeOAc] were also tested. 1,1,3,3-tetramethylguanidinium methoxyacetate was liquid at room temperature, it was very viscous and it was able to dissolve up to 10% cellulose at 60ºC in 5h and at 70ºC in less than 2h. The ionic liquid [dbuH][MeOAc] was also liquid at room temperature, was very viscous and was able of dissolved up to 10%wt of cellulose at 70ªC in 5h.

3.2. *Acid character and Purity of the Ionic liquid*

The acid character of the ionic liquid is very important in the dissolution process of cellulose. In this work, this acidity was determined by running ^{1}H NMR to the neat acid and to the ionic liquid. The ^{1}H NMR plots are shown in figure 1 a) and c) respectively. It is observed that the acidic proton shift from 10.64 ppm in the neat acid form to 11.82 ppm in the ionic liquid.

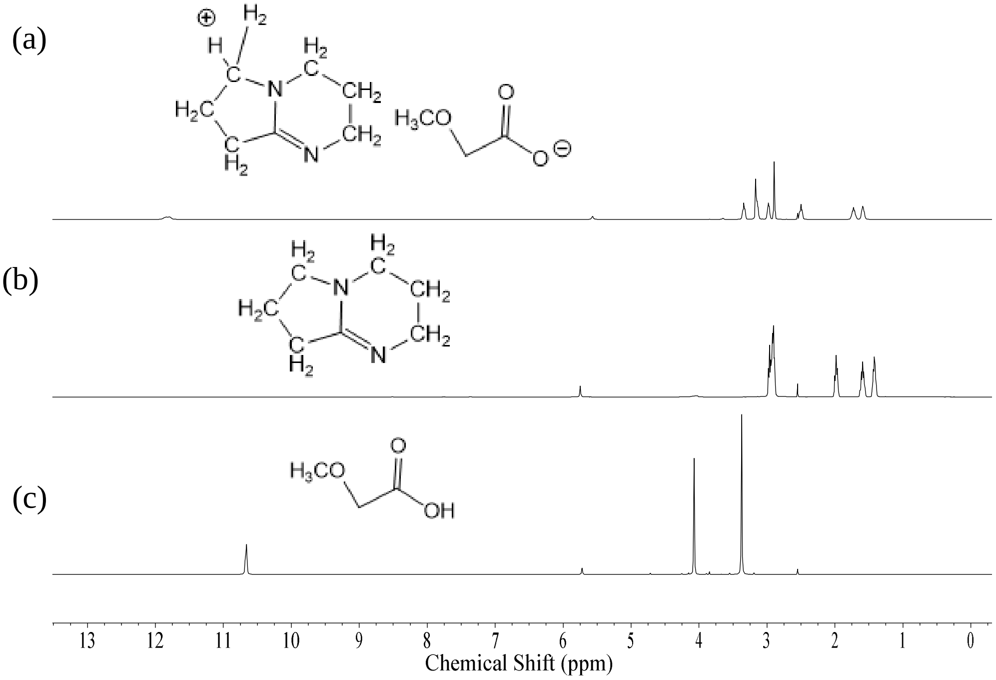


Figure 1.^{1}H-NMR spectra (δ_{solv}=2.5 ppm) of: (a) [dbnH][MeOAc], (b) 1,5-Diazabicyclo(4.3.0)non-5-ene (dbn), (c) methoxyacetic acid (MeOAc)

In addition, the ionic liquid was characterised by proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR), viscosity, density, Fourier transform infrared spectroscopy (FT-IR), TGA and DSC.

The thermal stability of this new ionic liquid, shown in figure 2, is worse than in aprotic ionic liquid, as indicated by the thermogravimetry analysis (TGA) which shows a decomposition temperature at 5% weight loss of 361 K.

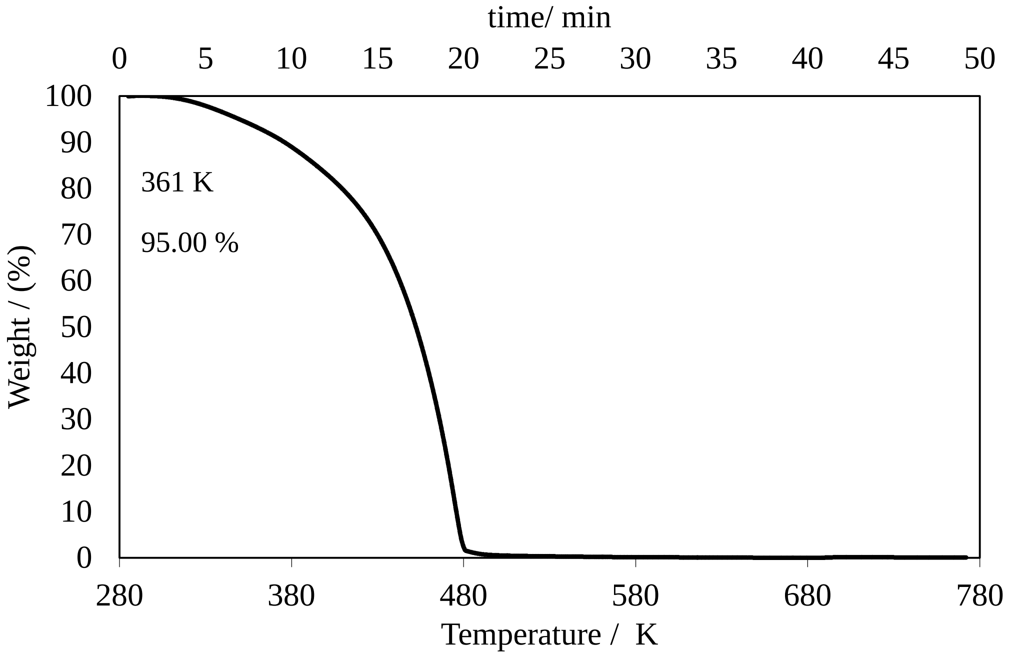


Figure2. TGA Analysis of the ionic liquid

The melting point of the ionic liquid 1,5-diazabyciclo[4.3.0]-non-5ene methoxyacetate [dbnH][MeOAc] (see figure 3), determined by DSC is 304 K. The asymmetry structure of the anion methoxyacetate favours this low melting point.

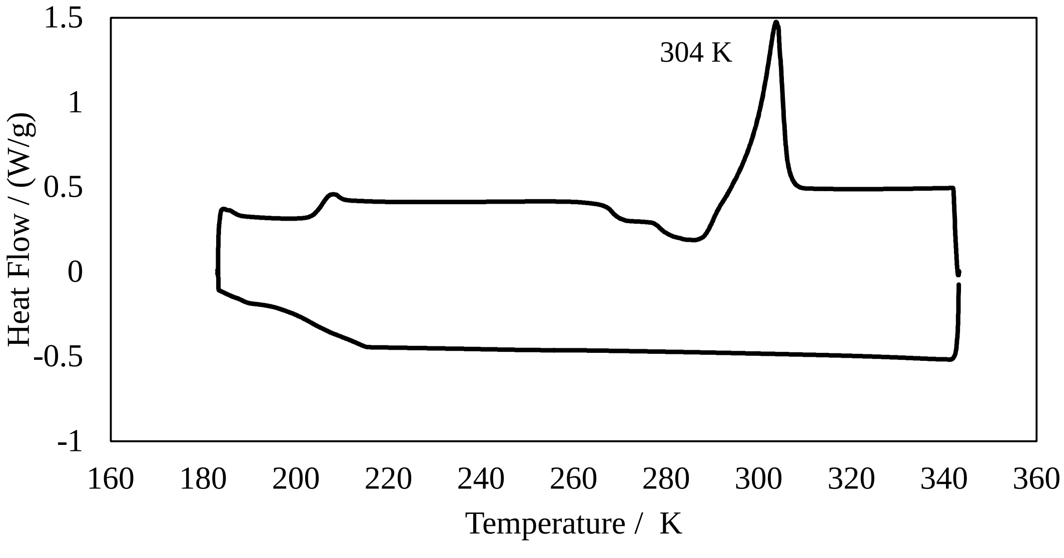


Figure 3. DSC curve of the ionic liquid from -183.15 K till 343.15 K

The water content of the ionic liquid is 0.34 wt%. It was neither dried nor purified. In order to be sure the amount of water in the ionic liquid was constant all the samples were prepared under nitrogen atmosphere.

The viscosityof the ionic liquid at 303.15 K is 189 mPa·s and decreases to 19mP·s at 353.15ºC, values similar to [emim][Ac], 180 mPa·s at 293.15 K and 17 mPa·s at 353.15 K, but much lower than [bmim][Cl] 142 mPa·s at 353.15 K [4], as shown in figure 4. In this way the lower viscosity favours proper stirring of the solution.

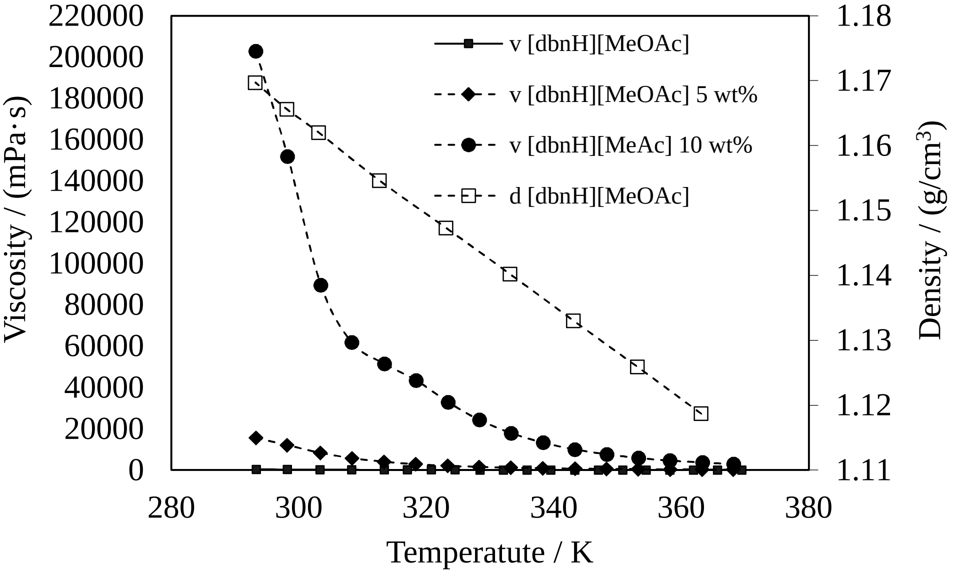


Figure 4. Viscosity (v) and density (d) of the pure [dbnH][MeOAc] and viscosity (v) of solutions of [dbnH][MeOAc]with different concentrations of cellulose disolved

3.3. Dissolution of cellulose in the ionic liquid

Different dissolution experiments are summarized in table 2.

Table 2.Characteristics of the different experiments of solubility.

IL (g)	**Cellulose (g)**	**Cellulose (wt%)**	**Temperature (ºC)**	**Time (h)**	**Observations**
1	0.02	2	40	0.7	Well stirring
1	0.05	5	40	1	Well stirring
1	0.08	8	40	2	As cellulose was dissolved, viscosity increased and it was more difficult to stir the solution
1	0.1	10	40	3	As cellulose was dissolved, viscosity increased and it was more difficult to stir the solution

It was observed that as cellulose is dissolved in the ionic liquid the viscosity of the solution increases, as it is shown in figure 4, and difficult solution stirring.

Ionic liquid with a 2:1 (DBN:MeOAc) molar equivalence mixture were also prepared and a 5 wt% of cellulose was dissolved at 40 ºC in less than 1h. The molar ratio 1:2 (DBN:MeOAc) was not good for cellulose dissolution. Figure 5 shows a comparative study of the ^{1}H-NMR spectra of the pure ionic liquid prepared with a molar ratio of 1:1 (DBN:MeOAc) and the spectra of a 5 wt% cellulose in the ionic liquid prepared with a 2:1 (DBN:MeOAc) molar ratio and there are some changes in the proton shift.

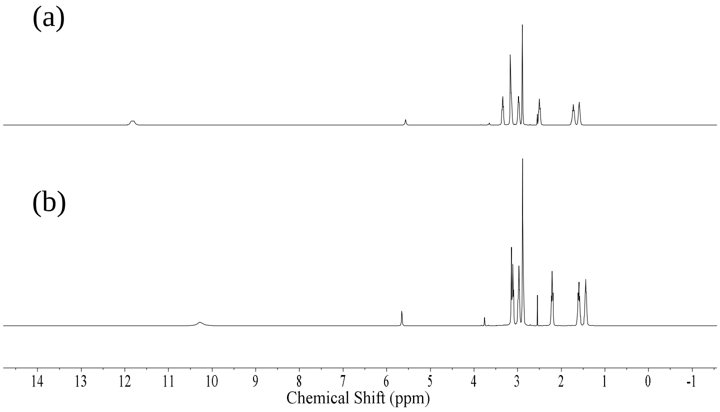


*Figure 5.^{1}H-NMR spectra (δ_{solv}=**2.5** ppm) of: (a) [dbnH][MeOAc] 1:1, (b) [dbnH][MeOAc] 2:1 with 5 wt% dissolved cellulose.*

In order to know if the ionic liquid suffers some decomposition during the dissolution process ^{1}H and ^{13}C NMR were carried out to the pure ionic liquid and to the ionic liquid with cellulose dissolved. Figures 6 and 7 show the spectra for neat ionic liquid and ionic liquid with 2 wt% cellulose dissolved and there was not any change in the spectrums. In both, chemical shift and integration peak ratio are in concordance**.** There is only a different in the broad of the peak that is produced for the interactions between the ionic liquid and the cellulose.

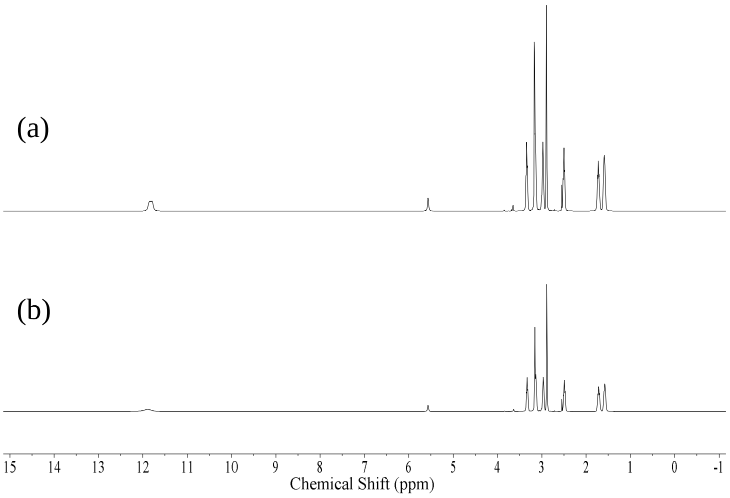


Figure 6.^{1}*H-NMR spectra (*δ_{solv}*=**2.5** ppm) of: (a) pure [dbnH][MeOAc], (b) [dbnH][MeOAc] with 2 wt% dissolved cellulose.*

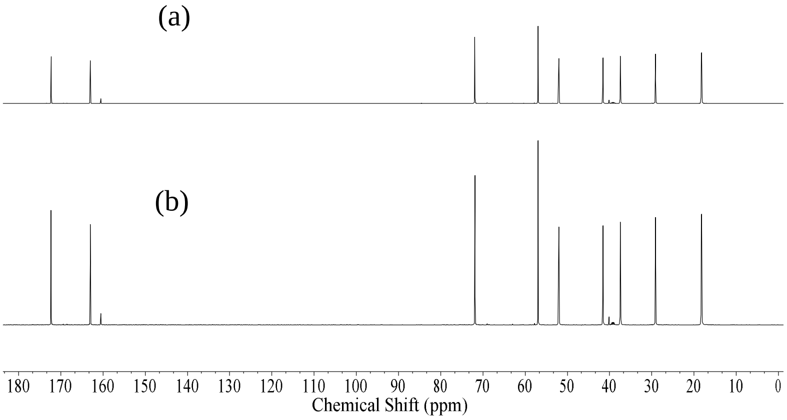
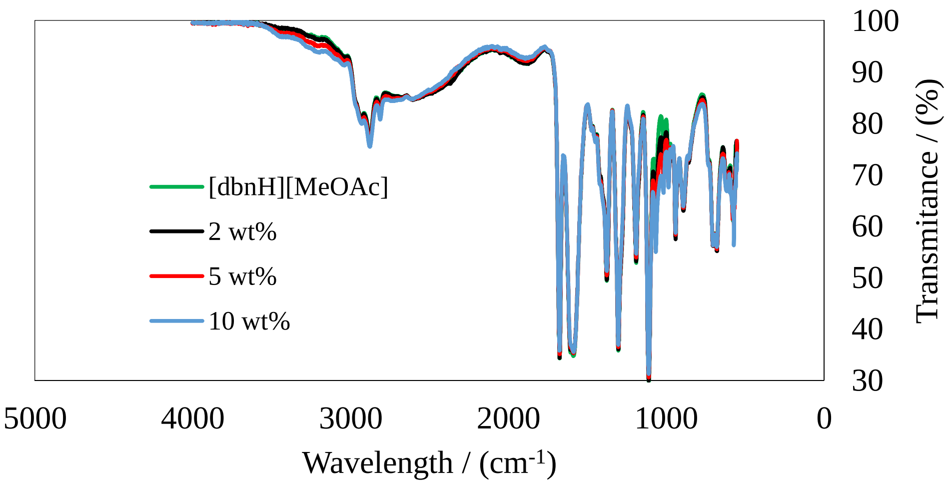


Figure 7.^{13}*C-NMR spectra (*δ_{solv}*=39.52 ppm) of: (a) pure [dbnH][MeOAc], (b) [dbnH][MeOAc] with 2 wt% dissolved cellulose.*

Cellulose dissolution process was followed by IR, analysing samples of different amounts of dissolved cellulose in the ionic liquid. In figure 8 the evolution in the range of the IR spectra between 3400-3200 ppm, where the peak of the OH is detected, is presented. When the amount of dissolved cellulose increases the transmittance decreases showing and increment of the OH presented in the dissolution.



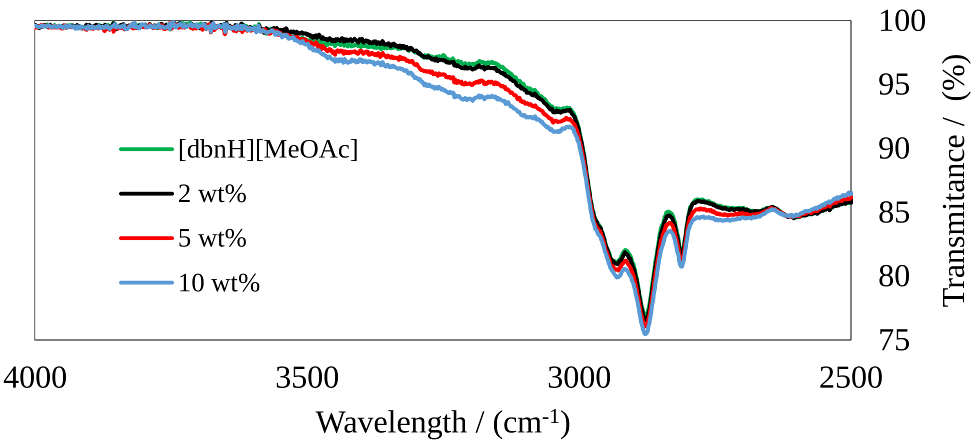


Figure 8. IR spectra of the ionic liquid [dbnH][MeOAc] pure and with different amounts of dissolved cellulose.

Cellulose dissolution was also followed visually. Figure 9 presents different photographs of the pure ionic liquid with dispersed cellulose and with the completely dissolution of cellulose is achieved.

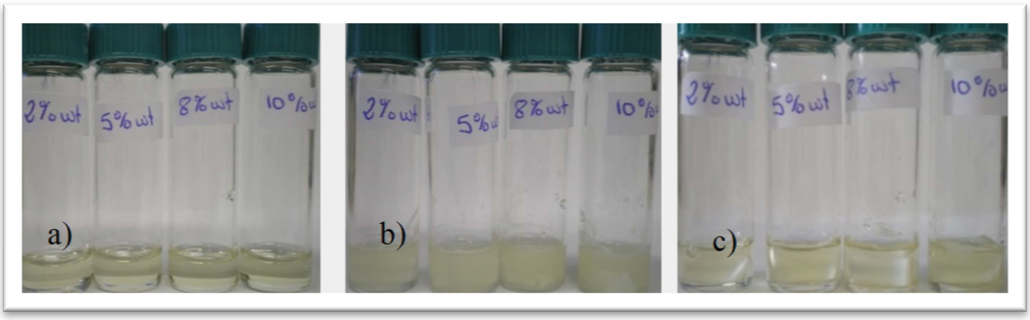


Figure 9.a) Pure ionic liquid [dbnH][MeOAc], b) Ionic Liquid with different concentrations of dispersed cellulose after 10 minutes of dissolution, c) different concentrations of dissolved cellulose in [dbnH][MeOAc]

IR spectra of the recovered precipitated cellulose and the original microcrystalline cellulose were recorded in order to compare. These spectra are shown in figure 10 and the peaks of both samples seem to be the same.

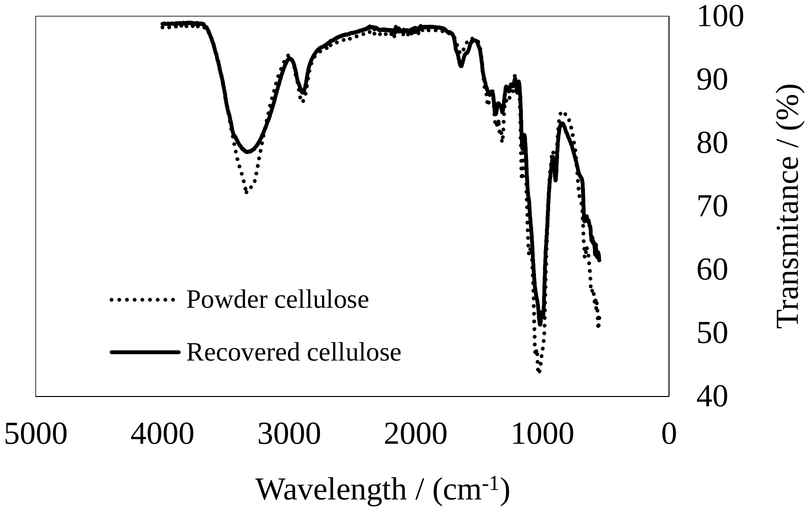


Figure10. IR analysis of the microcrystalline cellulose purchases by Sigma Aldrich, and the recovered cellulose after been dissolved in [dbnH][MeOAc]

The effect of the dissolution process in the molecular weight of the cellulose was also studied. The results are summarized in table 3.

Table 3. GPC data from pure powder cellulose and from cellulose recovery after being dissolved in the ionic liquids [dbnH][MeOAc], [emim][Ac] and [bmim][Cl].

Sample	**Elution Volume**	**MP**
Pure cellulose	6.053	77387
[dbnH][MeOAc]	6.057	76361
[bmim][Cl]	6.061	75568
[emim][Ac]	6.061	75492

The molecular weight of precipitated cellulose slightly decreases in all the cases and these decreases are not significant. According to the analysis performed this dissolution process does not cause any important change in cellulose structure.

3.4. Functionalization of cellulose to obtain cellulose acetate

Cellulose acetate with a degree of substitution (DS) of 1.89 at 40ºC in 24 h reaction timewas reached. These spectra of the obtained cellulose acetate and the commercial one are represented in figure 11 where it can be distinguished that the peak of the OH coming from the cellulose disappear and a new peak from the functional group C=O of the cellulose acetate at 1737 cm^{-1}appear.

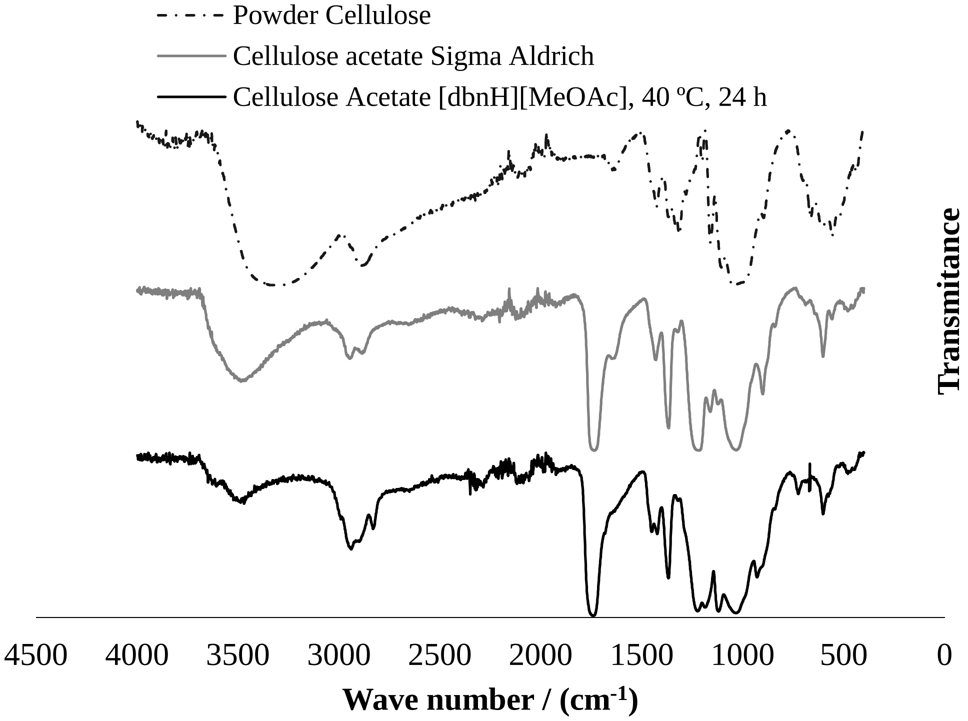


Figure 11.IR of the powder cellulose, cellulose acetate purchased by Sigma Adrich and the cellulose acetate obtained in the homogeneous media [dbnH][MeOH] (24h, 40 ºC, 4 mol acetic anhydride/mol AGU)

4. CONCLUSIONS

A new protic ionic liquid [dbnH][MeOAc] for the processing of cellulose was developed. The main advantages of these kind of ILs is their easy recyclability by distillation and subsequent mixing of the components without further purification making the final process more economical and sustainable. This ionic liquid improves the performance of other ionic liquid in cellulose processing due to it is possible to dissolve cellulose under mild conditions, up to 10 %wt at 40 ºC in 3 h, cellulose can be recovered in a high yield without molecular changes and it is also possible to carry out acetylation reactions.

5. REFERENCES

[1] D. Klemm, B. Heublein, H.-P. Fink, A. Bohn,Cellulose: fascinating biopolymerand sustainable raw material, Angewandte Chemie International Edition 44 (2005) 3358–3393.

[2] A. Pinkert, K.N. Marsh, S. Pang, Reflections on the solubility of cellulose, Industrial & Engineering Chemistry Research, 49 (2010) 11121-11130.

[3] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of Cellose with Ionic Liquids, Journal of the American Chemical Society J Am Chem Soc. 124 (2002) 4974-4975.

[4] M. Gericke, P. Fardim, T. Heinze, Ionic liquids-promising but challenging solvents for homogeneous derivatization of cellulose, Molecules 17 (2012) 7458-7502.

[5] C. Jiménez, A. Navarrete, M.D. Bermejo, M. J. Cocero, Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids Recent Patents on Engineering 6 (2012) 159 – 181.

[6] H. Wang, G. Gurau, R. D. Rogers,Ionic liquid processing of cellulose, Chem. Soc. Rev.41 (2012) 1519-1537.

[7] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: Recent progress from knowledge to applications, Applied Catalysis A: General 373 (2010) 1-56

[8] M. Zavrel, D. Bross, M. Funke, J. Büchs, High-throughput screening for ionic liquids dissolving (ligno-)cellulose.A. C- Spiess, Bioresource Tecnology 100 (2009) 2580-2587.

[9] A.W.T. King, J. Asikkala, I. Mutikainen, P. Järvi, I. Kilpeläinen, Distillable Acid–Base Conjugate Ionic Liquids for Cellulose Dissolution and Processing, Angewandte Chemie International Edition, 50 (2011) 6301-6305.

[10] B. Zhao, L. Greiner, W. Leitner, Cellulose solubilities in carboxylate-based ionic liquids RSC Adv. 2 (2012) 2476-2479.

[11] Y. Fukaya, K. Hayashi, M. Wada, H. Ohno, Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions, Green Chem. 10 (2008) 44-46.

[12] H. Zhao, G. A. Baker, Z. Song, O. Olubajo, T. Crittle, D. Peters, Designing enzyme-compatible ionic liquids that can dissolve carbohydrates, Green Chem. 10 (2008) 696-705.

[13] N. Bicak, A new ionic liquid: 2-hydroxy ethylammonium formateJournal of Molecular Liquids 116 (2005) 15-18.

[14] E. Achinivu, R. Howard, G. Li, H. Gracz, W. Henderson, Lignin extraction from biomass with protic ionic liquids Green Chemistry 16 (2014) 1114-1119.

[15] A.W.T. King, I. Kilpeläinen, Method of dissolving lignocellulosic materials (2011) Patent WO2011161326.

[16] L.S. Giovanni D'Andola, K.Massonne, V. Stegmann, Ionic liquids for solubilizing polymers, (2008) Patent WO 2008043837.

[17] L.C. Fidale, S. Possidonio, O. A. El Seoud, Application of 1-allyl-3-(1-butyl)imidazolium chloride in the synthesis of cellulose esters: properties of the ionic liquid, and comparison with other solvents Macromol. Biosci. 9 (2009) 813-821

[18] R. Evans, R.H. Wearne, A.F.A. Wallis, Molecular weight distribution of cellulose as its tricarbanilate by high performance size exclusion chromatography, Journal of Applied Polymer Science 37 (1989) 3291-3303.

Part IV. Analysis of the influence of CO_2 as a co-solvent for viscosity reduction in cellulose processing using [bmim][Cl]

Chapter 4. Properties of [bmim][Cl]. Densities, viscosities and phase equilibria.

Abstract

In this work a summaryof some properties of the ionic liquidmainly used in this work, 1-butyl-3-methylimidazolium chloride [bmim][Cl], are presented: density, viscosity, melting point, and CO_2 solubility. Density and viscosity were experimentally determined at different temperatures and atmospheric pressure, compared to literature data and correlated. Density and viscosity decreased with temperature as happens with all the ionic liquid found in literature. Data of the solubility of CO_2 in [bmim][Cl] were collected from literature. It was also found that the Skjold-Jørgensen Group Contribution EoS has available parameters for the characteristic group of this ionic liquid.

1. INTRODUCTION

Since Swatlosky et al [1] took up the use of Ionic Liquids (ILs) for cellulose dissolution,and found that 1-butyl-3-methylimidazoliumchloride [bmim][Cl] was able to dissolve up to 25% cellulose, the properties of [bmim][Cl] has been widely studied. It has been chosen in this study due to it is one of the most viscous ionic liquids using for processing cellulose. In the NIST Ionic Liquids DataBase [2] there are plenty of experimental data of pure [bmim][Cl] and mixtures containing this ionic liquid. In table 1 the viscosity of [bmim][Cl] and other ILs are compared and even at 5 ºC higher than the other ILs, viscosity of [bmim][Cl] is 10 times higher.

Table 1. Viscosities at room temperature of four ILs widely used for cellulose processing

IL	Temperature / K	Viscosity / mPa·s	Reference
[emim][Ac]	298.15	124	This work
[emim][DEP]	298.15	321	Normazlan et al (2014) [3]
[amim][Cl]	298.15	1884	This work
[bmim][Cl]	303.15	11000	Seddon (2002) [4]

As it has been already said, this IL is very viscous and besides it has a high melting point. Some normal melting point data [5-10] are shown in table 2.

Table 2. Melting Point of [bmim][Cl]

Reference	Temperature/ K
Wilkes at al (1982) [5]	340.1 ± 2.0
Domanska, Mazurowka (2004) [6]	341.9 ± 0.5
Guan et al (2006) [7]	340.1 ± 2.0
Alves et al (2010) [8]	338.1 ± 1.0
Morais et al (2013) [9]	341.9 ± 1.6
Kick et al (2013) [10]	342.9 ± 0.5

To the best of my knowledge the only available data of CO_2 solubilty in [bmim][Cl] or in any other ionic liquid (IL) of the imidazolium chloride family were determined by Jang et al. (2010) [11]. In this work the authors investigated the solubility of carbon dioxide in [bmim][Cl] with a variable volume cell in a temperature range from 353.15

to 373.15K and at pressure up to 40MPa, and they predicted solubility lower than 30% molar. Using these data Lopes et al [12] adjusted parameters for using the the Group Contribution Equation of State (GC-EoS) of Skjold-Jørgensen for predicting CO_2 solubility in imidazolium chloride ionic liquids as well as phase equilibria of imidazolium chloride ionic liquids with other substances.

In this chapter a compilation of different properties of the [bmim][Cl] necessary for the realization of this thesis has been carried out. To do so a bibliographical search was performed. In addition, densities up to 383.15 K and viscosities up to 373.15 K of [bmim][Cl] were experimentally determined.

2. MATERIALS AND METHODS

2.1. Materials

For density and viscosity measurement [bmim][Cl] with a purity of 95% was purchased by Sigma Aldrich and it was dried at 95 ºC for 48h in a vacuum heater before use.
Water content of IL was determined by Karl-Fischer titration using a Mettler Toledo C20 coulometric KF titrator.

2.2. Viscosity and Density determination

An Anton Paar (model SVM 3000) automated rotational Stabinger viscometer-densimeter was used to measure density and viscosity of [bmim][Cl] in a wide temperature range up to 373.15 K at atmospheric pressure. The SVM 3000 Stabinger viscometer has a cylindrical geometry, and it is based on a modified Couette principle with a rapidly rotating outer tube and an inner measuring bob that rotates more slowly. The SVM 3000 apparatus also has a density measuring cell that employs the oscillating U-tube principle. Both density and viscosity cells are filled in one cycle, and the measurements are carried out simultaneously. With this apparatus measurements can be done from 233.15 to 373.15 K in a viscosity range from 0.2 mPa·s to 20,000 mPa·s and in a density range from 0.65 $g\cdot cm^{-3}$ to 2 $g\cdot cm^{-3}$. The temperature uncertainty is ± 0.02 K from (278.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35

%, and the standard uncertainty of the density is ± 0.0005 $g\cdot cm^{-3}$. Every measure at each temperature was made in triplicate.

Densitity of [bmim][Cl] at temperatures higher than 373.15 K were measured using a vibrant tube Anton Paar DMA 602. Measured parameters were T, P (atmospheric) and τ (period of vibration). The basis of a vibrating tube densimeter is that the resonance frequency of a body immersed in a fluid depends on its density. The vibrating tube densimeter is a device consisting mainly of a thin "U" tube filled with the liquid which density we want to determine. The tube is surrounded by mineral oil bath, Julabo F 25, whose purpose is merely to keep constant its temperature. A Pt100 temperature meter is placed in the curved part of the "U" (where the resonance frequency is precisely measured) and a temperature controller, Julabo HE, integrated in the above mentioned thermal bath keeps the temperature constant. To determine the density of the ionic liquid is necessary to measure the response of the equipment in two different conditions, density of air and decane were measured and used as standard.

Calculation of Uncertainty

In this work, the calibration method for the vibrating tube densimeter developed by Lagouretteet al [13] and modified by Comuñas et al [14] was used. In this method, the density of one fluid depends on the oscillation period as is described in equation (1):

$$\rho(T,P) = A(T)\tau^2(T,P) - B(T,P) \qquad (1)$$

Where A and B are calibration constants that are calculated with equations (2) and (3), respectively, and it is necessary to get two sets of data, in our case air (compound 1) and decane (compound 2), a fluid of known density, to determine the characteristic parameters of the apparatus.

$$A = \frac{\rho_1 - \rho_2}{\tau_1^2 - \tau_2^2} \qquad (2)$$

$$B = \tau_1^2 \frac{\rho_1 - \rho_2}{\tau_1^2 - \tau_2^2} - \rho_1 \qquad (3)$$

Equations of uncertainty of the vibrating tube densimeter can be calculated from Segovia et al [15] due to it follows the law of propagation of uncertainty described in JCGM 100: 2008 [16]. Density of air and decane are obtained from the program

REFPROP from NIST [17] and these values have an associated uncertainty u(ρ), which depends on uncertainty of REFPROP and uncertainty of temperature.

The uncertainty of the Stabinger densimeter - viscometer measurements was provided by the apparatus.

3. RESULTS AND DISCUSSION

3.1. Densities

Densities of the same IL from the same batch were measured two following days with Anton Paar (model SVM 3000) Stabinger densimeter-viscometer in order to check its reproducibility and if the measured are affected by water content. In both cases water content was measured with KF before and after carrying out the measurement. All data are shown in table 3.

During the measurement of the first day the amount of water practically did not increase after the measurement,$x_{H2O\_initial}$=1758 ppm and $x_{H2O\ \_final}$=1763.8 ppm. But the second day the amount of water increased after the measurements were carried out:$x_{\_H2O\ initial}$= 1689.5 ppm and x_{H2O_final}= 3855.77 ppm. At observed in table 2 both measurements were very similar, thus the water increase in the sample was thought to produce during the extraction of the sample from the Stabinger.

Table 3. Experimental measure of density of [bmim][Cl] at different temperatures at atmospheric pressure with the Stabinger. Temperature uncertainty 0.02 K. Standard uncertainty of the density is ± 0.0005 g·cm $^{-3}$

Specific density/ g/cm^3		
Temperature/ K	**Day 1**	**Day 2**
373.15	1.0407	1.0418
363.15	1.0459	1.0473
353.15	1.0511	1.0530
343.15	1.0565	1.0589
333.15	1.0621	
323.15	1.0678	
318.15	1.0706	
313.15	1.0734	
308.15	1.0762	

Results of density measurement using the vibrating tube densimeter are presented in table 4. It is observed that, at common temperatures, measurements are consistent with those made using the Stabinger.

Table 4. Experimental measure of density of [bmim][Cl] at different temperatures at Atmospheric Pressure with the vibrating tube densimeter. Temperature uncertainty is 0.02 K.

Temperature/ K	**Specific density/ g/cm^3**
	VibrantTube
383.15	1.0354± 0.0098
373.15	1.0410 ± 0.0098
363.15	1.0462 ± 0.0085
353.15	1.0522 ± 0.0098

Figure 1shows the experimental data compared to bibliography data. Experimental data obtained in this work are similar to other authors' data: Mc Dowell et al [18], Machida et al [19], He at al [20] and Huddleston et al [21]. The measurements of Govinda et al [22] and Kavitha et al [23] substantially differ from our data. Differences could be attributed to differences on the amount of water, which significantly decrease the density of [bmim][Cl] [24].

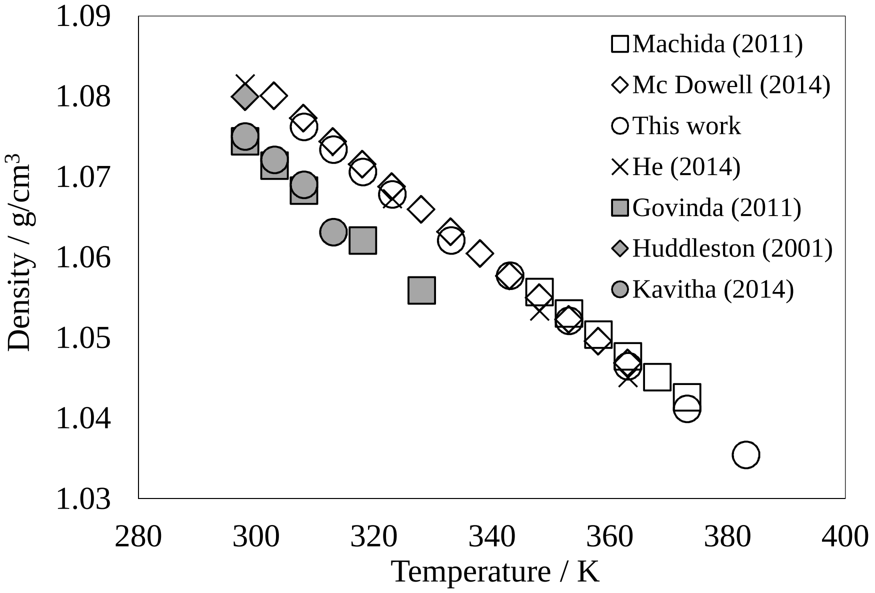


Figure 1. Comparison of experimental density of [bmim][Cl] obtained in this work and bibliography data.

3.2. Viscosity

Viscosities of [bmim][Cl] obtained from Stabinger viscometer at temperatures from 308.15 up to 373.15 K are summarized in table 5.

Table 5. Viscosity of pure [bmim][Cl] measured with an Stabinger densimeter-viscometer at atmospheric pressure and up to 373.15 K. Temperature uncertainty 0.02 K.

T/K	**μ/ mPa·s**
373.15	56.71 ±0.2
363.15	88.98 ±0.31
353.15	149.16 ± 0.52
343.15	270.07± 0.95
333.15	536.78 ± 1.88

T/ K	**μ/ mPa·s**
323.15	1194.80 ± 4.18
318.15	1873.67 ± 6.56
313.15	3052.43 ± 10.68
308.15	5194.23 ± 18.18

As it is shown in figure 2, our data are consistent with the data obtained by Seddon et al [4] and at high temperatures withdata from Fendt et al [25]. As it happened with density values, results from Govinda et al [22] and Kavitha et al [23] were not in consonance with our results, and again it is attributed to the content of water that can affect significantly the viscosity in this IL [24].

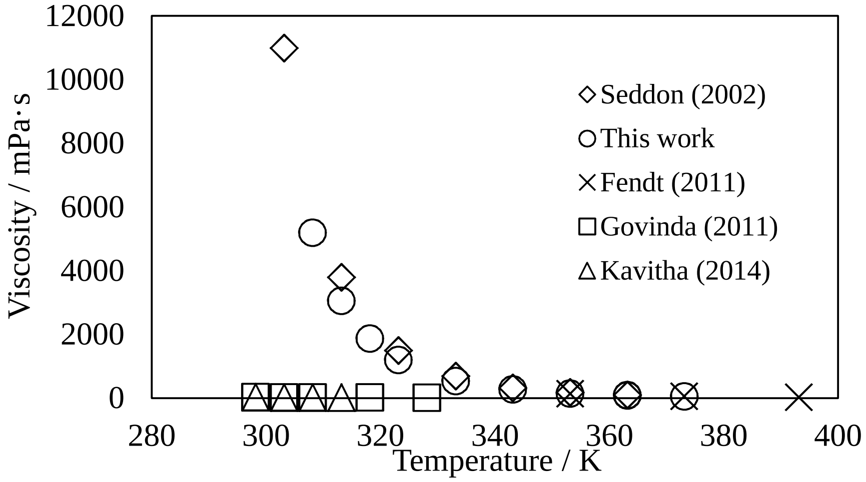


Figure 2. Comparison of viscosity of [bmim][Cl] obtained in this work using a Stabinger viscosimeter-densimeter and bibliography data.

3.3.Solubility of CO_2 in [bmim][Cl]

The solubility of [bmim][Cl] measured by Jang et al [12] and that predicted by the GC EoS are plotted and compared in Figure 3.

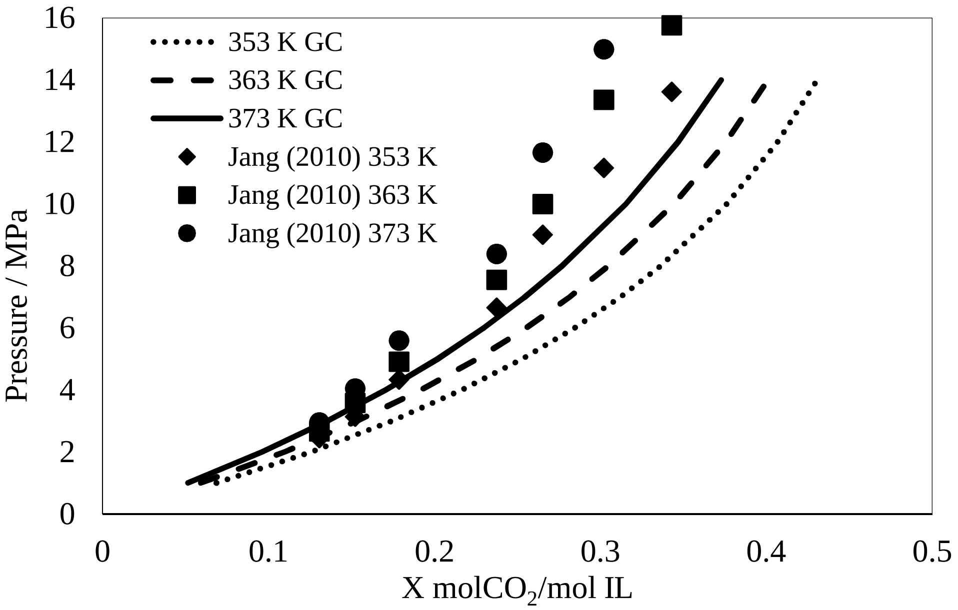


Figure 3. Comparison of solubilities of [bmim][Cl] at 353 K, 363 K and 373 K of our experimental data and data from Jang et al [3] and data obtained by the group contribution correlation adjusted by Lopes et al [12]

The solubility of CO_2in [bmim][Cl] is lower than in other Ionic Liquids. These data would be used in Chapter 5.

4. CONCLUSIONS

Main properties of [bmim][Cl] were compiled and presented. The melting point of this ionic liquid is around 340.8 K and CO_2 has a solubility up to 40.6 % mol at 373.15 K and 36.94 MPa.

Densities and viscosities of pure [bmim][Cl] were experimentally determined. Density and viscosity decrease with increasing temperature as expected and the determined values are consistent with most literature data. Viscosity varies from 5194 mPa·s at 308.15 K to 56.7 mPa·s at 373.15 K and density from 1.0762 g/cm^3 at 308.15K and 1.0354 g/cm^3 at 383.15K.

5. REFERENCES

[1] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of Cellose with Ionic Liquids, J Am Chem Soc. 124 (2002) 4974-4975.

[2] Ionic Liquids Database - ILThermo (v2.0) http://ilthermo.boulder.nist.gov/ (Last accessed 19th August 2016).

[3] W.M.D.W. Normazlan, N.A. Sairi, Y. Alias, A.F. Udaiyappan, A. Jouyban, M. Khoubnasabjafari, Composition and Temperature Dependence of Density, Surface Tension, and Viscosity of EMIM DEP/MMIM DMP + Water + 1-Propanol/2-Propanol Ternary Mixtures and Their Mathematical Representation Using the Jouyban Acree Model, J. Chem. Eng. Data 59(2014) 2337-2348.

[4] K.R Seddon, A. Stark, M.J. Torres, Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids, ACS Symp. Ser., 819 (2002) 34-49.

[5] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis, Inorg. Chem. 21 (1982) 1263-1264.

[6] U. Domanska, L. Mazurowska, Solubility of 1,3-dialkylimidazolium chloride or hexafluorophosphate or methylsulfonate in organic solvents: effect of the anions on solubility, Fluid Phase Equilib. 221 (2004) 73-82.

[7] W. Guan, J.Z. Yang, L. Li, H. Wang, Q.G. Zhang, Thermo-chemical properties of aqueous solution containing ionic liquids 1. The heat of reaction mixed 1-methyl-3-butylimidazolium chloride with InCl3, Fluid Phase Equilib. 239(2006) 161-165.

[8] M.B. Alves, A.P. Umpierre, V.O.J. Santos, V.C.D. Soares, J. Dupont, J.C. Rubim, P.A.Z. Suarez, Characterization of phase-diagrams of ionic mixtures of 1-n-butyl-3-methylimidazolium chloride and niobium chloride or zinc chloride by differential scanning calorimetry,Thermochim. Acta 502 (2010) 20-23.

[9] A.R.C Morais, A.M.d.C.Lopes, E. Bogel-Lukasik, R. Bogel-Lukasik, Ionic Liquids Cation and Anion Influence on Aromatic Amine Solubility, Ind. Eng. Chem. Res. 52(2013) 14722-14726.

[10] M. Kick, P. Keil, A. Konig, Solid liquid phase diagram of the two Ionic Liquids EMIMCl and BMIMCl, Fluid Phase Equilib. 338 (2013) 172-178.

[11] S. Jang, D.W. Cho, T. Im, H. Kim, High-pressure phase behavior of CO_2 and 1-butyl 3-methylimidazolium chloride system, Fluid Phase Equilibria 299 (2010) 216-221.

[12] J.M. Lopes, S. Kareth, M.D. Bermejo, A. Martín, E. Weidner, M.J. Cocero, Experimental determination of viscosities and densities of mixtures carbon dioxide + 1-allyl-3-methylimidazolium chloride. Viscosity correlation, J Supercrit Fluids 111 (2016) 91-96.

[13] B. Lagourette, C. Boned, H. Saint-Guirons, P. Xans, H. Zhou, Densimeter calibration method versus temperature and pressure, Measurements Science Technologie, (1992) 699-703.

[14] M.J.P. Comuñas, J.P. Bazice, A. Baylaucq, C. Boned, Density of Diethyl Adipate using a New Vibrating Tube Densimeter from (293.15 to 403.15) K and up to 140 MPa. Calibration and Measurements, Journal of Chemical Engineering Data, 53 (2008) 986-994.

[15] J.J. Segovia, O. Fandiño, E.R. López, Martín, M.C. Martín, J. Fernandez, Automated densimetric system: Measurements and uncertainties for compressed fluids,J. Chem. Thermodynamics, 41 (2009) 632-638.

[16] Joint Committee for Guides in Metrology (JCGM), Evaluation of measurement data - Guide to the expression of uncertainty in mesurements, 2008.

[17] E.W. Lemmon, M.L. Huber, M.O. McLinden, NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, 2013.

[18] N. Mac Dowell, F. Llovell, N. Sun, J.P. Hallett, A. George, P.A. Hunt, T. Welton, B.A. Simmons, L.F. Vega,. New Experimental Density Data and Soft-SAFT Models of Alkylimidazolium ($[CnC1im]^+$) Chloride (Cl^-), Methylsulfate ($[MeSO_4]^-$), and Dimethylphosphate ([Me2PO4]-) Based Ionic Liquids, J. Phys. Chem. B, 118 (2014) 6206-6221.

[19] H. Machida, R. Taguchi, Y. Sato, R.L. Smith Jr., Pressure Densities of Ionic Liquids, 1-Ethyl-3-methylimidazolium l-Lactate ([emim][Lactate]), 2-Hydroxyethyl-trimethylammonium l-Lactate ([(C2H4OH)(CH3)3N][Lactate]), and 1-Butyl-3-methylimidazolium Chloride ([bmim][Cl]), J. Chem. Eng. Data, 56(2011) 923-928.

[20] R.H. He, B.W. Long, Y.Z. Lu, H. Meng, C.X. Li, Solubility of Hydrogen Chloride in Three 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids in the Pressure Range (0 to 100) kPa and Temperature Range (298.15 to 363.15) K, J. Chem. Eng. Data, 57 (2011) 2936-2941.

[21] J.G Huddleston, A.E. Visser, W. M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, Green Chem., 3 (2001), 156-164.

[22] V. Govinda, P. Attri, P. Venkatesu, P. Venkateswarlu, Thermophysical properties of dimethylsulfoxide with ionic liquids at various temperatures Fluid Phase Equilib., 304 (2011) 35-43.

[23] T. Kavitha, T. Vasantha, P. Venkatesu, R.S.R. Devi, T. Hofman, Thermophysical properties for the mixed solvents of N-methyl-2-pyrrolidone with some of the imidazolium-based ionic liquids, J. Mol. Liq., 198 (2014) 11-20.

[24] V. S. Nandhibatla, M. V. Nilesh, M. M. Pradip, Densities, excess molar and partial molar volumes for water + 1-butyl- or, 1-hexyl- or, 1-octyl-3-methylimidazolium halide room temperature ionic liquids at T = (298.15 and 308.15) K, J. Mol. Liq., 180 (2013) 12–18.

[25] S. Fendt, S. Padmanabhan, H.W. Blanch, J.M. Prausnitz, Viscosities of Acetate or Chloride-Based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents, J. Chem. Eng. Data, 56 (2011) 31-34.

Chapter 5. Analysis of the influence of CO_2 use as a co-solvent for viscosity reduction in cellulose processing using [bmim][Cl]

Abstract

In this chapter the use of CO_2 as a co-solvent for viscosity reduction in biomass processing using ionic liquids is analyzed. To do so, the ionic liquid selected was the 1-butyl-3-methylimidazolium chloride [bmim][Cl]. This ionic liquid has been widely applied for biomass processing due to its high solubility but present the inconvenient of its high viscosity and melting point.

The processes for cellulose processing considered in this chapter were: hydrolysis and synthesis of cellulose acetate.

In first place it was proved that CO_2 was not causing cellulose precipitation of cellulose, by keeping a cellulose solution of [bmim][Cl] under CO_2 atmosphere for several days without observing cellulose precipitation.

No difference was found in hydrolysis with and without CO_2 atmosphere. This can be explained because in the hydrolysis process water is used as a reagent and the reduction of viscosity caused by water is higher than that caused by CO_2. Nevertheless at pressures of CO_2 higher than 40 bar a reduction in the hydrolysis yield was observed.

The production of cellulose acetate is highly decreased when performed under CO_2 atmosphere. It was hypothesised that part of the acetylating reagent (acetic anhydride) could be in the CO_2 phase. Because, under the P-T conditions used, it presents a solubility of 70% in mol in CO_2 phase. Nevertheless there are not data available of the influence of [bmim][Cl] in this equilibrium. When experiments in a volume variable cell were performed in order to completely dissolve the CO_2 phase in the ionic liquid phase the cellulose conversion to acetate was even lower. The preliminary experiments performed this work are not sufficient to explain the reason why the CO_2 is decreasing conversion in this reaction.

1. INTRODUCTION

Due to the depletion of fossil fuels, cellulose and some other polysaccharides are used as renewable sources of valuable chemicals and energy. Cellulose is the most abundant natural source of organic carbon. But its current industrial use is reduced due to that it is not possible to treat cellulose using classical solvents. Thus, ionic liquids (ILs) able to dissolve cellulose and other biopolymers became an alternative for cellulose treatment since 2002, when Swatlosky et al took the use of ionic liquid for cellulose dissolution up [1].

This discovery has opened new perspectives for cellulose valorization: cellulose processing pretreatments before a fermentation or enzymatic process [2], [3], hydrolysis to produce biofuels and chemicals [4] or production of biopolymers derived from cellulose such as cellulose acetate [5]-[8].

For all these processes the high viscosity of the ionic liquids has become a challenge. What it is more, when the biopolymer is dissolved into it, viscosity of the mixture increases and even non-newtonian behaviours were observed [9]. It is known that the use of molecular co-solvents can highly reduce viscosity of ionic liquids [10], [11]. In the case of cellulose processing caution must be taken that the co-solvent is not producing the precipitation of the biopolymer. The most frequently used co-solvents in cellulose processing with ionic liquids are dimethylsulfoxide (DMSO) and dimethylformamide (DMF) [9], [12]-[14].

In this work the use of CO_2 as a co-solvent for viscosity reduction of IL media is proposed. CO_2 is an inert gas without environmental limitations that can be dissolved in ILs in concentrations as high as 70-80% in mol under moderate pressures [15]-[17]. It is known that it is able to reduce the melting points [18]-[22] as well as the viscosity of the ionic liquids [23]-[26]. Even when cellulose is dissolved into it the viscosity can be reduced as much as 80% at 80ºC in the case of [bmim][Ac] [25]. In most cases, ionic liquid cannot be dissolved in CO_2 [27]-[29]. Thus, after the process, CO_2 could be easily separated of the ionic liquid and recovered by depressurization.

1-butyl-3-methylimidazolium chloride [bmim][Cl] is a very viscous IL able to dissolve up to 25% of cellulose [1]. It is known that CO_2 at 150 bar can decrease the melting point of [bmim][Cl] in 10ºC, much less than in the case of other ionic liquids [19]. The recent measurements of melting point depression induced by CO_2 performed by Lopes et al [22] confirmed that for this family of ILs the melting point depression induced by

CO_2 was of the order the magnitude of 10ºC under 100 bar of CO_2. Lopes et al [26] also observed 60-100% viscosity reduction with respect the viscosity of the pure ionic liquid when it is mixture with CO_2 molar fractions up to around 0.5 mol. What it is more, Qi et al proved that the viscosity reduction induced by molecular solvents, included sc-CO_2 can improve the transformation of fructose to 5-hydroximethylfurfural [30].

There is a lot of literature data of cellulose dissolving in ILs. In general it is a slow process [1], [31]-[32]. FitzPatrick et al [33] studied the effect of low pressures of CO_2 which produces an increment up to 75% in the dissolution of up to 4% of cellulose in [emim][Ac]. Iguchi et al [25] observed that CO_2 can be added to solutions with up to 1.2% cellulose in [bmim][Ac], without producing the precipitation of cellulose. On the other hand, other authors have observed that CO_2 can precipitate the cellulose dissolved in [emim][Ac] from concentrations of 5-6% wt to 10% wt due to the formation of the zwitterion compound 1-butyl-3-methylimidazolium-2-carboxylate. In this case a bond between the acetate anion and the CO_2 that breaks the bonds between cellulose and IL is formed and produces its precipitation [34]- [35].

Acidic hydrolysis in IL has been widely studied obtaining good results [2], [4], [37]-[40]. It has been proved that the use of ILs increase the acid hydrolysis yield and selectivity. For example De la Rosa et al [37] concluded that a very high selectivity to glucose + cellobiose can be obtained by this method. Bian et al [39] suggested that pretreatment led to effective disruption of useful cellulose for subsequent enzyme hydrolysis as evidenced by high glucose conversion yield of 95.2 %, that is an increase in glucose content from 80-83.3% to 91.6-92.8 % and a decrease in the degree of polymerization from 974 to 511. This is due to that the IL pretreatment produces an increase in the surface area accessible to water and cellulases. Amarasekara et al [41] demonstrated that Brönsted acidic ionic liquids are effective in dissolution and hydrolysis of cellulose under mild reaction temperatures in a single operation without any pretreatment. Rinaldi et al [42] proposed cellulose hydrolysis by use of acid resins such as Amberlyst 15 DRY in [bmim][Cl] obtaining glucose as the major product.

The functionalization of cellulose for producing other high value products has been thoroughly studied for different authors and many patents have been developed [43]. In literature there are a number of examples of production of cellulose ester and ethers in ILs [5]- [8]. In special a lot of data exist on the production of cellulose acetate, mainly in [bmim][Cl] and other imidazolium ILs with chloride anions [5], [8], [44], [45]-[50]. It is known that reaction can be completed with a degree of substitution of 2.5-3 in a time between 2-8 h at temperatures of 80-110ºC depending on the IL, the acetylation reagent and its excess. Authors as Ignatyev et al [49] combined hydrolysis and acetylation processes for synthesizing glucose ester obtaining the high yield when the hydrolysis was carried out using a ratio IL:Cellulose:acid catalyst 1:0.05:0.001 in mass.

In this work, the influence of CO_2 in several cellulose processing reactions is going to be experimentally studied. In first place it was proved that CO_2 was not causing cellulose precipitation of cellulose. Based on those previous works, different experiments of cellulose hydrolysis were performed using different amount of CO_2, which besides of decreasing viscosity, presents a weak acid character what could enhances the hydrolysis reaction. To do so the use of an acid resin has been chosen instead of the use on an acid, because it can be more easily separated and reused. These experiments were similar to those presented by Rinaldi et al [42] in order to compare. Similar results were obtained in hydrolysis with and without CO_2 atmosphere. In the case of the cellulose acetate production is highly decreased when performed under CO_2 atmosphere.

2. EXPERIMENTAL

2.1. Materials

The IL used was 1-butyl-3-methylimidazolium chloride, [bmim][Cl], (> 95% purity) purchased from sigma Aldrich and produced by BASF. Prior to its first used was dried in the rotary evaporator to eliminate volatile impurities and before each experiment it was dried in a vacuum oven at 100 ºC for 24 h. The water content was measured with a Karl Fisher Mettler Toledo C20 and it was under 0.24 %wt. Cellulose used in all the experiments was micro-crystalline cellulose with a particle size of between 20 and 137 μm, purchased from VWR. It was dried at 90ºC in a vacuum heater before use. Amberlyst 15DRY , acetic anhydride (> 99% purity) were purchased by sigma Aldrich. Reagents for DNS analysis, 3,5-dinitrosalicylic acid (> 98% purity), sodium hydroxide (>98 % purity) and potassium sodium tartrate tetrahydrate (>99 % purity) were also purchased by Sigma Aldrich and used as received. Cellulose acetate was supplied by Sigma Aldrich and it was used as standard. Carbon dioxide (99.5% purity) was supplied by Carburos Metalicos (Spain) and was used without further purification.

2.2. Precipitation

A solution of 5% cellulose was prepared and placed in a vial inside a high pressure visual cell (SITEC 740.2120) with an inner volume of 25 mL, and kept at 80ºC and under 60 bar of CO_2 for 5 days.

2.3. Hydrolysis Experiments

The experiments were carried out in a stainless steel reactor of 35 mL designed in our laboratory situated on a magnetic stirrer hot plate. The scheme of the experimental set up is shown in Figure 1. Temperature was measured with a thermocouple provided by RS Amidata with a precision of ± 0.1 K. Pressure was measured with a pressure transducer supplied by Gems with a range of 0-160 bar. Reactor was heating using 2 wall heaters with a power of 100 W each, which were controlled by a PID controller connected with the thermocouple. The system was isolated with glasswool and foil.

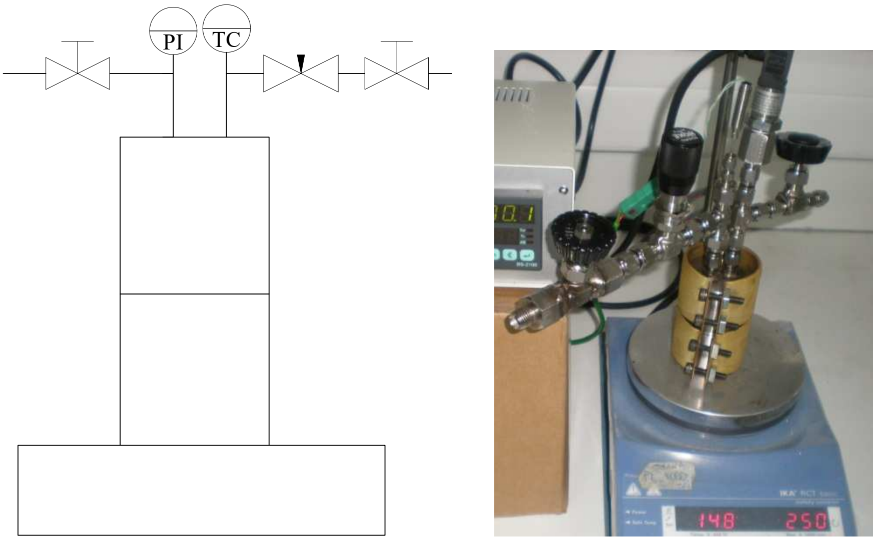


Figure 1. Apparatus set up used for carrying out the hydrolysis of cellulose.

A ratio of cellulose: Amberlyst 15DRY 5:1 was selected according to Rinaldi et al [42] The samples were prepared in a nitrogen filled glove box. The reactor was filled with 1 g of 1-butyl-3-methylimidazolium chloride, 0.05 g of cellulose, 0.001 g Amberlyst and 20 μL of water. Vaccum was made in the reactor and then it was heated till the desired temperature and stabilized for 20-30 minutes. A known amount of CO_2 was then charged into the reactor through a reservoir tank and the stirrer was turn on with a speed of 250 rpm and reaction was carried out for 5 h. After that time, the reactor was slowly depressurized till atmospheric pressure. Then the reactor was opened and 5 mL of water was added to the solution in order to precipitate the non-reacted cellulose. The solution was centrifuged at 8000 rpm for 10 minutes in order to separate the solid and liquid phases. Supernatant was kept for further analysis and solid was washed and dried, in order to know the amount of unreacted cellulose. Some experiments were repeated several times at similar conditions to ascertain the reproducibility of the measurements.

Total reducing sugars were analyzed by DNS method. DNS reagent was prepared by dissolving 10g/L of 3,5-Dinitrosalicylic acid, 16 g/L of sodium hydroxide and 300 g/L of potassium sodium tartrate. 1 mL of sample was mixture with 1 mL of water. The solution was kept at 95 ºC for 10 minutes then it was cooled down in ice and mixed with 10 mL of water. After that, the solution was analyzed at a wave length of 540 nm in a Shimadzu Espectrophotometer UV-2550. Glucose was used as standard.

2.4. Acetylation Experiments

10 g of ionic liquid [bmim][Cl] and 0.5 g of mycrocrystalline cellulose were mixed for cellulose dissolution. In all the experiments acetic anhydride was used as acetylation reagent in a ratio 4.5:1 of Anhydroglucose Units of Cellulose (AGU). The acetic anhydride was added after the total dissolution of cellulose. After a fixed time of reaction, the reaction is stopped by adding to the solution milliQ water while stirring. Thus, the solid was precipitated in this moment. Solid was separated from by centrifugation and later washed with water by filtration under vacuum. The recovered solid was dried at 90 ºC overnight. The degree of substitution was determined by FT-IR.

Different experiments were carried out in different high pressure equipment and conventional devices.

- Device (A). Reactions without CO_2 were carried out in an open beaker, 100 mL.
- Device (B). Stainless steel reactor. This reactor has a volume of 330 mL and it is able to work at temperatures and pressures as high as 473 K and 10 MPa. In these experiments the cellulose is dissolved under CO_2 atmosphere and when considered it is dissolved, (3 h) the acetic anhydride is added by pumping a known volume using a HPLC pump. In this way the CO_2 is dissolved in the IL media at the beginning of the reaction. In some experiments to add the acetic anhydride the reactor was depressurized, opened and added with a pipette, and

later close again and pressurized. In these experiments, the CO_2 is not dissolved in the solution in the beginning of the reaction, but the volume of acetic anhydride is added with a higher precision. Water was pumped after the reaction is finished in order to stop the reaction and precipitate the products.

- Device (C). Variable volume high pressure visual cell (SITEC 740.2120) with an inner volume of 25 mL. In the experiment performed in the device the volume of the visual cell is reduce to avoid the existence of a gaseous phase. Thus, all the CO_2 is dissolved in the liquid phase.

2.5. Determination of the degree of substitution by FTIR analysis

The degree of substitution was determined by FT-IR. It is known that the peak corresponding to OH bond appears at 3327 cm^{-1}. During the acetylating reaction this peak is reduced while a new peak corresponding to C=O bond appears at 1737 cm^{-1} [47, 48]. This can be observed in figure 2. The degree of substitution was obtained using the same method described in chapter by comparing the size of the area of the new peak with the area of the peak of the cellulose acetate provided by Sigma area of the new peak with the area of the peak of the cellulose acetate provided by Sigma Aldrich (DS=2.46; X=0.82) and used as standard , as shown in eq. (1):

$$X = \frac{A_P - A_C}{A_{A.C.} - A_C} \cdot 0.82 \qquad (1)$$

$$DS=3 \cdot X \qquad (2)$$

Where, A_i is the Area of the FT-IR spectra at 1737 cm^{-1}. The subindex P is referred to the solid product of reaction, C to the cellulose and A.C. to the pure cellulose acetate. X is the reaction conversion. As in each AGU unit there are three OH positions that can be substituted by and Acetyl group maximum Degree of Substitution (DS) of 3 could be achieved, thus DS is three times the conversion (eq.2).

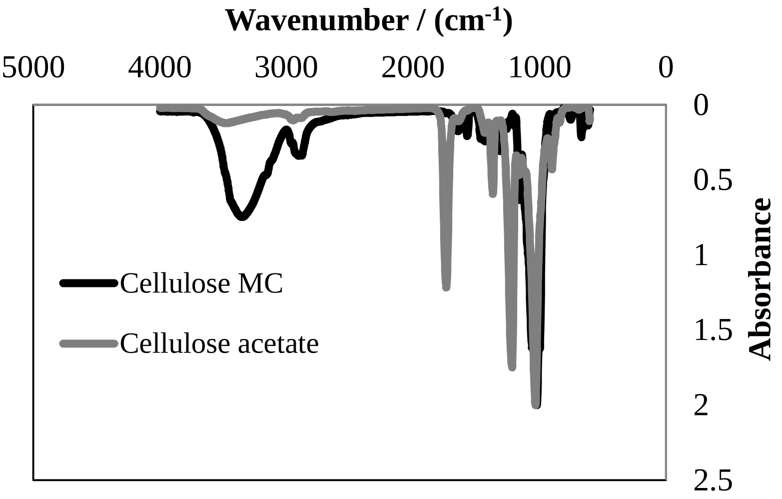


Figure 2. FTIR Spectra of cellulose and acetate of cellulose

The FTIR spectra of cellulose, ionic liquid and cellulose esters were recorded on a Fourier Transform infrared instrument (Bruker Platinum-ATR) equipped with software of OPUS Optik GmBH in the range from 400 to 4400 cm^{-1} of wavelength.

3. RESULTS

3.1. Precipitation

After 5 days under a pressure of CO_2=60 bar, no precipitation was observed in a solution of 5% cellulose in [bmim][Cl]. In figure 3 the vial containing the solution and the aspect of the solution in the visual cell under pressure can be observed.

Figure 3. Solution of 5% cellulose under a PCO2=60 bar for 5 days.

3.2. Hydrolysis

The different hydrolysis experiments, carried out at 80 ºC and 100 ºC at different CO_2 pressures from 1 to 45 bar are listed in table 1 and plotted in Figure 4. The solubility of CO_2 estimated at these conditions using the Group Contribution EoS [22] is also listed in table 1. It is observed that up to pressures of 15 bar both conversion and yield of reducing sugars determined by DNS analysis seems not to be influenced by the presence of CO_2, while at pressures of 45 bar (when the maximum concentration of CO_2 reach a value of 23%) it seems that a slight reduction both in cellulose conversions and in reducing sugars yield is produced.

Table 1. Hydrolysis experiments at about 80ºC and different CO_2 pressures at a reaction time of t=5 h

T (ºC)	P (bar)	Cellulose Conversion (%)	Reducing Sugars Yield (%)	Max x_{CO2}
80	1	84%	56.2%	0.0074
81	2.8	82.7%	53.9%	0.0202
83	9.3	77.8%	59.2%	0.0613
84	10.1	85.6%	57.1%	0.0651
80	15.4	85.2%	56.5%	0.1007
81	44.8	65%	39.6%	0.2317

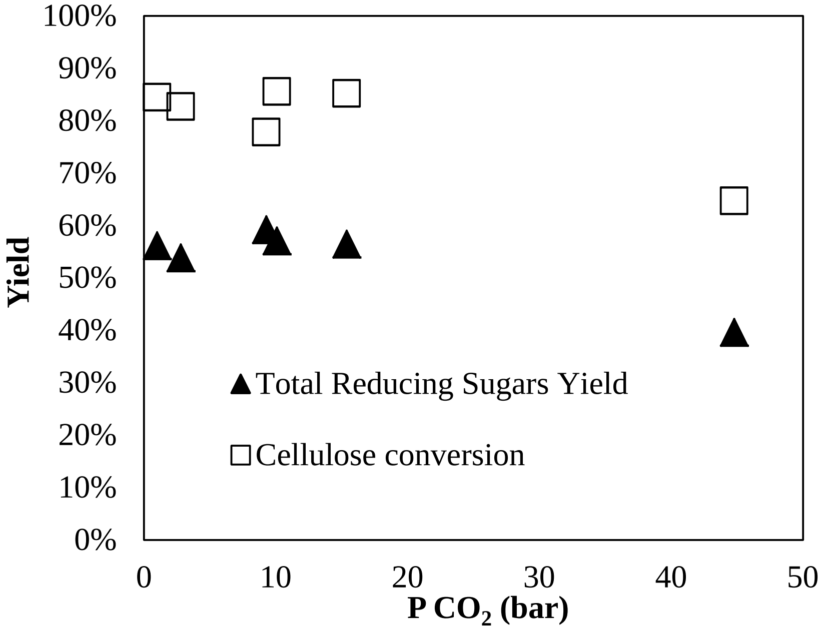


Figure 4. Cellulose conversion and yield of reducing sugars as a function of CO_2 pressure

In order to go deep on this phenomena, experiments at different times were performed keeping a constant temperature of 80 ºC and a constant pressure of 45 bar. These results are listed in table 2. It is observed that the yield of reducing sugars is increasing rapidly from 2 to 3 h of reaction time and keeping constant to increase again from 24% to almost 40%.

Table 2. Hydrolysis experiments at about 80ºC and P_{CO2}=45 bar

Time (h)	**x_{CO2}**	**Cellulose Conversion (%)**	**Reducing Sugars Yield (%)**
1	18.60%	13.2%	4.8%
2	16.26%	17.1%	6.6%
3	8.47%	34.06%	21.3%
3	18.93%	46.3%	23.9%
3	24.85%	34.44%	25.0%
4	57.59%	39%	24.4%
5	30.35%	64.7%	39.6%

It is observed that when the reaction is proceeding the color of the final solution (after precipitation of unreacted cellulose) showed a progressively darker color, as shown in figure 5.

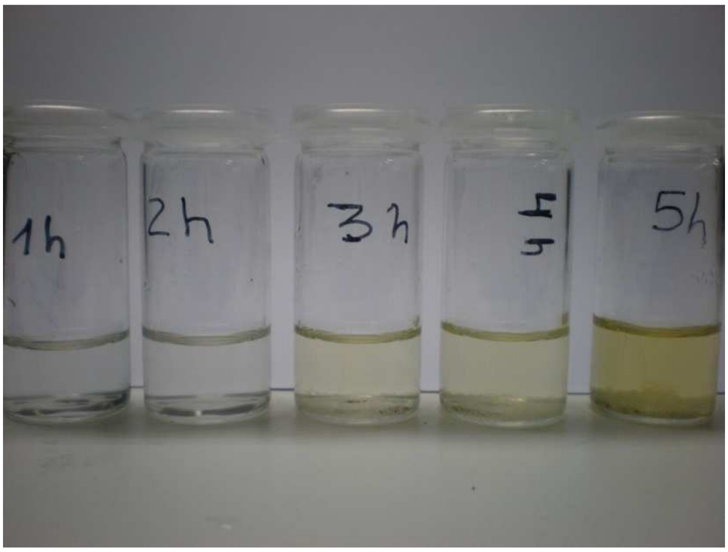


Figure 5. Final solutions of hydrolysis after precipitation of unreacted cellulose at 80ºC, P_{CO2}=45 bar and different reaction times.

Further hydrolysis experiments were performed at 100ºC, reaction time 5 hours and different CO_2 pressures up to 15 bar (see Table 3). Cellulose conversions of about 95% with reducing sugars yields of around 70% were obtained with independence of the CO_2 pressure. Nevertheless, these results cannot be considered totally reliable because at 100 ºC the solution became black, which provide some error to the DNS method, which is a colorimetric analysis.

Table 3. Hydrolysis experiments at 100º C and different P_{CO2}. Reaction time 5 h

T (ºC)	**P (bar)**	**time (h)**	**Cellulose Conversion (%)**	**Reducing Sugars Yield (%)**	**Max x_{CO2}**
104	15	5	94.4%	70.3%	0.0707
100	10.2	5	96.0%	83.1%	0.0523
100	5.3	5	97.0%	69.0%	0.0281
100	1.1	2	97.6%	70.7%	0.0060

In general not significant differences were appreciated when CO_2 was added to the system. The amount of TRS and the amount of transformed cellulose did not change when CO_2 is presented, except for a reduction in the conversion and yield at 45 bar. This can be explained because an amount of water of 20 mg/g [bmim][Cl] was added to the mixture, this means that together with the original humidity of the IL (0.24% ww), the final content of water in the [bmim]Cl is 2.2%wt, what means almost a 18% in mol. Viscosities at different temperatures at 0% and 18% mol in water are listed in table 4 and they were calculated according to the correlation presented in chapter 2 for viscosities in mixtures H_2O + [bmim][Cl]. It is observed that the viscosities of [bmim][Cl] are much lower at high temperatures, typical from hydrolysis, and what it is more, at these temperatures the viscosity reduction caused by a molecular solvent passes from 1/6 of the value of viscosity of the dry IL at 25ºC to only 1/3 at 80-100ºC.

In the case of CO_2, in the best case, the maximum solubility of CO_2 is 23% (estimated with the GC EoS) and in most of the experiments is lower than 10%. What it is more, as the dissolution kinetics of CO_2 in the IL is quite slow, it is possible that this maximum concentration is only reached at the end of the 5 h of the experiment. This causes that the effect of reduction in viscosity induced by CO_2 is much lower than that produced by the presence of water or the temperature increase.

Table 4. Viscosities of [bmim][Cl] dry and with 18% mol H_2O according to the correlation developed in chapter 2.

H_2O mol	0%	18%
T (K)	**μ (mPa·s)**	
298	19864.2	3315.3
313	3868.9	818.5
328	1011.9	259.8
343	335.8	100.9
353	181.2	59.4
373	64.2	24.3

This effect is not explaining why the conversion of cellulose is reduced at concentrations of CO_2 of 23 %mol. It is known that at moderate pH and in aqueous media CO_2 can be found in aqueous media as HCO_3^+ or even as a CO_3^{2+}. It may be hypothesized that the CO_2 is causing a kind of buffer effect in hydrolysis medium, moderating the acidity and reducing the hydrolysis rate.

3.3. Synthesis of cellulose acetate

The acetylation experiments performed are summarized in table 5. Looking at experiments 1 and 2 it is observed that when the reaction is performed without CO_2 DS=3 (that is, total conversion) was achieved in 8 h, under a pressure of 50 bar of CO_2 a degree of substitution of only DS= 1.94 was achieved. According to the results presented by Heinze and coworkers [44], [45], [46] in the same IL ([bmim][Cl]), at 80ºC and with a molar ration 5:1 of acetic anhydride:AGU, DS=2.7 could be achieved in only 2 h while at molar rations 3:1 conversions were reduced to 1.7. Reaction times much longer that those needed in our experiments under CO_2 atmosphere. However, no experiments at lower reaction time without CO_2 atmosphere could be performed in this work in order to compare. Nevertheless other authors report experiments at 8 h, T=80ºC and molar ration 4.5:1 in other imidazolium chloride ILs. ie. Possidonio et al [8] using 1-allyl-3-butylimidazolium chloride obtained a DS=2.2 and Wu et al [50] with a molar ratio of 5 obtained a DS=2.49 in 8 h using AmimCl and needed 23 h to obtain a DS=2.74, results that are more in agreement with our experimental data. In general, observing the literature data, it is found that while the results found in the same laboratory with the same IL are consistent, when comparing results of different authors and different ILs of the same imidazolium Cl family very different results were obtained.

Several experiments were performed at 30 bar (exp. 3 and 7) and 50 bar (exp. 2,4 and 5) of CO_2, dissolving the cellulose under CO_2 atmosphere. This means that when the acetic anhydride was added and the reaction time started to count the CO_2 was already dissolved in the solution. Comparable DS between 0.49 and 1.94 were obtained. Nevertheless, the addition of acetic anhydride was performed with a pump and it was considered that the precision of the volume added could be lower. It is known, according to literature data that acetylating reagent is strongly affected by the molar ratio Acetic anhydride: AGU. For example in experiment 6 the cellulose was dissolved without CO_2 and pressurized with CO_2 after adding the acetic anhydride with a pipette. In exp 6 the ratio was more precise but the conversion was lower than in exp 3-5 where the reagent was added with a pump.

It is known that acetic anhydride can be soluble up to 70% mol in the CO_2 at the conditions used in the experiments [51], but there are not experimental data about the influence of the IL in this equilibria. In order to determine if this assumption was right other experiment was developed adding an excess of acetic anhydride equal to the solubility of acetic anhydride in CO_2 at that conditions to compense possible lost~~.~~ This experiment was not satisfactory because solution become black and any conclusion was not achieved.

Another experiment at a higher pressure of 100 bar and longer reaction time, Exp 8, was carried out at in a variable volume equilibrium cell, and a DS of 0.88 was achieved. The initial objective of this experiment was decreasing the volume of the cell up to a value where the entire gas phase was dissolved in the liquid, thus ensuring that all the CO_2 phase was dissolved in the IL phase. By that time the piston of the cell broke down and it was also not possible to solve this challenge during the realization of this thesis, and the experiment with performed in two phases media. Thus the dissolution of the reagent in the gas phase can be still considered the reason of the lower conversion. Other reason could be that CO_2 is producing a different effect in the reaction. Nevertheless, the preliminary experiments performed this work are not sufficient to explain the reason why the CO_2 is decreasing conversion in this reaction.

Table 5. Experiments of synthesis of cellulose acetate using acetic anhydryde as acylating agent. T=80ºC, Ratio mol acetic anhydryde/mol AGU=4.5

Exp	Device	Cel Dissolution Conditions	time (h)	P_{CO2} (bar)	DS	Acetic Anhydride Addition
1	A	80ºC, 6 h, no CO_2	8	0	2.46	Pipette
2	B	80ºC, 1 h, P_{CO2}= 35 bar	8	50	1.94	Pipette
3	B	80ºC, 1 h, P_{CO2}=30 bar	7	30	1.11	Pump
4	B	80ºC, 2 h, P_{CO2}=22.7 bar	8	46.6	0.98	Pump
5	B	80ºC, 1 h, P_{CO2}=55 bar	7	50	1.16	Pump
6	B	80ºC, 5 h, no CO_2	8	50	0.74	Pipette
7	B	80ºC, 15 h, PCO_2=46 bar	8	31	0.49	Pump
8	C	80ºC, 5 h, no CO_2	20	100	0.88	Pump

4. CONCLUSIONS

Several experiments were performed in order to check if CO_2 can improve the processing of cellulose in the ionic liquid [bmim][Cl].

It was found that CO_2 did not cause cellulose precipitation in [bmim][Cl].

No appreciable effect of CO_2 was found in cellulose hydrolysis.

CO_2 decreased the degree of substitution of cellulose acetate synthethyzed in [bmim][Cl]. When the reaction was carried out without CO_2 a degree of substitution of 2.49 was achieved in 8 h, while 1.94- 0.49 were achieved at 80ºC in 7-20h and CO_2 pressures between 30-100 bar.

5. REFERENCES

[1] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, Journal of the American Chemical Society. 124 (2002) 4974–4975.

[2] A.P. Dadi, C.A. Schall, S. Varanasi, Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment, Applied Biochemistry and Biotechnology,137 (2007) 407-421.

[3] Watanabe, H, (2010), The study of factors influencing the depolymerisation of cellulose using a solid catalyst in ionic liquids, Carbohydrate Polymers, 80 (2010) 1168-1171.

[4] O.J. Olusola, M. Sudip, A. U. Lamidi, O. A. Kolawole,O. A. Olayinka, O. S. Tolu, S. Satanand, C. Rashmi, “Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxylmethylfurfural,” Energy Environ. Sc., 3 (2010) 1833-1850.

[5] Y. Cao, J. Wu, T. Meng, J. Zhang, J.S. He, H.Q. Li, Y. Zhang, Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl), Carbohydrate Polymers, 69 (2007) 665-672.

[6] C.F. Liu, R.C. Sun, A.P. Zhang, M.H. Qin, J.L. Ren, X.A. Wang, XA, Preparation and characterization of phthalated cellulose derivatives in room-temperature ionic liquid without catalysts, J. Agricultural and Food Chemistry, 55 (2007a) 2399-2406.

[7] C.F. Liu, R.C. Sun, A.P. Zhang, J.L. Ren, Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium, Carbohydrate Polymers, 68 (2007) 17-25.

[8] S. Possidonio, L.C Fidale, O.A. El Seoud, Microwave-assisted derivatization of cellulose in an ionic liquid: An efficient, expedient synthesis of simple and mixed carboxylic esters, J. Polymer Science Part A: Polymer Chemistry , 48 (2009) 134-143.

[9] Y. Lv, J. Wu, J. Zhang, Y. Niu, C. Liu, J. He, J. Zhang, Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions, Polymer, 53 (2012) 2524–2531.

[10] S. Fendt, S. Padmanabhan, H. W. Blanch, J. M. Prausnitz, Viscosities of Acetate or Chloride-Based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents, J. Chem. Eng. Data, 56 (2011) 31–34.

[11] K.R. Seddon, A. Stark, M.J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem. 72 (2000) 2275–2287.

[12] M. Gericke, T. Liebert, O.A. El Seoud, T. Heinze, Tailored media for homogeneous cellulose chemistry: ionic liquid/ co-solvent mixtures. Macromol Mater Eng 296 (2011) 483–493.

[13] R. Rinaldi, Instantaneous dissolution of cellulose in organic electrolyte solutions. Chem Commun 47 (2011) 511–513.

[14] J.M. Andanson, E. Bordes, J. Devémy, F. Leroux, A.A.H. Pádua, M.F. Costa Gomes, Understanding the role of co-solvents in the dissolution of cellulose in ionic liquids, Green Chem., 16 (2014) 2528-2538.

[15] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, scientific correspondence A stimulatory phalloid organ in a weaver bird Green processing using ionic liquids and CO2, Nature. 399 (1999) 28–29.

[16] S. Raeissi, C.J. Peters, Carbon dioxide solubility in the homologous 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family, Journal of Chemical & Engineering Data. 54 (2009) 382–386.

[17] S. Jang, D.-W. Cho, T. Im, H. Kim, High-pressure phase behavior of CO2+1-butyl-3-methylimidazolium chloride system, Fluid Phase Equilibria, 299 (2010) 216–221.

[18] S.G. Kazarian, N. Sakellarios, C.M. Gordon, High-pressure CO_2-induced reduction of the melting temperature of ionic liquids, Chemical Communications. (2002) 1314–1315.

[19] A.M. Scurto, W. Leitner, Expanding the useful range of ionic liquids: melting point depression of organic salts with carbon dioxide for biphasic catalytic reactions., Chemical Communications. (2006) 3681–3683.

[20] A.M. Scurto, E. Newton, R.R. Weikel, L. Draucker, J. Hallett, C.L. Liotta, et al., Melting point depression of ionic liquids with CO_2: Phase equilibria, Industrial & Engineering Chemistry Research, 47 (2008) 493–501.

[21] A. Serbanovic , Z. Petrovskia, M. Manic, C. Carolina, S. Marques, G.V.S.M. Carrera, L. Branco, C. A.M. Alfonso, M.N. da Ponte, Melting behaviour of ionic salts in the presence of high pressure CO2, Fluid Phase Equilibria. 294 (2010) 121–130.

[22] J. M. Lopes, F. A. Sánchez, S. B. Rodríguez Reartes, M. D. Bermejo, Á. Martín, M. J. Cocero, Melting point depression effect with CO_2 in high melting temperature cellulose dissolving ionic liquids. Modeling with group contribution equation of state, J Supercrit. Fluids, 107(2016) 590–604.

[23] Z.M. Liu, W.Z. Wu, B.X. Han, Z.X. Dong, G.Y. Zhao, J.Q. Wang, T. Jiang, G.Y. Yang, Study on the phase behaviours, viscosities, and thermodynamic properties of CO_2/[C4mim][PF_6]/methanol system at elevated pressures, Chem. Eur. J. 9 (2003) 3897-3903.

[24] A. Ahosseini, B. Ortega, B. Sensenich, A.M. Scurto, Viscosity of n-alkyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ionic liquids saturated with compressed CO_2, Fluid Phase Equilib. 286 (2009) 72-78.

[25] M. Iguchi, K. Kasuya, Y. Sato, T. M. Aida, M. Watanabe, R. L. Smith Jr., Viscosity reduction of cellulose + 1-butyl-3-methylimidazolium acetate in the presence of CO_2, Cellulose, 20 (2013)1353–1367.

[26] J.M. Lopes, S. Kareth, M.D. Bermejo, A. Martín, E. Weidner, MJ Cocero, Experimental determination of viscosities and densities of mixtures carbon dioxide + 1-

allyl-3-methylimidazolium chloride. Viscosity correlation, J Supercrit. Fluids, 111 (2016) 91-96

[27] A. Shariati, C.J. Peters, High-pressure phase equilibria of systems with ionic liquids, J. Supercrit. Fluids 34 (2005) 171-176.

[28] K.I. Gutkowski, A. Shariati, C.J. Peters, High-pressure phase behavior of the binary ionic liquid system 1-octyl-3-methylimidazolium tetrafluoroborate + carbon dioxide, J.Supercrit. Fluids 39 (2006) 187-191.

[29] L.A. Blanchard, Z. Gu, J.F. Brennecke, High-Pressure Phase Behavior of Ionic Liquid/CO2 Systems, J.Phys. Chem. B 105 (2001) 2437-2444.

[30] X.H. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Efficient catalytic conversion of fructose into 5-hydroxymethylfurfural in ionic liquids at room temperature, Chemsuschem 2 (2009) 944–946

[31]. A. Pinkert, K.N. Marsh, S. Pang, M.P. Staiger, Ionic liquids and their interaction with cellulose, Chem. Rev. 109 (2009) 6712–6728.

[32] D.A. Fort, R.C. Remsing , R.P. Swatloski, P. Moyna, G. Moyna , R.D. Rogers, Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride, Green Chem. 9 (2007) 63-6.

[33] M. FitzPatrick, P. Champagne, M. F. Cunningham, The effect of subcritical carbon dioxide on the dissolution of cellulose in the ionic liquid 1-ethyl-3-ethylimidazolium acetate, Cellulose, 19 (2012) 37–44.

[34] P. S. Barber, C. S. Griggs, G. Gurau, Z. Liu, S. Li, Z. Li, X. Lu, S. Zhang, R. D. Rogers, Coagulation of Chitin and Cellulose from 1-Ethyl-3-methylimidazolium Acetate Ionic-Liquid Solutions Using Carbon Dioxide, Angew. Chem., 125 (2013) 12576 –12579.

[35] G. Gurau, H. Rodríguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers, Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids, Angew. Chem. Int. Ed., 50 (2011) 12024 –12026.

[36]. X. Sun, Y. Chi, T. Mu, Studies on staged precipitation of cellulose from an ionic liquid by compressed carbon dioxide. Green Chem., 16 (2014) 2736-2743.

[37] S. Morales-de la Rosa, J. M. Campos-Martín, J. L.G. Fierro, High glucose yields from the hydrolysis of cellulose dissolved in ionic liquids, Chem. Eng. J. 181– 182 (2012) 538– 541

[38] Dadi A.P., Varanasi S., Schall C.A., Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step, Biotechnology and Bioengineering, 95 (2006) 904-10.

[39] J. Bian, F. Peng, X. P. Peng, X. Xiao, P. Peng, F. Xua, R.C. Sun, Effect of [Emim]Ac pretreatment on the structure and enzymatic hydrolysis of sugarcane bagasse cellulose. Carbohydrate Polymers, 100 (2014) 211– 217.

[40] H. Ma, B. Zhou, Y. Li, D.S. Argyropoulos, Conversion of Fructose to 5-hydroxymethyl-fyrfural with Functionalized Ionic Liquids, BioResources, 7 (2012) 533-544.

[41] A.S. Amarasekara, S. Onome, O.S. Owereh,. Hydrolysis and Decomposition of Cellulose in Brönsted Acidic Ionic Liquids Under Mild Conditions, Ind. Eng. Chem. Res., 48 (2009) 10152–10155.

[42] Rinaldi R., Palkovits R., Schüth F. Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids, Angew. Chem. Int. Ed. 47 (2008) 8047-8050.

[43] C. Jiménez de la Parra, A. Navarrete, M.D. Bermejo, M.J. Cocero, Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids, Recent Patents on Engineering, 2012, 6, 159-181.

[44] S. Barthel, T. Heinze, Acylation and carbanilation of cellulose in ionic liquids, Green Chem., 8 (2006) 301–306.

[45] T. Heinze, K. Schwikal, S. Barthel, Ionic Liquids as Reaction Medium in Cellulose Functionalization, Macromol. Biosci., 5 (2005) 520–525.

[46] B. Kosan, S. Dorn, F. Meister, T.S. Heinze, Preparation and Subsequent Shaping of Cellulose Acetates Using Ionic Liquids, Macromol. Mater. Eng., 295 (2010) 676–681

[47] D.A. Cerqueira , G. R. Filho, C.d.S. Meireles, Optimization of sugarcane bagasse cellulose acetylation, Carbohydrate Polymers 69 (2007) 579–582.

[48] H.S. Barud, A. M. de Araújo Júnior, D.B. Santos, R. M.N. de Assunção, C. S. Meireles, D.A. Cerqueira, G. R. Filho, C. A. Ribeiro, Y. Messaddeq, S.J.L. Ribeiro, Thermal behavior of cellulose acetate produced from homogeneous acetylation of bacterial cellulose, Thermochimica Acta, 471 (2008) 61–69.

[49] I.A. Ignatyev, C. Van Doorslaer, G.N. Pascal, P.G.N. Mertens, K. Binnemans, D.E. de Vos, Synthesis of glucose esters from cellulose in ionic liquids, Holzforschung, 66 (2012) 417–425.

[50] J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren, M. Guo, Homogeneous acetylation of cellulose in a new ionic liquid. Biomacromolecules, 5(2004) 266-268.

[51] L. Calvo, T. W. de Loos, High pressure vapour–liquid equilibria of the binary and some of the ternary and multicomponent mixtures of the carbon dioxide + acetic anhydride + α-methylbenzyl alcohol + acetic acid + α-methylbenzyl acetate system: Experimental and modelling results,Fluid Phase Equilibria 244 (2006) 179–187.

Conclusions and future work

1. CONCLUSIONS

In this work the main problems associated with cellulose processing in ionic liquids were identified and some solutions to these problems were proposed.

- The main aspects of cellulose processing with ionic liquids were studied and the main process developed so far thoroughly analyzed. It was found that the high hygroscopicity of ionic liquids for cellulose processing, the high viscosity and the difficulty to be recycled were the main problems associated to cellulose processing and some solutions to these problems were proposed.

- The influence of water content in densities and viscosities of two of the most characteristic ionic liquids used for cellulose processing 1-allyl-3-methyilimidazolium chloride and 1-ethyl-3-methylimidazolium acetate were experimentally determined in the temperature range from 298.15 to 373.15 K, at atmospheric pressure and for water molar fractions lower than 0.35.

  Viscosity of 1-ethyl-3-methylimidazolium acetate decrease with water content at 298.15 K from 124 to 75 mPa·s and at 373.15 from 8.19 to 6.47 mPa·s, and density slightly increase with water molar fraction at 298.15 K from 1.0983 to 1.1018 g/cm^3 and at 373.15 K from 1.0538 to 1.0571 g/cm^3. Viscosities and densities of the system H_2O +1-ethyl-3-methylimidazolium acetate were consistent with existent literature data. In the case of 1-allyl-3-methyilimidazolium chloride, viscosity decreases with water at 298.15 K from 1884 to 258.7 mPa·s and at 373.15 K from 22.21 to 10.98 mPa·s. Density slightly decrease at 373.15 from 1.1459 to 1.1430 g/cm^3 and at 373.15 K from 1.1036 to 1.1009 g/cm^3. Data of this system H_2O + 1-allyl-3-methyilimidazolium chloride, present inconsistencies with the scarce literature data existent.

  Excess molar volumes of the mixtures were calculated obtaining negative values, being more negative for the system H_2O +1-ethyl-3-methylimidazolium acetate, what indicates a strongly packed structure attributed to the formation of hydrogen bonds.

  Seddon and Grunberg and Nissan equations were modified to describe the highly no ideal viscosity behaviour as well as the temperature dependence.

Logarithm of viscosities of pure ionic liquids has been correlated as a quadratic equation instead of the traditional lineal equations. The equation has been extended successfully to describe the viscosity of other aqueous imidazolium chloride binary systems as well as to the system ethanol + 1-ethyl-3-methylimidazolium acetate using literature data, obtaining an average deviations lower than 15% in the viscosity in most systems considered.

- In chapter 3, protic ILs were proposed as a solution for recyclability of ILs. A new protic IL for cellulose processing at mild conditions was developed. This , new protic ionic liquid, [dbnH][MeOAc] was able to dissolve up to 10% wt of cellulose in 3h at 40 ºC. Cellulose can be recovered by precipitation without observed any change neither in its structure nor in its depolymerisation degree. Besides it is possible to obtain cellulose acetate with a degree of substitution of 1.9 at 40 ºC in 24 h.

- As a solution to the high viscosity of ionic liquids in cellulose processing the use of CO_2 as a co-solvent is proposed. To do so, the influence of CO_2 was experimentally studied in several celluloses modification processes. The IL 1-butyl-3-methylimidazolium chloride [bmim][Cl] was selected because of it has a high capacity for dissolving cellulose and also important challenges such as high viscosities and melting points. It was considered that the effect on viscosity reduction would be especially remarkable using this IL. The viscosity of this IL at 293. 15 K is 41000 mPa·s, while others ILs, also used in biomass processing present less viscosity, [amim][Cl] 1884 mPa·s at 298.15 K and [emim][Ac] 124 mPa·s at 298.15 K

- Most important physical properties of 1-butyl-3-methylimidazolium chloride [bmim][Cl] were compiled and experimentally determined. The melting point is around 340.6 K, and experimental viscosity and density decrease with temperature increased and measured values were similar to bibliography data. Viscosity varies from 5194.23 mPa·s at 308.15 K to 56.71 mPa·s at 383.15 K and density ranges between 1.0762 g/cm^3 at 308.15K and 1.0354 g/cm^3 at

383.15K. According to literature, it presents solubilities of CO_2 between 30-40% mol at moderate pressures.

- The influence of CO_2 for cellulose processing using ionic liquids was analysed in two process involving cellulose and [bmim][Cl]: hydrolysis and acetylation reaction.
    - It was determined that cellulose precipitation in a solution of 5 % of cellulose in [bmim][Cl] was not induced by pressures of CO_2 up to 60 bar.
    - The presence of CO_2 did not improve hydrolysis of cellulose using Amberlyst as acid. What it is more, in a range between 1-15 bar the cellulose conversion was about 85 % but at 45 bar it decreased till 65 %.
    - The presence of CO_2 decreased the production of cellulose acetate in [bmim][Cl] using acetic anhydride as an acetylating reagent. A degree of substitution of only 1.16 was achieved in 7 h at 50 bar and 80 ºC. This might be caused by the high solubility of acetic anhydride in CO_2, 70% mol at 80 ºC and 40 bar, which may separate the reagents in different phases, or it could be due to CO_2 is producing a different effect in the reaction. But these assumptions could not be proved during the realization of this thesis.

1. FUTURE WORK

- To experimentally determine the viscosity of different cellulose dissolving ionic liquids with water, carbon dioxide and co-solvents and made a comparison of the viscosity reduction by using water or CO_2 as co-solvents.

- To complete the study of the PIL developed in chapter 3, [dbnH][MeOAc in order to prove the high yield recovery and its real degree of reciclability. Also new applications of [dbnH][MeOAc] would need to be proposed. For example the use of this IL for other biomass processes like lignocellulosic material pretreatment, and, for example, the study the solubility of CO_2 in [dbnH][MeOAc].

- To develop a high pressure equilibrium cell to experimentally determine the solubility of CO_2 and other gases in ILs. During the realization of this thesis solubility measurements were carried out in an equilibrium cell, based on the determination of pressure decreases by gas dissolution, which was designed and constructed by our group but results were neither reproducible nor in accordance with the obtained by Jang et al. New pressure vessels were constructed and a new calibration method of the volume of the CO_2 added should be developed in order to complete the development of this equipment.

- In order to better understand the possible effect of acetic anhydride dissolution into CO_2 phase more experiments need to be done in a high pressure variable volume equilibrium cell where all the reagent are in an unique phase.

- To further investigate the use of the ionic liquid [bmim][Cl] in cellulose dissolution with and without CO_2 atmosphere. During the realization of this thesis it was observed that in different kind of cellulose dissolution experiments (cotton, pellets, powder) a kind of "coat" of IL around the cellulose was formed preventing its dissolution in the IL. The same happened when dissolution experiments were carried out in device B (described in chapter 5). A much faster dissolution of cellulose was under CO_2 atmosphere (sometimes in less than 1 h). Nevertheless, even when this phenomenon was qualitatively observed, a quantitative determination was not successful during the realization of this thesis.

- To further validate FTIR method of determining DS of cellulose acetate comparing to other widely spread quantitative methods such as titration or ^{1}H NMR for obtaining the degree of substitution.

- To develop a more detailed analysis method of compounds obtained during hydrolysis or by cellulose degradation after its precipitation from the IL. During the realization of this work, HPLC analysis with different columns was tested but the results were not neither reproducible or nor consistent. It would be interesting to continue this study.

Resumen

ESTUDIO DE LA MEJORA DEL PROCESADO DE BIOMASA EN LÍQUIDOS IÓNICOS

1. INTRODUCCIÓN

Debido al agotamiento de las fuentes de energía actuales, petróleo principalmente, se ha empezado a considerar la biomasa como una materia prima prometedora para la producción de productos químicos y combustibles que anteriormente se obtenían del petróleo. La lignocelulosa es la biomasa vegetal más abundante y está compuesta de tres fracciones: celulosa (30-60%), hemicelulosa (20-40%) y lignina (10-30%).

La celulosa es el polisacárido más abundante, con una producción anual de of 75×10^9 toneladas/año. Está constituida por cadenas de β-D-glucosa que forman una estructura cristalina debido a los puentes de hidrógeno intermoleculares que se crean entre cadenas contiguas de celulosa. El procesado y la disolución de celulosa son procesos más complicado que en el caso de otros polisacáridos ya que las moléculas de glucosa están enlazadas fuertemente unas a otras. No es soluble en agua ni en otros disolventes convencionales a temperatura ambiente, sino que es necesario utilizar bases o ácidos fuertes y/o altas temperaturas, lo que hace que estos procesos sean contaminantes, y que se hayan investigado nuevos procesos y tratamientos alternativos.

En el año 2002 Swatloski retomó la utilización de líquidos iónicos (LIs) como solventes limpios para el tratamiento de biomasa, ya que eran capaces de disolver altas concentraciones de celulosa.

Los líquidos iónicos son sustancias compuestas exclusivamente por iones que son líquidos a temperatura ambiente. Son muy asimétricos y voluminosos, por lo que presentan fuerzas atractivas más débiles que las sales convencionales. Se han considerado solventes "verdes" debido a su baja presión de vapor y a su reciclabilidad. Poseen muy buenas propiedades: alto calor específico, y poder disolvente, elevada conductividad iónica, estabilidad electroquímica frente a reacciones redox y la mayoría son no inflamables y son térmica y químicamente estables. Eligiendo el anión y el catión apropiados se puede obtener un líquido iónico con unas propiedades específicas. Los líquidos iónicos son un buen medio de reacción y también pueden actuar como catalizadores en algunos procesos. Presentan un alto grado de solvatación lo que hace que sea posible una reducción del tamaño de los reactores.

En general los líquidos iónicos son viscosos, y la viscosidad se incrementa aún más cuando se disuelve celulosa en él. Se sabe que el uso de CO_2 como co-solvente ayuda a disminuir la viscosidad de la solución ya que se mejora el movimiento de los iones y la transferencia de materia, y también disminuye el punto de fusión del líquido iónico.

Durante el proceso de disolución el líquido iónico compite con los puentes de hidrógeno intermoleculares y separa las cadenas del polímero. Los grupos OH^- de la celulosa crean un complejo donor-aceptor de enlaces de hidrógeno con el líquido iónico cargado.

En el proceso de disolución ambos, catión y anión juegan un papel importante. Los cationes tienen la habilidad de deslocalizar la carga positiva, participan en los enlaces de hidrógeno y el anión a su vez actúa como un aceptor de H^+ que interactúa con los grupos hidroxilo de la celulosa.

2. OBJETIVOS

El **objetivo** de este trabajo mejorar el tratamiento de celulosa en medio líquido iónico solventando alguno de los principales problemas como es la elevada viscosidad. Para llevar a cabo esta tarea se han propuesto los siguientes objetivos parciales:

- Estudio detallado del estado del arte para entender los procesos e identificar las principales limitaciones. Revisión de los procesos y tratamientos de celulosa en medio líquido iónico patentados. Este objetivo se desarrolló en el Capítulo 1.

- Medida experimental y modelado de algunas propiedades físicas de los líquidos iónicos más usados para el tratamiento de biomasa. Se ha seleccionado un líquido iónico de la familia de los cloruros de imidazolio y otro de la familia de acetato de imidazolio. Una de las principales limitaciones de los líquidos iónicos es que son muy higroscópicos por lo que se estudiará la influencia del contenido de agua en la viscosidad y densidad de esos dos líquidos iónicos y se buscará una correlación para determinar la viscosidad en función del contenido de agua. Este objetivo se trabajó en el Capítulo 2.

- Búsqueda de un nuevo líquido iónico prótico capaz de disolver celulosa en condiciones suaves y que sea fácil de reciclar. Este objetivo fue llevado a cabo en colaboración con el grupo del Profesor Kenneth R. Seddon en el Queen´s

University Ionic Liquid Laboratory (QUILL) en la Universidad de Queen´s en Belfast (UK) y se explica en el capítulo 3.

- Desarrollo de un método para solventar uno de las principales limitaciones del proceso, la elevada viscosidad de los líquidos iónicos. Se propone el uso de dióxido de carbono como co-solvente en lugar de disolventes orgánicos. El CO_2 es un solvente verde, capaz de disolverse en el LI en concentraciones de hasta un 70 % mol disminuyendo la viscosidad y el punto de fusión de algunos líquidos iónicos. Además puede separarse fácilmente del LI sin dejar residuos. El líquido iónico seleccionado es el [bmim][Cl] ya que se ha demostrado que tiene una alta capacidad de tratamiento de biomasa y además posee un elevado punto de fusión y es mucho más viscoso que la mayoría de los LIs utilizados para procesar biomasa. Este objetivo se llevó a cabo en los Capítulos 4 y 5 y se divide en dos objetivos parciales:
    - En el Capítulo 4 se realizó una revisión bibliográfica y la determinación experimental de algunas propiedades físicas del [bmim][Cl] como el punto de fusión, la viscosidad, la densidad y solubilidad de CO_2 en él.
    - En el Capítulo 5 se analizó la influencia del CO_2 utilizado como co-solvente en un proceso de hidrólisis y en otro de acetilación de celulosa en [bmim][Cl].

3. RESULTADOS Y DISCUSIÓN

CAPÍTULO 1. REVISIÓN DE PATENTES DEL PROCESADO DE BIOMASA LIGNOCELULÓSICA USANDO LÍQUIDOS IÓNICOS.

En este capítulo se realizó una revisión bibliográfica de las patentes desarrolladas para diversos procesos en los que se utilizan líquidos iónicos en el tratamiento de biomasa. En primer lugar se realizó una introducción sobre los conceptos de celulosa y líquidos iónicos así como del mecanismo de disolución de la celulosa en los líquidos iónicos. En segundo lugar se llevó a cabo un análisis de las nuevas tecnologías desarrolladas para procesar biomasa en líquidos iónicos, prestando especial atención a las patentes publicadas por empresas involucradas en la implantación de estos procesos.

Estas tecnologías se han dividido en 6 grupos principales: disolución y precipitación de celulosa; fraccionamiento de biomasa, deslignificación o pretratamiento de celulosa para reacciones de hidrólisis o procesos de fermentación para la producción de bioetanol; reacciones para la obtención de productos de bio-refinería y químicos; preparación de composites de celulosa y reacciones de sustitución para la obtención de compuestos derivados de celulosa.

Los líquidos iónicos han generado mucho interés como una alternativa limpia a los procesos tradicionales más contaminantes que utilizan disolventes orgánicos y ácidos o bases fuertes.

Los procesos patentados son simples y relativamente fáciles de implementar, aunque presentan algunas limitaciones como son la elevada viscosidad de la mezcla biopolímero/LI y la capacidad de recuperación y reciclaje del LI. Desde el año 2005 se han publicado más de 70 patentes sobre el procesamiento de biomateriales para producir diferentes productos químicos, combustibles, composites y polímeros derivados de la celulosa. Un gran número de estas patentes son propiedad de BASF y Eastman Chemical Companies, aunque aún ninguno de estos procesos ha sido desarrollado a escala industrial.

CAPÍTULO 2. INFLUENCIA DE LA CONCENTRACIÓN DE AGUA EN LAS VISCOSIDADES Y DENSIDADES DE LÍQUIDOS IÓNICOS QUE DISUELVEN CELULOSA. CORRELACIÓN DE LOS DATOS DE VISCOSIDAD.

En colaboración con el grupo TERMOCAL de la Escuela de Ingenierías Industriales se ha utilizado un viscosímetro-densímetro Stabinger para medir experimentalmente la densidad y la viscosidad de diferentes mezclas acuosas de dos líquidos iónicos ampliamente estudiados en el tratamiento de biomasa, cloruro de 1-alil-3-metilimidazolio [amim][Cl] + agua y acetato de 1-etil-3-metilimidazolio [emim][Ac] + agua. Las medidas se han llevado a cabo con concentraciones de agua de hasta un 35% mol a presión atmosférica y en un rango de temperatura de 298.15 a 373.15. Los resultados obtenidos se muestran en el conjunto de figuras 1.

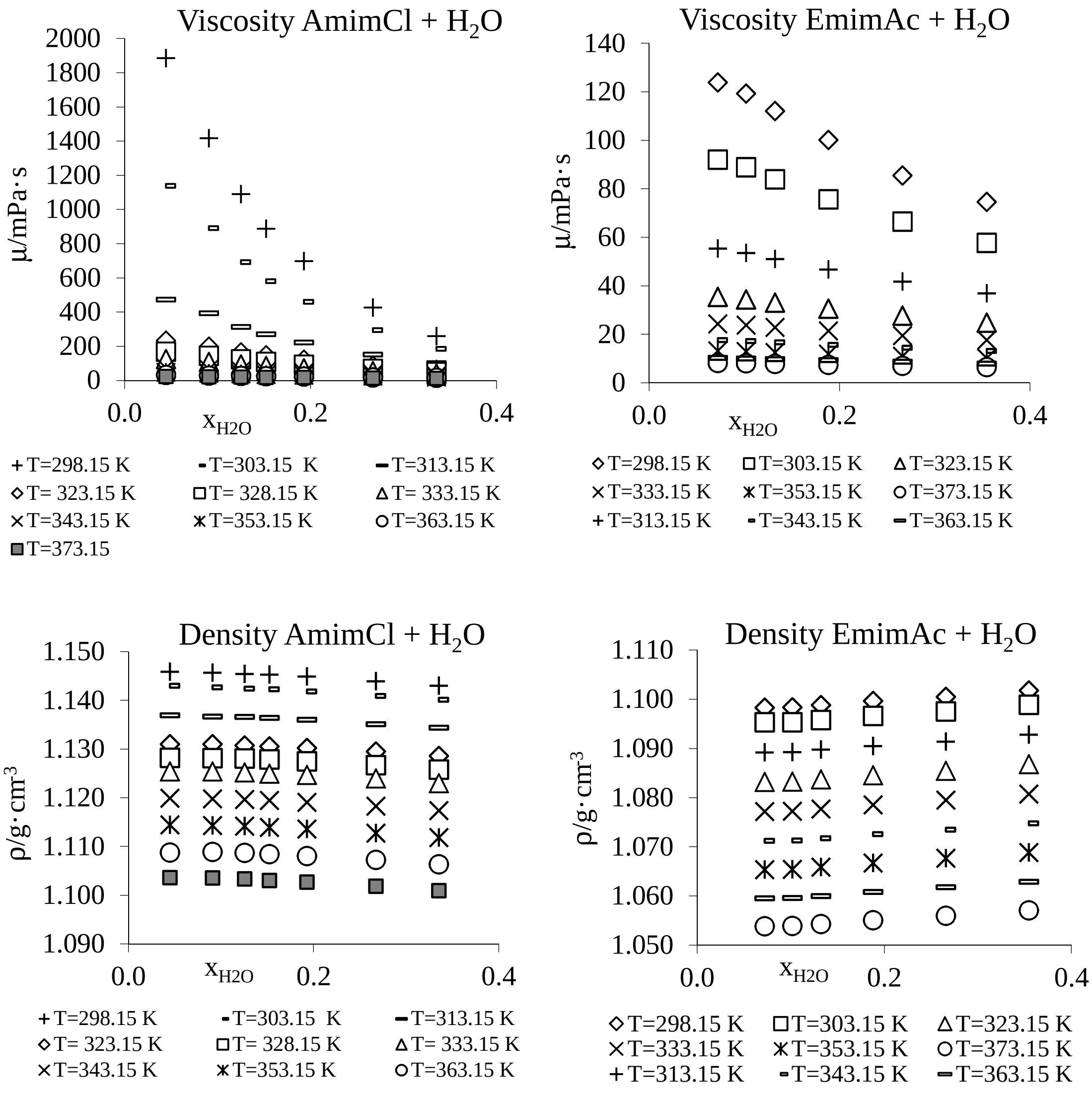


Figura 1. Medida de viscosidad y densidad a distintas temperaturas de distintas mezclas [emim][Ac] – agua y [amim][Cl] – agua.

Los volúmenes de exceso se calcularon a través de los datos de densidad y resultaron valores negativos, esto se explica porque los volúmenes molares de ambos líquidos no son aditivos. Los componentes están más empaquetados, por lo que la densidad es mayor de la esperada. El acetato de 1-etilo-3metilimidazolio presenta valores más negativos, la estructura está más fuertemente empaquetada, lo que puede atribuirse a la formación de puentes de hidrógeno.

En este capítulo también se ha propuesto una correlación para $x_{H2O}<0.4$ y otra para todo el rango de concentraciones que relaciona la viscosidad con la temperatura y con la concentración de agua. Las viscosidades logarítmicas del líquido iónico puro han sido correlacionadas con ecuaciones cuadráticas en lugar de lineales. Las ecuaciones de Seddon y Grunberg y Nissan se han modificado para describir el comportamiento altamente no lineal y la dependencia de la temperatura. Esta ecuación se ha utilizado también satisfactoriamente para describir la viscosidad de otras soluciones acuosas de cloruros de imidazolio y agua así como los del sistema etanol + acetato de 1-etil-3metilimidazolio. De esta forma se han obtenido desviaciones medias menores del 15% en la viscosidad de la mayoría de los sistemas que se han considerado.

CAPÍTULO 3. USO DE LÍQUIDOS IÓNICOS PRÓTICOS EN EL PROCESADO DE BIOMASA.

Este trabajo fue llevado a cabo en Queen´s University Ionic Liquid Laboratory (QUILL) Research Center en la Universidad de Queen en Belfast (UK).

Se estudió el uso de líquidos iónicos próticos (LIP) para disolver biomasa. Se probaron distintas mezclas de ácidos y bases para obtener un líquido iónico prótico que fuese líquido a temperatura ambiente y que fuese capaz de disolver celulosa. El LIP óptimo que se consiguió fue el obtenido mezclando la base fuerte 1,4-diazabicyclo[4.3.0]non-5-ene, DBN (pka=12.7) y el ácido metoxiacético MeOAc (pK_a=3.54). Este líquido iónico, [dbnH][MeOAc] fue fácilmente sintetizado transfiriendo un protón del ácido a la base. La pureza del [dbnH][MeOAc] fue determinada por análisis NMR (Resonancia Magnética Nuclear). La figura 2 muestra el espectro ^{1}H NMR del ácido, la base y el líquido iónico sintetizado.

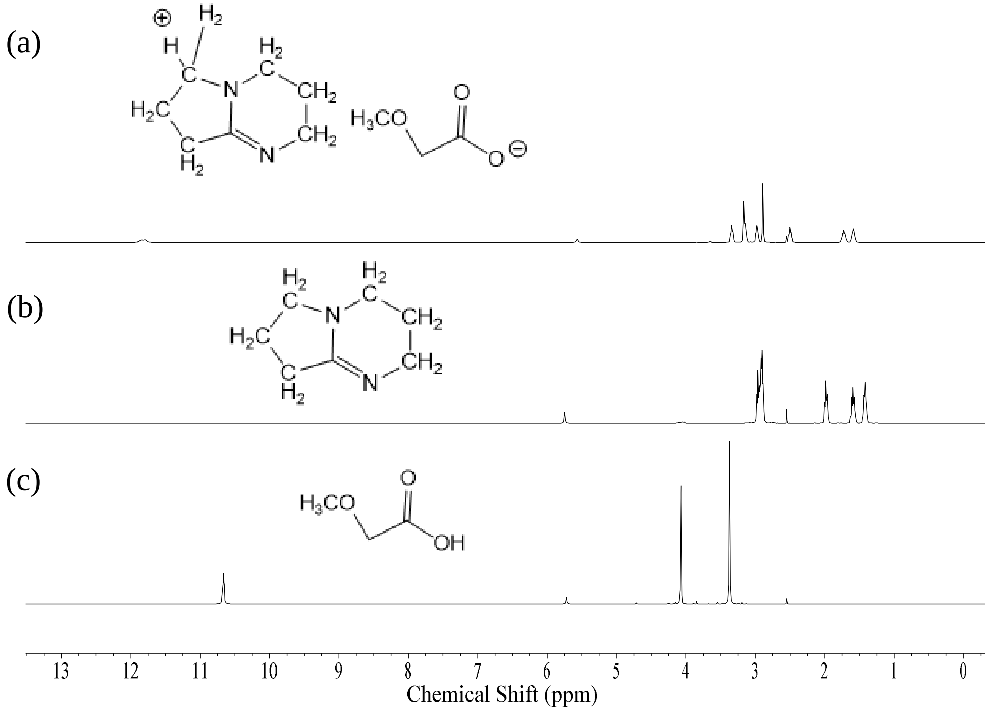


Figura 2. Espectro ^{1}H-NMR (δ_{solv}=2.5 ppm) de: (a) [dbnH][MeOAc], (b) 1,5-Diazabicyclo(4.3.0)non-5-ene (dbn), (c) Ácido metoxiacético (MeOAc)

Este líquido iónico fue capaz de disolver 10 % en peso de celulosa a 40 ºC en 4 horas con agitación obteniéndose una solución perfectamente clara. Se estudió también la precipitación de la celulosa disuelta y se observó que es posible recuperar celulosa sin que esta sufra ningún cambio significativo ni en su estructura atómica ni en su grado de polimerización. En este líquido iónico es posible llevar a cabo reacciones de acetilación, y obtener acetato de celulosa con un grado de sustitución de 1.9 en 24 h a 40 ºC y con un ratio de 4 mol anhídrido acético/ mol AGU.

Se determinó también la viscosidad del [dbnH][MeOAc] puro y con celulosa disuelta, (ver figura 3). La viscosidad del LI puro es similar a la del [emim][Ac] 189.2 mPa·s a 303.15 K y la viscosidad de la solución con un 10% wt de celulosa disuelta aumenta hasta los 89540 mPa·s.

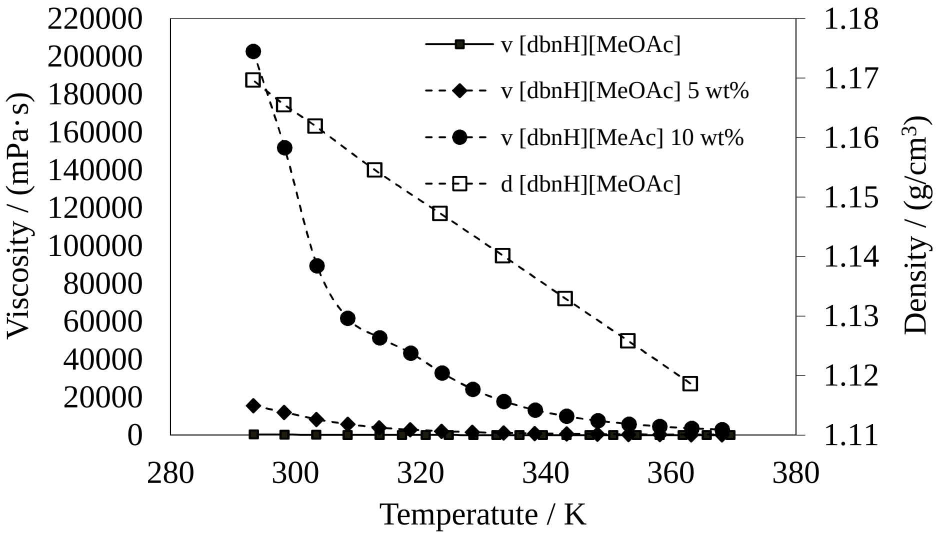


Figura 3. Viscosidad (v) y densidad (d) del LI puro [dbnH][MeOAc] y viscosidad (v) de soluciones de [dbnH][MeOAc] con diferentes concentraciones de celulosa disuelta.

CAPÍTULO 4. PROPIEDADES DEL LÍQUIDO IÓNICO [bmim][Cl]. DENSIDAD, VISCOSIDAD Y EQUILIBRIO DE FASES.

En colaboración con el grupo TERMOCAL de la Escuela de Ingenieros Industriales se determinaron experimentalmente dos propiedades del líquido iónico cloruro de 1-butil-3-metilimidazolio [bmim][Cl] a presión atmosférica, la densidad de 308.15 a 383.15K y la viscosidad de 308.15 a 373.15 K. Los datos se han contrastado con los obtenidos en literatura y los resultados se muestran en el grupo de figuras 4.

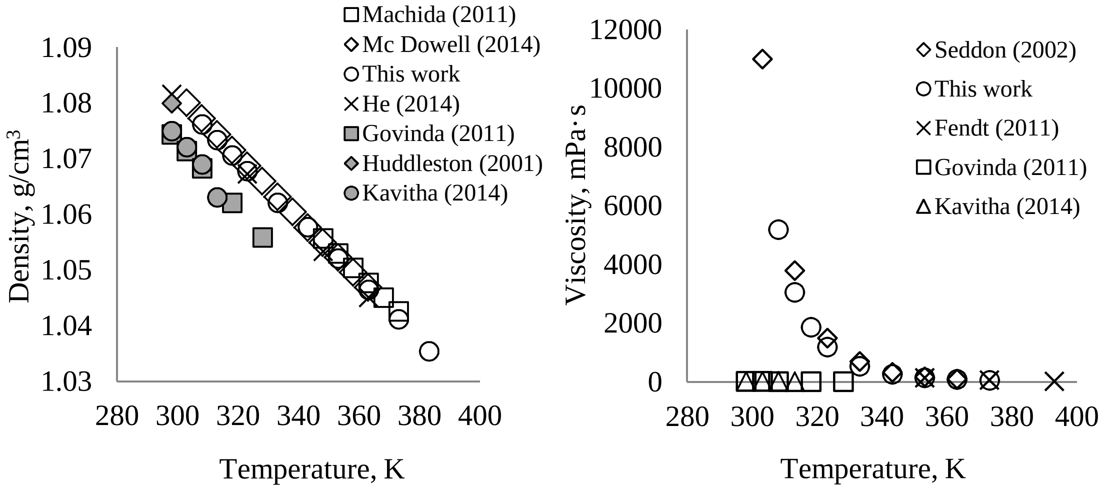


Figure 4. Comparación de los valores experimentales de densidad y viscosidad de [bmim][Cl] obtenidos en este trabajo y los obtenidos de bibliografía.

También se ha llevado a cabo una recopilación de datos bibliográficos de puntos de fusión y de solubilidad de CO_2 en [bmim][Cl]. El punto de fusión de este líquido iónico está entorno a las 340.8 K y es capaz de disolver hasta un 40.6% mol de CO_2 a 373.15 K y 36.94 MPa, valores menores a los obtenidos con otros líquidos iónicos.

CAPÍTULO 5. ANÁLISIS DE LA INFLUENCIA DEL CO_2 USADO COMO CO-SOLVENTE PARA REDUCIR LA VISCOSIDAD DEL PROCESADO DE CELULOSA EN [bmim][Cl]

En este capítulo se ha analizado la influencia del CO_2 en las reacciones de hidrólisis y síntesis de acetato de celulosa en [bmim][Cl].

En primer lugar se ha probado que el CO_2 no causa la precipitación de celulosa, para ello se ha dejado una solución de celulosa disuelta en [bmim][Cl] en una atmósfera de CO_2 a presión de 60 bar varios días sin observarse ningún cambio.

En el caso de las reacciones de hidrólisis, se obtuvieron resultados similares trabajando en presencia y ausencia de CO_2. Esto puede deberse a que el agua que se utiliza como reactivo a su vez provoque una disminución de la viscosidad mayor que el propio CO_2. En la tabla 1 se muestran los resultados obtenidos después de 5h.

Tabla 1. Experimento de hidrólisis llevados a cabo a 80 ºC a diferentes presiones de CO_2 durante 5h.

T (ºC)	**P (bar)**	**Cellulose Conversion (%)**	**Reducing Sugars Yield (%)**	**Max x_{CO2}**
80	1	84%	56.2%	0.0074
81	2.8	82.7%	53.9%	0.0202
83	9.3	77.8%	59.2%	0.0613
84	10.1	85.6%	57.1%	0.0651
80	15.4	85.2%	56.5%	0.1007
81	44.8	65%	39.6%	0.2317

La producción de acetato de celulosa disminuyó cuando se llevó a cabo en atmósfera de CO_2. Todos los experimentos llevados a cabo condujeron a un grado de sustitución (GS) menor, obteniéndose valores de 1.94, 1.1 ó 0.49 frente a los 2.49 obtenido cuando se trabajó en ausencia de este co-solvente. El agente acilante, anhídrido acético, podría pasar a la fase del CO_2, ya que en las condiciones usadas en estos experimentos, la solubilidad del anhídrido acético en el CO_2 es del 70% en mol. Pero los experimentos llevados a cabo en este trabajo no son suficientes para explicar la razón por la que el CO_2 provoca una disminución del grado de conversión de la reacción.

4. CONCLUSIONES

A continuación se presentan las conclusiones más relevantes del presente trabajo de tesis doctoral en el que los principales problemas asociados con el procesado de celulosa en medio líquido iónico han sido identificados y se han propuesto algunas soluciones.

- Se han estudiado los principales aspectos del procesado de celulosa en medio líquido iónico y se han analizado los principales procesos que se han desarrollado en este tema. Se ha determinado que los principales problemas asociados son que la elevada higroscopicidad del proceso, la elevada viscosidad y también la dificultad para recuperar el líquido iónico puro y reciclarlo.

- Se ha determinado experimentalmente la influencia del contenido de agua en la viscosidad de dos de los líquidos iónicos más característicos en el tratamiento de celulosa con líquidos iónicos, cloruro de 1-alil-3metilimidazolio y acetato de 1-etil-3-metilimidazolio en un rango de temperaturas de 298.15 a 373.15 K, a presión atmosférica y para fracciones molares de agua menores de 0.35.
  La viscosidad del acetato de 1-etil-3-metilimidazolio disminuye con el contenido de agua a 298.15 K baja de 124 a 75 mPa·s y a 373.15 de 8.19 a 6.47 mPa·s. La densidad aumenta ligeramente con la fracción molar de agua a 298.15 K desde 1.0983 a 1.1018 g/cm^3 y a 373.15 K desde 1.0538 a 1.0571 g/cm^3. Los valores de viscosidad y densidad obtenidos son consistentes con los datos experimentales existentes. En el caso del cloruro de 1-alil-3metilimidazolio, la viscosidad también disminuye con el contenido de agua, a 298.15 K desde 22.21 a 10.98 mPa·s y la densidad, al contrario de lo que sucedía con el otro líquido iónico, disminuye ligeramente, a 298.15 K de 1.1459 a 1.1430 g/cm^3 y a 373.15 K de 1.1036 a 1.1009 g/cm^3. Los datos presentan inconsistencias con los escasos datos presentes en bibliografía.

Se han obtenido volúmenes molares de exceso negativos y se han correlacionado además datos bibliográficos de agua + cloruro de 1-alquilo-3-metilimidazolio y de etanol + acetato de 1-etil-3metilimidazolio. Los datos se ajustan y reproducen bien datos de otros líquidos iónicos obteniendo desviaciones medias menores de un 15% en la mayoría de los casos.

- En el capítulo 3 se propuso la utilización de líquidos iónicos próticos para el tratamiento de celulosa debido principalmente a su reciclabilidad. Se consiguió sintetizar un nuevo líquido iónico prótico capaz de procesar celulosa en condiciones suaves. [dbnH][MeOAc] es capaz de disolver hasta un 10%wt de celulosa en 3h a 40 ºC. La celulosa puede ser recuperada por precipitación sin que se produzca ningún cambio ni en su estructura ni en su grado de polimerización. Además también es posible sintetizar acetato de celulosa con un grado de sustitución de 1.9 a 40 ºC en 24 h.

- Se propuso el uso de CO_2 como co-solvente como solución a la elevada viscosidad de los líquidos iónicos utilizados en el tratamiento de celulosa. Para ello se estudió experimentalmente la influencia del CO_2 en diversos tratamientos de celulosa. Se eligió como LI el cloruro de 1-butil-3-metilimidazolio [bmim][Cl] porque ya se ha demostrado su capacidad para disolver celulosa y porque presenta elevada viscosidad y punto de fusión, por tanto se consideró que una reducción de viscosidad sería más apreciable en este líquido iónico. La viscosidad del [bmim][Cl] a 303.15 K es de 11000 mPa·s mientras que otros líquidos iónicos, también usados en el tratamiento de celulosa son menos viscosos: el cloruro de 1-alil-3metilimidazolio [amim][Cl] y el acetato de 1-etil-3metilimidazolio [emim][Ac], ambos estudiados en el capítulo 2, presentan una viscosidad a 298.15 K de 1884 mPa·s y de 124 mPa·s respectivamente.

- Las principales propiedades físicas del cloruro de 1-butil-3-metilimidazolio [bmim][Cl], se recopilaron de bibliografía y se estudiaron experimentalmente. Este líquido iónico presenta un punto de fusión de unos 340.6 K y los valores experimentales de viscosidad y densidad disminuían al aumentar la temperatura y eran similares a los obtenidos por otros autores. Se obtuvieron valores de viscosidad que variaban desde los 5194.23 mPa·s a 308.15 K hasta los 56.71

mPa·s a 383.15 K. La densidad oscilaba entre 1.0762 g/cm^3 a 308.15 K y 1.0354 g/cm^3 a 383.15 K.

- Se analizó la influencia del uso de CO_2 como co-solvente en dos procesos de tratamiento de celulosa en [bmim][Cl]. Se analizaron los procesos de hidrólisis y acetilación:
    - Se determinó que el CO_2 no inducía la precipitación de una solución de 5%wt de celulosa en una atmósfera de CO_2 de hasta 60 bar.
    - La presencia de CO_2 no mejoró el proceso de hidrólisis utilizando resina Amberlyst como ácido. Se obtuvieron valores similares de conversión de celulosa y de producción de azúcares totales reducidos trabajando en ausencia y en atmósfera de CO_2. De hecho en el rango entre 1 y 15 bar la conversión de celulosa es del 85% y a 45 bar baja hasta un 65 %.
    - La producción de acetato de celulosa en cloruro de 1-butil-3-metilimidazolio utilizando anhídrido acético como reactivo acetilante se ve perjudicada por la presencia de CO_2, obteniéndose tan solo grados de sustitución de 1.17 en 7 h trabajando a 80 ºC y 50 bar. Esto puede deberse a la solubilidad del anhídrido acético en CO_2, 70% mol a 80 ºC y 40 bar, lo que hace puede hacer que el reactivo se distribuya entre las diferentes fases, otra hipótesis es que el CO_2 produzca otro efecto en la reacción. Aún así, los experimentos llevados a cabo en esta tesis no son suficientes para explicar la razón por la que el CO_2 empeora la conversión de esta reacción.

5. TRABAJO FUTURO

- Determinar experimentalmente la viscosidad de otros líquido iónicos utilizados en el tratamiento de biomasa con agua, CO_2 y otros co-solventes y realizar un estudio comparativo de la reducción de viscosidad producida por el agua y por el CO_2.

- Completar el estudio del líquido iónico obtenido en el capítulo 3, [dbnH][MeOAc] para comprobar el alto rendimiento de recuperación y su grado de reciclabilidad. También es necesario ampliar el estudio de este líquido iónico y su aplicación en otros procesos como el pretratamiento de material lignocelulósico y, por ejemplo, estudiar la solubilidad del CO_2 en él.

- Desarrollar una celda de equilibrio a alta presión para poder determinar experimentalmente la solubilidad del CO_2 y de otros gases en diferentes líquidos iónicos. Durante la realización de esta tesis se llevaron a cabo medidas de solubilidad de CO_2 en [bmim][Cl], en una celda de equilibrio de volumen constante, basadas en la determinación de la disminución de presión causada por la disolución del gas en el LI. La celda de equilibrio de volumen constante fue diseñada y construida en nuestro grupo pero los resultados no se han mostrado porque no eran ni reproducibles ni eran del orden de los obtenidos por Jang et al. Se diseñó otro recipiente más sencillo, pero es necesario desarrollar un nuevo método de calibración más exacto del método de adición de CO_2 ya que era uno de los principales problemas que surgieron.

- Para entender mejor el posible efecto de la disolución de parte de anhídrido acético en el CO_2 sería necesario estudiar la reacción en una sola fase en una celda de equilibrio de volumen variable.

- Continuar el estudio del uso de [bmim][Cl] y otros líquidos iónicos en procesos de disolución de biomasa en ausencia y en presencia de CO_2. Durante la realización de esta tesis se llevaron a cabo diferentes tipos de experimentos de disolución de celulosa (pastillas, algodón, polvo…) y en muchos casos se formaba una capa de líquido iónico alrededor de la celulosa impidiendo su disolución en el líquido iónico. Este fenómeno se observó también en los experimentos de disolución llevados a cabo en el aparato B (descrito en el capítulo 5), donde se consiguieron disoluciones muy rápidas (en algunos casos en menos de 1h). Este fenómeno no pudo cuantificarse ya que no conseguimos reproducibilidad.

- Para validar el método FTIR de determinación del grado de sustitución del acetato de celulosa debería haberse comparado con otros métodos cuantitativos muy extendidos como son la titración o el ^{1}H NMR.

- Determinar de forma más detallada los compuestos obtenidos durante el proceso de hidrólisis. Durante la realización de este trabajo se llevaron a cabo diferentes análisis de HPLC con diferentes columnas pero los resultados obtenidos no eran ni reproducibles ni consistentes. Habría que continuar con este estudio.

Acknowledgements

“On ne voit bien
qu´avec le coeur.
L´essentiel
est invisible
pour
les yeux”

El Principito
Antoine de Saint Exupéry

Acknowledgements

I would like to thank the Spanish Economy and Competitiveness Ministry for the predoctoral grant BES-2011-046496, the National Project: “Despolimerizacion y valorizacion de biomasa para la obtencion de compuestos de alto valor añadido. Estudio de la disolucion e hidrolisis de biomasa en agua supercrítica” and Junta de Castilla y León for the Project:VA295U14

About the author

Cristina Jiménez de la Parra. Chemical Engineer
https://es.linkedin.com/in/cristinajimenezdelaparra
crisbaterna@gmail.com

Cristina was born in 1984 in Ávila, and lived in Baterna (Ávila) a small and nice village till 2002 when she moved out to Valladolid to begin her degree in Chemical Engineer. In 2007/2008 she got a scholarship in the Erasmus Program and went to Wageningen, The Netherlands, to carry out her master thesis with the topic "Effect of high salinity wastewater on extracellular polymeric substances production in UASB reactors fed with defined substrates". She completed her Master at Chemical Engineering in 2008 and from 2009 to 2010 she worked as Researcher at the High Pressure Process Group at the University of Valladolid working in the topic of supercritical water oxidation and coursed a Master's Degree in Research into Fluid Thermodynamic Engineering. In August 2011 she started the PhD in the same group with the topic "Study of the improvement of cellulose processing using ionic liquids" in 2013 she went for a 4 months stay to Queen´s University Ionic Liquids Laboratory (QUILL) in Belfast, UK. In 2015 she worked as Process Engineer at Envirohemp, an SME situated in Tudela de Navarra (Spain) where she was the technical responsible to set up a pilot plant for activated carbon production. She is currently studying a specialization course about metal stamping and metallurgic at IK4 Azterlan in Bizkaia.

RESEARCH PAPERS

1. S.B. Ismail, C.J. de La Parra, H. Temmink, J.B. van Lier "Extracellular polymeric substances (EPS) in upflow anaerobic sludge blanket (UASB) reactors operated under high salinity conditions" Water Research, 44 (2010) 1909–1917.

2. M.D. Bermejo, P. Cabeza, M. Bahr, R. Fernández, V. Ríos, C. Jiménez, M.J. Cocero "Experimental study of hydrothermal flames initiation using different static mixer configurations" J Supercrit Fluids, 50 (2009) 240-249.

3. M.D. Bermejo, P. Cabeza, J.P.S. Queiroz, C. Jiménez, M.J. Cocero. "Analysis of the Scale up of a Transpiring Wall Reactor with a Hydrothermal Flame as a Heat Source for the Supercritical Water Oxidation" J Supercritical Fluids, 56 (2011) 21–32.

4. P. Cabeza, M.D. Bermejo, C. Jiménez, M. J. Cocero. “Experimental Study of the Supercritical Water Oxidation of Recalcitrant Compounds under Hydrothermal Flames Using Tubular Reactors” Water Research , 45(2011), 2485-95.

5. M.D. Bermejo, C. Jiménez, P. Cabeza, A. Matias-Gago, M.J. Cocero. “Experimental study of hydrothermal flames formation using a tubular injector in a refrigerated reaction chamber. Influence of the operational and geometrical parameters”J Supercritical Fluids, 59 (2011), 140– 148.

6. C. Jiménez, A. Navarrete, M.D. Bermejo, M.J. Cocero. “Patents Review on Lignocellulosic Biomass Processing Using Ionic Liquids”. Recent Patents on Engineering, 6, (2012), 159-181.

7. P. Cabeza, J.P.S Queiroz, S. Arca, C. Jiménez, A. Gutiérrez, M.D. Bermejo, M.J. Cocero. “Sludge destruction by means of a hydrothermal flame. Optimization of ammonia destruction conditions” Chemical Engineering Journal, 232 (2013), 1–9.

8. C. Jiménez de la Parra, J.R. Zambrano, M.D. Bermejo, A. Martín, J.J. Segovia , M José Cocero. “Influence of Water Concentration in the Viscosities and Densities of Cellulose Dissolving Ionic Liquids. Correlation of viscosity data” J Chem Therm 91 (2015), 8-16.

9. P. Cabeza, J.P.S Queiroz, M. Criado, C. Jiménez, M.D. Bermejo, F. Mato, M.J. Cocero. “Supercritical water oxidation for energy production by hydrothermal flame as internal heat source. Experimental results and energetic study” Energy 90 (2015), 1584–1594.

CONTRIBUTION TO CONFERENCES.

Oral Communications as speaker

1. **10th RBB Renewable Resources and Biorefineries”** Valladolid, Spain. C. Jiménez, N.V. Plechkova, H.Q.N. Gunaratne, M.D. Bermejo, K.R. Seddon, M.J. Cocero “Cellulose Dissolution in Protic Ionic Liquids” 4-6 June 2014.
2. **II International Seminar on Engineering Thermodynamics of Fluids,** Universitat Rovira i Virgili, Tarragona, Spain. M. B. Bermejo, C. Jiménez, P. Cabeza, A. Matías, M.J. Cocero. 22-23 July 2010

Oral Communications

1. **Water & Industry 2011 IWA,** Valladolid, Spain. P. Cabeza, M. D. Bermejo, S. Arca, C. Jiménez, M. J. Cocero ”Experimental Study of the Destruction Wastewaters with High Ammonia Concentrations by SCWO in a Vessel Reactor as Preliminary Step for the Treatment of Waste Water Treatment Plant Sludge” 1-4 May 2011
2. **12th European Meeting On Supercritical Fluids**, Graz, Austria. P. Cabeza, M.D. Bermejo C. Jiménez, J. P. Silva, M.J. Cocero “Experimental study of the hydrothermal flame formation and behavior in a vessel reactor for supercritical water oxidation” 9-12 May 2010.
3. **Prosciba,** Natal, Brasil, J.P. Silva, M.D. Bermejo, P. Cabeza, C. Jiménez, M.J. Cocero “Behavior of SCWO Vessel Reactors with a Hydrothermal Flame: Modeling and Experimental results” 5-9 April 2010

4. **Proceedings of SENSE symposium on: Innovative Techniques for a Sustainable Environment,** Wageningen, Netherland. S. Ismail, C. Jiménez, H. Temmink, J.Van Lier “Effects of high salinity on extracellular polymeric substances: production and function in methanogenic granular sludge” 19-20 February 2009.

Poster

1. **X Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design**, Alicante, Spain, C. Jiménez, J. R. Zambrano, M. D. Bermejo, A. Martín, M.J. Cocero, J. J. Segovia “Influence of water concentration in the viscosities and densities of cellulose dissolving ionic liquids” 28 June-1 july 2015

2. **EXIL Workshop 2014. Liquid/liquid extraction with ionic Liquids.** IPHC Strasbourg (France). C. Jiménez, M.D. Bermejo, M.J. Cocero, ”Study the use of CO_2 for enhance biomass treatment in ionic liquids” April 24 – 26, 2014

3. **VI reunión de Expertos en Tecnología de Fluidos Comprimidos**, Madrid Spain. P. Cabeza, C. Jiménez, J. P. Silva, M. Criado, M.D. Bermejo, M.J. Cocero “Nuevo diseño de reactor para mejorar el aprovechamiento energético del proceso de oxidación en agua supercrítica en presencia de llama hidrotermal”, June 2012

4. **13th European Meeting on Supercritical Fluids**, The Hague, Netherlands, P. Cabeza, M.D. Bermejo, C. Jiménez, J. P. Silva, M.J. Cocero “Experimental study of the viability of the destruction of different kind of waste by supercritical water oxidation at hydrothermal flame regime” 9-12 October 2011

5. **13th European Meeting on Supercritical Fluids**, The Hague, Netherlands, J. P. Silva, M.D. Bermejo, P. Cabeza, C. Jiménez, M.J. Cocero “Numerical study of the influence of geometrical and operational parameters in behavior of a hydrothermal flame in vessel reactor” 9-12 October 2011

6. **8th European Conference in Chemical Engineering (ECCE)** Berlín, Germany. M.D. Bermejo, J. P. Silva, P. Cabeza, C. Jiménez, A. Gutiérrez, M.J. Cocero "Novel Vessel Reactor for Energy Production by Means of a Hydrothermal Flame" 26-29 September 2011.

7. **V Reunión de expertos en Tecnologías de Fluidos Comprimidos**, Burgos, Spain. P. Cabeza, C. Jiménez, M. D: Bermejo, S. Arca, A. Gutierrez, M.J. Cocero "Destrucción de diferentes aguas residuales por oxidación en agua supercrítica usando un reactor de tanque con llama hidrotermal" 15-17 June 2011

8. **IV Reunión de expertos en Tecnologías de Fluidos Comprimidos**, Ciudad Real, Spain. Castilla-La Mancha Oxidación en agua supercrítica con reactores de tanque en régimen de llama hidrotermal" M. D. Bermejo, P. Cabeza, J.P. Silva, C. Jiménez, A. Matías, M.J. Cocero, 10-12 February 2010.

9. **Supergreen,** Sendai, Japan. M.D. Bermejo, P. Cabeza, J.P. Silva, C. Jiménez, M.J. Cocero "Water Oxidation in Vessel Reactors with a Hydrothermal Flame Inside" 15-17 October 2009.

SHORT INTERNSHIPS IN OTHER RESEARCH CENTERS

Queen´s University of Belfast, UK. Queen´s University Ionic Liquids Laboratory (QUILL) (Prof. Kenneth Richard Seddon)

- Protic Ionic Liquids for biomass treatment
- 4 months stay (July- October 2013)

Wageningen University, **Netherlands**. Sub-department of Environmental Technology (Prof. Jules Van Lier)

- Topic: "Effect of high salinity wastewater on extracellular polymeric substances production in UASB reactors fed with defined substrates".
- 9 month stay (Sept 2007-July 2008) Erasmus Program.