

Solvation of Starch by Ionic Liquid

Monika Knotková

Bachelor thesis
2012



Tomas Bata University in Zlín
Faculty of Technology

Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů

akademický rok: 2011/2012

ZADÁNÍ BAKALÁŘSKÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Monika KNOTKOVÁ**

Osobní číslo: **T090035**

Studijní program: **B 2808 Chemie a technologie materiálů**

Studijní obor: **Chemie a technologie materiálů**

Téma práce: **Solvatace škrobu pomocí iontových kapalin.**

Zásady pro vypracování:

I. Teoretická část

1. Charakterizace iontových kapalin.
2. Charakterizace škrobu.
3. Vybraná metoda stanovení a její popis.

II. Praktická část

1. Solvatace škrobu iontovými kapalinami.



Rozsah bakalářské práce:

Rozsah příloh:

Forma zpracování bakalářské práce: **tištěná/elektronická**

Seznam odborné literatury:

[1] Bastioli, C. (2005). Handbook of Biodegradable Polymers. Smithers Rapra Technology.

[2] Endres, H. J.; Siebert-Raths, A. (2011). Engineering Biopolymers - Markets, Manufacturing, Properties and Applications. Hanser Publishers.

[3] Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to applications, Appl. Catal. A-Gen. 373 (2010) 1?56.

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

Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. Chem. Soc. Rev. 37 (2008) 123?150.

[5]

http://www.knovel.com/web/portal/browse/display_EXT_KNOVEL_DISPLAY_bookid=4223&VerticalI

Vedoucí bakalářské práce:

doc. Ing. Roman Čermák, Ph.D.

Ústav inženýrství polymerů

Datum zadání bakalářské práce:

10. února 2012

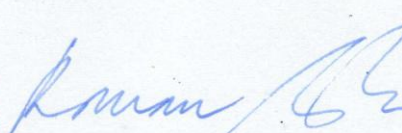
Termín odevzdání bakalářské práce:

1. června 2012

Ve Zlíně dne 10. února 2012


doc. Ing. Roman Čermák, Ph.D.
děkan




doc. Ing. Roman Čermák, Ph.D.
ředitel ústavu

Příjmení a jméno: Monika Knotková

Obor: Polymerní materiály

PROHLÁŠENÍ

Prohlašuji, že

- beru na vědomí, že odevzdáním diplomové/bakalářské práce souhlasím se zveřejněním své práce podle zákona č. 111/1998 Sb. o vysokých školách a o změně a doplnění dalších zákonů (zákon o vysokých školách), ve znění pozdějších právních předpisů, bez ohledu na výsledek obhajoby¹⁾;
- beru na vědomí, že diplomová/bakalářská práce bude uložena v elektronické podobě v univerzitním informačním systému dostupná k nahlédnutí, že jeden výtisk diplomové/bakalářské práce bude uložen na příslušném ústavu Fakulty technologické UTB ve Zlíně a jeden výtisk bude uložen u vedoucího práce;
- byl/a jsem seznámen/a s tím, že na moji diplomovou/bakalářskou práci se plně vztahuje zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, zejm. § 35 odst. 3²⁾;
- beru na vědomí, že podle § 60³⁾ odst. 1 autorského zákona má UTB ve Zlíně právo na uzavření licenční smlouvy o užití školního díla v rozsahu § 12 odst. 4 autorského zákona;
- beru na vědomí, že podle § 60³⁾ odst. 2 a 3 mohu užít své dílo – diplomovou/bakalářskou práci nebo poskytnout licenci k jejímu využití jen s předchozím písemným souhlasem Univerzity Tomáše Bati ve Zlíně, která je oprávněna v takovém případě ode mne požadovat přiměřený příspěvek na úhradu nákladů, které byly Univerzitou Tomáše Bati ve Zlíně na vytvoření díla vynaloženy (až do jejich skutečné výše);
- beru na vědomí, že pokud bylo k vypracování diplomové/bakalářské práce využito softwaru poskytnutého Univerzitou Tomáše Bati ve Zlíně nebo jinými subjekty pouze ke studijním a výzkumným účelům (tedy pouze k nekomerčnímu využití), nelze výsledky diplomové/bakalářské práce využít ke komerčním účelům;
- beru na vědomí, že pokud je výstupem diplomové/bakalářské práce jakýkoliv softwarový produkt, považují se za součást práce rovněž i zdrojové kódy, popř. soubory, ze kterých se projekt skládá. Neodevzdání této součásti může být důvodem k neobhájení práce.

Ve Zlíně 23. 8. 2012


.....

¹⁾ zákon č. 111/1998 Sb. o vysokých školách a o změně a doplnění dalších zákonů (zákon o vysokých školách), ve znění pozdějších právních předpisů, § 47 Zveřejňování závěrečných prací:

(1) Vysoká škola nevýdělečně zveřejňuje disertační, diplomové, bakalářské a rigorózní práce, u kterých proběhla obhajoba, včetně posudků oponentů a výsledku obhajoby prostřednictvím databáze kvalifikačních prací, kterou spravuje. Způsob zveřejnění stanoví vnitřní předpis vysoké školy.

(2) Disertační, diplomové, bakalářské a rigorózní práce odevzdané uchazečem k obhajobě musí být též nejméně pět pracovních dnů před konáním obhajoby zveřejněny k nahlížení veřejnosti v místě určeném vnitřním předpisem vysoké školy nebo není-li tak určeno, v místě pracoviště vysoké školy, kde se má konat obhajoba práce. Každý si může ze zveřejněné práce pořizovat na své náklady výpisy, opisy nebo rozmnoženiny.

(3) Platí, že odevzdáním práce autor souhlasí se zveřejněním své práce podle tohoto zákona, bez ohledu na výsledek obhajoby.

²⁾ zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, § 35 odst. 3:

(3) Do práva autorského také nezasahuje škola nebo školské či vzdělávací zařízení, užije-li nikoli za účelem přímého nebo nepřímého hospodářského nebo obchodního prospěchu k výuce nebo k vlastní potřebě dílo vytvořené žákem nebo studentem ke splnění školních nebo studijních povinností vyplývajících z jeho právního vztahu ke škole nebo školskému či vzdělávacímu zařízení (školní dílo).

³⁾ zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, § 60 Školní dílo:

(1) Škola nebo školské či vzdělávací zařízení mají za obvyklých podmínek právo na uzavření licenční smlouvy o užití školního díla (§ 35 odst. 3). Odpírá-li autor takového díla udělit svolení bez vážného důvodu, mohou se tyto osoby domáhat nahrazení chybějícího projevu jeho vůle u soudu. Ustanovení § 35 odst. 3 zůstává nedotčeno.

(2) Není-li sjednáno jinak, může autor školního díla své dílo užít či poskytnout jinému licenci, není-li to v rozporu s oprávněnými zájmy školy nebo školského či vzdělávacího zařízení.

(3) Škola nebo školské či vzdělávací zařízení jsou oprávněny požadovat, aby jim autor školního díla z výdělku jím dosaženého v souvislosti s užitím díla či poskytnutím licence podle odstavce 2 přiměřeně přispěl na úhradu nákladů, které na vytvoření díla vynaložily, a to podle okolností až do jejich skutečné výše; přitom se přihlídáne k vyšší výdělku dosaženého školou nebo školským či vzdělávacím zařízením z užití školního díla podle odstavce 1.

ABSTRAKT

Iontové kapaliny používané pro rozpouštění celulózy získávají v posledních letech rostoucí pozornost, ale množství odborných článků zabývajících se použitím iontových kapalin pro škrob je stále omezené. V této práci bylo použito třináct iontových kapalin s odlišnými kationty a anionty pro rozpouštění škrobu. Rozpouštění kukuřičného, pšeničného a kasavového škrobu pomocí iontových kapalin založených na imidazoliu, amoniu, fosfoniu a choliniu bylo kvalitativně studováno a porovnáno s želatinačním procesem ve vodě. Přítomnost vody v systému iontová kapalina – škrob, byla zkoumána v závislosti na teplotě, při které nastalo rozpouštění.

Byly použity iontové kapaliny s kationty jako 1-butyl-3-methylimidazolium, N, N – dimethyl – N - (2-hydroxyethyl) amonium, trihexyl (tetradecyl) fosfonium, 1-ethyl-3-methylimidazolium, propylcholinium, trimethylbutylamonium a anionty jako levulinát, acetát, methyl fosfit, dimethyl fosfát, methyl sulfát, chlorid, tetrachloroaluminát, bis (trifluoromethansulfonyl) imid, ethylsulfát, triflát.

Rozpustnost škrobu byla zkoumána pomocí optického mikroskopu s vyhřívaným stolcem. U iontových kapalin, ve kterých byl škrob rozpustný, byla určena hustota, viskozita a tepelné vlastnosti. Entalpie rozpouštění kukuřičného škrobu v 1-butyl-3-methylimidazolium methyl fosfitu byla zkoumána pomocí mikro diferenciálního skenovacího kalorimetru. Reologické vlastnosti 1-butyl-3-methylimidazolium methyl fosfitu a směsi 1-butyl-3-methylimidazolium methyl fosfit - kukuřičný škrob a 1-butyl-3-methylimidazolium methyl fosfit - kukuřičný škrob - voda byly zkoumány pomocí reometru.

Klíčová slova: iontová kapalina, škrob, rozpouštění, hustota, viskozita, tepelné vlastnosti, reologické vlastnosti, entalpie rozpouštění, želatinace, diferenciální skenovací kalorimetr, optický mikroskop

ABSTRACT

Ionic liquids (ILs) utilized for cellulose dissolution have gained increasing attention in recent years, but the number of the reports using ILs for starch is still limited. In this study, thirteen ionic liquids with different cations and anions were used to dissolution of starch. Solvation of corn, wheat and cassava starch by ionic liquids based on imidazolium, ammonium, phosphonium and cholinium was qualitatively studied and compared with gelatinization process in water. Presence of water in the system ionic liquid – starch was also examined in dependence of temperature at which dissolution occurred.

Ionic liquids with cations as 1-butyl-3-methylimidazolium, N, N – dimethyl – N - (2-hydroxyethyl) ammonium, trihexyl (tetradecyl) phosphonium, 1-ethyl-3-methylimidazolium, propylcholinium, trimethylbutylammonium and anions as levulinate, acetate, methyl phosphite, dimethyl phosphate, methyl sulfate, chloride, tetrachloroaluminate, bis (trifluoromethanesulfonyl) imide, ethylsulfate, triflate were used.

Solubility of starch was investigated by optical microscope using the hot stage system. Density, viscosity and thermal properties of some ionic liquids capable to dissolve the starch were examined. Enthalpy of dissolution of corn starch in 1-butyl-3-methylimidazolium methyl phosphite was examined by micro differential scanning calorimetry. Rheological properties of 1-butyl-3-methylimidazolium methyl phosphite and mixture 1-butyl-3-methylimidazolium methyl phosphite - corn starch and 1-butyl-3-methylimidazolium methyl phosphite - corn starch - water were examined by rheometer.

Keywords: ionic liquid, starch, dissolution, density, viscosity, thermal properties, rheological properties, enthalpy of dissolution, gelatinization, differential scanning calorimetry, optical microscopy

ACKNOWLEDGEMENTS

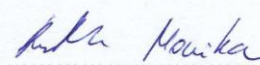
I would like to thank to supervisor of my bachelor thesis Roman Čermák for mentoring, for assistance, for time that gave me during my traineeship and for guidance and help during writing.

This study was performed in cooperation with institution Ecole Nationale Supérieure de Chimie de Clermont-Ferrand in France. I would like to thank to coordinators of this project, Margarida Costa Gomes, Sophie Commereuc, Vincent Verney for mentoring during my traineeship, working on experiments and writing science article.

This study was financially supported by Tomas Bata University in Zlin, Faculty of Technology.

I hereby declare that the print version of my Bachelor's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

In Zlín: 23. 8. 2012


.....

CONTENTS

INTRODUCTION	55
I. THEORY	11
1 IONIC LIQUIDS	12
1.1 PROPERTIES AND SYNTHESIS OF ILS	13
1.2 APPLICATIONS OF IONIC LIQUIDS	18
2 STARCH	21
2.1 PROPERTIES OF STARCH	22
2.2 APPLICATION OF STARCH	28
3 SOLVATION OF STARCH	30
3.1 SOLVATION OF STARCH IN CONVENTIONAL SOLVENTS	30
3.2 SOLVATION OF STARCH IN IONIC LIQUIDS	30
II. ANALYSIS	32
4 EXPERIMENT INTRODUCTION	33
MATERIALS	33
METHODS	37
<i>OPTICAL MICROSCOPY</i>	37
<i>DENSIMETRY</i>	37
<i>VISCOMETRY</i>	38
<i>KARL FISCHER COULOMETRY</i>	40
<i>DIFFERENTIAL SCANNING CALORIMETRY</i>	40
<i>MICRO DIFFERENTIAL SCANNING CALORIMETRY</i>	41
5 RESULTS AND DISCUSSION	42
CONCLUSION	54
BIBLIOGRAPHY	55
LIST OF ABBREVIATIONS	58
LIST OF FIGURES	59
LIST OF TABLES	60

INTRODUCTION

Starch is the most abundant reserve carbohydrate in plants [Kaur et al., 2004]. From availability point of view, the starch occupies the second place, after the cellulose. The most industrial sources of starch are corn, wheat, potato, tapioca and rice. Starches from different botanical sources, growing conditions, mutations, or maturity can vary in their chemical structures and physicochemical properties. Starch is mainly composed of a mixture of amylose and amylopectin [Kuakpetoon & Wang, 2007]. Amylose and amylopectin have different structures and properties. Amylose is relatively long, linear α -glucan. Amylose has a molecular weight of approximately $1 \times 10^5 - 1 \times 10^6$. Amylopectin is a much larger molecule than amylose with a molecular weight of $1 \times 10^7 - 1 \times 10^9$ and a heavily branched structure [Karkalas et al., 2004].

Ionic liquids (ILs) are salts having a melting point below 100 °C. ILs typically consist of bulky organic cations and inorganic anions. The constituents of ILs are constrained by high coulombic forces, exhibiting practically no vapor pressure. This unique property gives them the capability to expand traditional laws of chemistry [Depaoli, 2003]. For nearly two dozens of years ILs attract the quickly growing attention due to outstanding properties: negligible vapor pressure, excellent thermal stability, wide interval of hydrophilic-hydrophobic balance, good dissolution properties with many organic and inorganic compounds including polymers or cellulose, and low flammability [Aslanov, 2011].

A growing interest in applying ILs as polysaccharide solvent has been observed. ILs are good solvents and can dissolve various substances including biomass (cellulose, lignin, wood, chitin, starch). Most publications are focused mainly on cellulose, lignin, monosaccharides, different kinds of polysaccharides or on wood dissolution [Biswas et al., 2009; Blanch et al., 2011; Carneiro et al., 2012; Chen & Feng, 2008]. Solubility of starch depends on structure of ILs, temperature, starch origin and content of amylose and amylopectin in starch.

The aim of the present work is to study dissolution of six kinds of starches in thirteen ILs and enthalpy of starch dissolution in ionic liquid.

I. THEORY

1 IONIC LIQUIDS

Ionic liquids (ILs) having a melting point below 100 °C have recently attracted considerable attention as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic, and electrochemical applications. ILs are salts that typically consist of bulky organic cations and inorganic anions. These ionic solvents are composed entirely of ions. The constituents of ILs are constrained by high coulombic forces, exhibiting practically no vapor pressure. This unique property gives them the capability to expand traditional laws of chemistry. For example, these liquids are highly polar, yet noncoordinating (ideal for catalytic reactions), they can be made immiscible with water and/or a number of organic solvents (providing flexibility for a number of reaction and separation schemes), and they are nonvolatile even at elevated temperatures. The physical and chemical properties (e.g. density, conductivity, viscosity, Lewis acidity, hydrophobicity, and hydrogen-bonding capability) of ILs can be tuned by varying the structure of the component ions to obtain desired solvent properties [Depaoli, 2003].

In the opinion of many researchers, investigations of ILs would be more fruitful if the principles of structure formation for ILs were known. Some results of the ionic liquid (IL) structure investigations were published during last decade, but regular investigations of IL structures started since 2005 after development of empirical potentials for molecular dynamics simulations, which are appropriate to ionic interactions in ILs [Aslanov, 2011].

The earliest discovery of an IL can be dated to the middle of the nineteenth century, when some 'red oil' was observed in a Friedel-Crafts reaction. A few decades later, in 1914, the first room-temperature IL ethylammonium nitrate, $[\text{EtNH}_3][\text{NO}_3]$, was synthesized. In 1951 AlCl_3 -based ILs were developed by Hurley and Wier at Rice Institute in Texas as a bath solution for electroplating aluminium. In 1963 the U.S. Air Force Academy became interested in that work and developed it further with the aim of finding new electrolytes for batteries. In the 1970s Osteryoung and Wilkes succeeded in preparing room-temperature liquid chloroaluminate melts. In the 1980s Hussey and Seddon started to use these alkylpyridinium tetrahalidoaluminate, $[\text{Rpy}][\text{AlCl}_3\text{X}]$, ILs as solvents in transition metal complex studies. The first organic reaction that was carried out in an acidic tetrachloroaluminate IL was Friedel-Crafts alkylation, and since then ILs have been used as reaction solvents in various organic reactions. The first generation of ILs that contain

aluminium are very hygroscopic and air-sensitive, and therefore they are not easy to handle. A few years later this problem was solved when new air- and water-stable anions, such as halides, $[\text{PF}_6]^-$, $[\text{BF}_4]^-$ and $[\text{CF}_3\text{CO}_2]^-$, were discovered by Wilkes and Zaworotko. Since then, a wide selection of different ILs has been synthesized. These ILs are the second generation of ILs [Karkkainen, 2007].

1.1 Properties and synthesis of ILs

An IL is formed from organic cations and inorganic or organic anions, and it is possible to make even 10^{18} different ILs. Commonly used cations are large and asymmetric, e.g. derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium (Fig. 1). Typical inorganic anions are e.g. halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis (trifluoromethylsulfonyl) imide and typical organic anions are alkylsulfate, alkylsulfonate, p-toluenesulfonate (tosylate) and trifluoroacetate (Fig. 2) [Karkkainen, 2007].

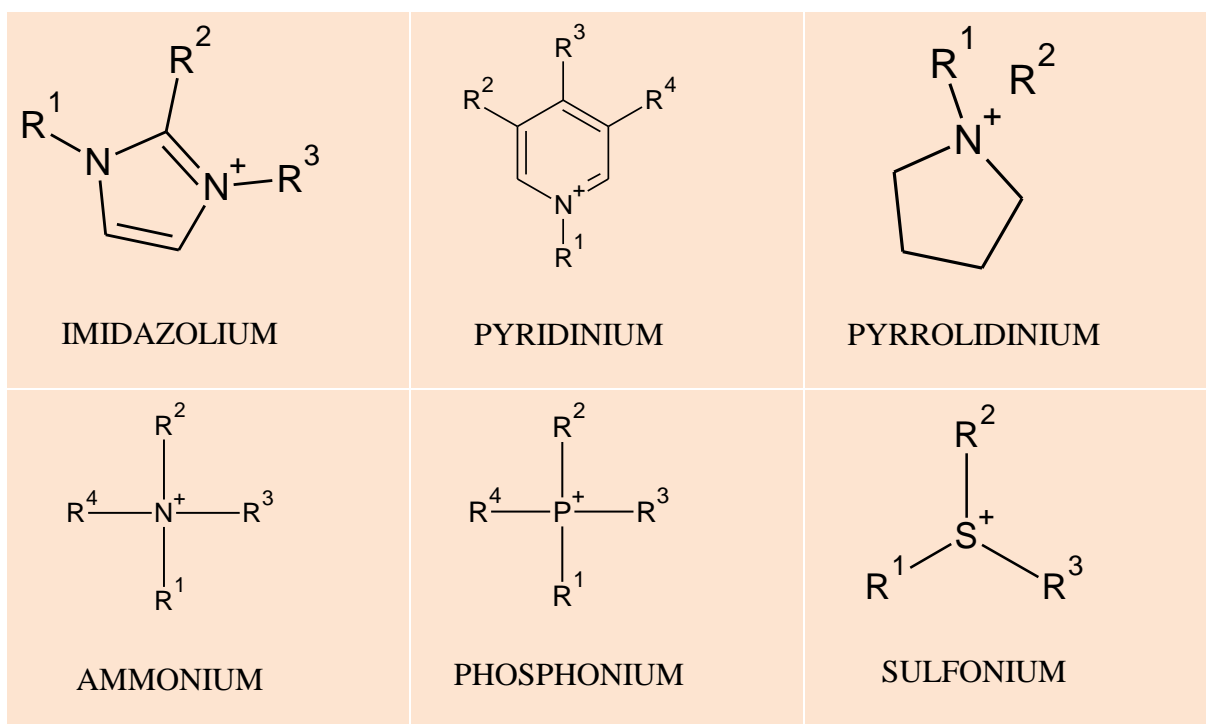


Table 1. Commonly used cations in ILs [Karkkainen, 2007].

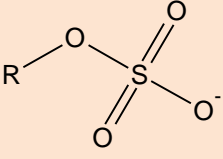
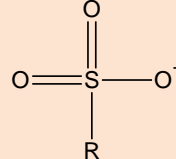
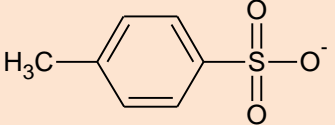
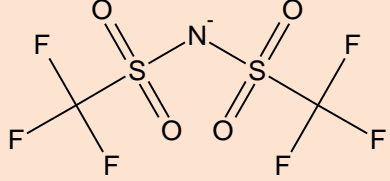
Cl ⁻ Br ⁻ I ⁻ Halides	NO ₃ ⁻ Nitrate	PF ₆ ⁻ Hexafluorophosphate
BF ₄ ⁻ Tetrafluoroborate	AlCl ₄ ⁻ Tetrachloroaluminate	Al ₂ Cl ₇ ⁻
CF ₃ CO ₂ ⁻ Triflate	 Alkylsulfate	 Alkylsulfonate
 Tosylate	 Bis (trifluoromethylsulfonyl) imide	

Table 2. Commonly used anions in ILs [Karkkainen, 2007].

Polymeric ILs are defined as the polymers obtained by polymerization of ILs having polymerizable groups (polymerizable ILs). Thus, ‘polymeric ILs’ are termed just the polymeric forms of ILs, but they are not necessary to show liquid form at room temperature or even at some ambient temperatures. The polymeric ILs, therefore, are often called ‘polymerized ILs’ too. The major advantages for providing the polymeric ILs are to be enhanced stability, and improved processability and feasibility in application as practical materials. Polymerizable ILs as a source of the polymeric ILs can be available by incorporating the polymerizable groups at both anionic and cationic sites in the IL structures. The polymerizable ILs have been employed for the preparation of polysaccharide-polymeric IL composite materials [Kokorin, 2011].

For nearly two dozens of years ILs attract the quickly growing attention due to outstanding properties: negligible vapor pressure, excellent thermal stability, wide interval of hydrophilic-hydrophobic balance, good dissolution properties with many organic and

inorganic compounds including polymers or cellulose, and low flammability [Aslanov, 2011].

ILs are low-melting-point molten salts, defined as which form liquids at room temperature or even at temperatures lower than a boiling point of water. The property is owing to that the liquid state is thermodynamically favorable due to the large size and conformational flexibility of the ions, in which these behaviors lead to small lattice enthalpies and large entropy changes that favor the liquid state. In the past more than a decade, ILs have attracted much attention due to their specific characteristics such as a negligible vapor pressure, excellent thermal stabilities, and controllable physical and chemical properties. Beyond these traditional properties of ILs, recently, interests and applications on ILs have been extended to the researches related to biomolecules such as naturally occurring polysaccharides, because of specific good affinities of ILs for them [Kokorin, 2011].

The structure of the IL cation influences the physical properties of the ILs, such as density and viscosity. Generally, an increase in the alkyl chain length leads to a decrease in the density and an increase in the viscosity of the IL [Kokorin, 2011].

The purity of an IL is of paramount importance, since impurities influence its chemical and physical properties. Prior to use, ILs should be carefully characterized with several methods, such as NMR, MS (ESI⁺ and ESI⁻) and elemental analysis. ILs have a very low vapour pressure and, therefore, cannot be purified by distillation. It is important to use purified starting materials in their preparation in order to get a pure IL. The main contaminants of ILs are halides, water, organic compounds or inorganic salts. The application where an IL will be use determines the level of purity of the IL required. Solid ILs can be characterized by determining their crystal structure, and the determined structures can be found in the Cambridge Crystal Database [Karkkainen, 2007].

Miscibility with water depends on the nature of the IL. Some ILs are totally soluble in water, while others are not miscible at all. Most ILs content some water that might originate from its preparation or purification process. In addition, many ILs are hygroscopic. A large amount of water can be detected by ¹H NMR spectroscopy, and a small amount by using a Karl-Fisher titrator [Karkkainen, 2007].

Water is removed from ILs by heating at 60-80 °C in a high vacuum for at least three hours, preferably overnight. Recently, it has been noticed that some ILs have a tendency to

decompose when heated in the presence of water. For example, ILs that contain hexafluorophosphate ions will form hydrogen fluoride when heated. This can be detected through pH measurement directly from the IL or from aqueous washings. Hydrogen fluoride is toxic, and consequently the use of hexafluorophosphate-based ILs should be avoided [Karkkainen, 2007].

Impurities sometimes affect the coloration of ILs. The chemical nature of coloring impurities is not clear, but they are assumed to be oxidation products or thermal degradation products of starting materials. Even if the amount of the impurity is so small that it cannot be detected by ^1H NMR or CHN microanalysis it might have significance on the application IL is used. Colored impurities can be eliminated by using distilled reagents and a low reaction temperature. Especially amines very easily take on a yellowish color upon standing, but distillation removes the color. When the prepared IL is colored, it can be purified with activated charcoal followed by filtration through activated alumina or silica [Karkkainen, 2007].

Considering the different applications where ILs can be used, it is essential to know their stability. Stability can be evaluated in terms of thermal or chemical reactivity according to the temperatures and reaction conditions they withstand. The stability of ILs also depends on their purity. Especially water and halide impurities will affect physical properties such as density, viscosity, melting point and degradation temperature. In reference to these it can be concluded that impurities also affect chemical properties, and hence thermal stability and reactivity [Karkkainen, 2007].

The thermal stability of an IL is determined by the strength of the formed heteroatom-carbon or heteroatom-hydrogen bonds and the stability of the formed ion species. A N-C bond is stronger than a N-H bond and accordingly, the stability of ammonium cations decreases in the following order: quaternary > tertiary > secondary > primary [Karkkainen, 2007].

The general trend between different cations seems to be that a phosphonium cation is more stable than an imidazolium cation, and an ammonium cation is least stable in terms of thermal degradation. The stability of an imidazolium cation increases when nitrogen atoms and the carbon atom between nitrogens in the ring have alkyl substituents. Stability

increases with straight alkyl chains compared with branched ones, not to mention the hydrogen atom as a substituent [Karkkainen, 2007].

The stability of ILs depends largely on the anion. ILs containing weakly coordinating anions are most resistant to thermal decomposition [Karkkainen, 2007].

The chemical stability of ILs has been studied with acids, bases and some other reagents. An IL is considered to be chemically stable when it does not react or decompose under reaction conditions. Until now, imidazolium-based ILs have been the most studied and used. Research has shown that most imidazolium-based ILs withstand acidic conditions, but not basic ones. The reason is the acidic proton at the carbon atom between nitrogen atoms in the imidazolium ring. Even a mild base can remove it and decompose the IL. Stability towards bases slightly increases when this carbon atom is alkylated. When higher stability is needed, phosphonium-based ILs are a good choice, since they are compatible even with strong bases [Karkkainen, 2007].

The chemical and physical properties of ILs have been studied intensively since their discovery. Diverse modifications of cations and anions have provided ILs with desired properties for many technical applications. Yet, the design of an IL with suitable properties for a specific application in view is not enough, and more attention needs to be paid to the total life-cycle impacts of ILs. Studies on the biodegradation of ILs and their potential accumulation in the environment have begun only recently. Degradation of organic compounds can be either aerobic or anaerobic. In both processes micro-organisms require a source of nitrogen and other essential nutrients in order to decompose an organic substrate into carbon dioxide and water. A difference of the processes is that an aerobic treatment requires a source of oxygen and an anaerobic treatment requires an electron acceptor such as Fe^{3+} [Karkkainen, 2007].

It is very important to develop biodegradable ILs to prevent them from accumulating in the environment [Karkkainen, 2007].

Since certain ILs are highly soluble in water, their release into an aquatic environment may lead to water pollution, but owing to their very low vapour pressure, their accumulation into the atmosphere is not expected [Karkkainen, 2007].

Environmental considerations require the recovery of ILs after their use. ILs are quite expensive, and hence their recycling is also necessary due to economic reasons. Several

procedures for recycling ILs have been reported, and the efficiency of the recycling varies from poor to very good recovery [Karkkainen, 2007].

Typical procedure of synthesis is: into a round bottom flask, anion and cation were added. The reaction was conducted under refluxing for 8-48 h. After reaction, the mixture was extracted with ether for several times to remove the residual cation. The ILs can be obtained after being dried at 80 °C (vacuum: 0.08 MPa) for 24 h (yield: > 90 %) [Kokorin, 2011].

1.2 Applications of Ionic Liquids

ILs are expected as superior environmentally friendly solvents for chemical synthesis, homogeneous catalysis, biocatalysis, separation technologies, nanomaterial preparations, templates for production of porous solids, hydraulic fluids, and lubricants. In addition, the high ionic conductivity and wide electrochemical windows make ILs excellent candidates for electrolytes avoiding corrosion or leakage. Unique collection of IL properties promises wide range of applications of ILs in electrochemical technologies as solvent-free electrolytes in various devices and processes, such as rechargeable lithium batteries, fuel cells, chemical sensors, electrochemical capacitors, dye-sensitized solar cells, and the electrodeposition [Aslanov, 2011].

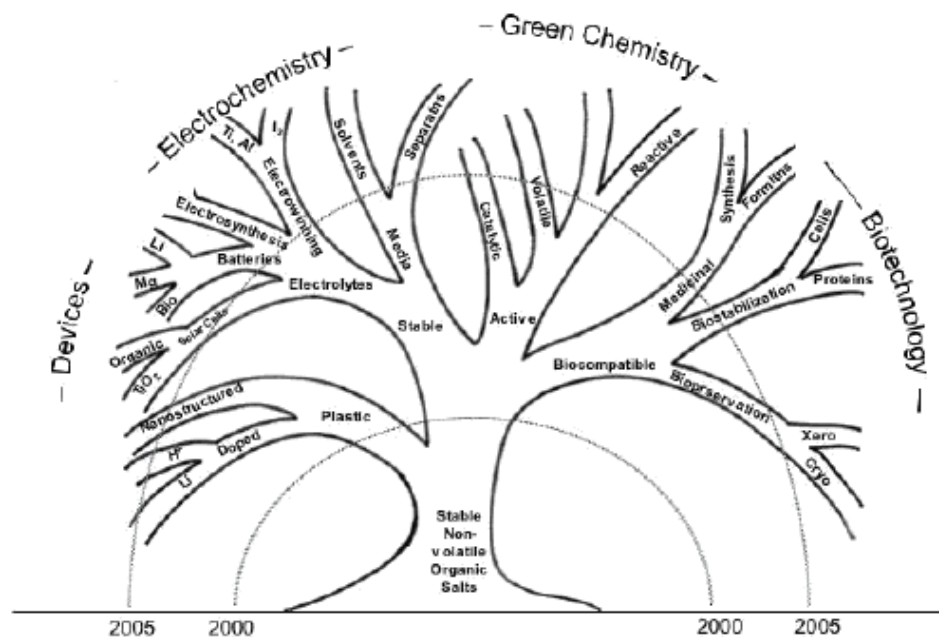


Figure 1. Use of ILs [Lišková, 2008].

Recently, ILs have received worldwide academic and industrial attention as replacements for organic solvents in catalysis. Attractive features of ILs for catalysis include:

- the IL can act as both catalysts and solvent;
- solvation, solvolysis, reaction rates, and selectivity can be increased;
- and side reactions can be reduced [Depaoli, 2003].

The potential to reduce pollution in industrial processes have led to investigations of ILs as alternative reaction media for a variety of application that conventionally use organic solvents [Depaoli, 2003].

Recent efforts by a number of investigators have focused on the application of ILs in separations, typically as replacements for the organic diluents employed in traditional liquid-liquid extraction or in membrane-based separations of organic solutes, metal ions, and gases. ILs exhibit several properties that make them attractive as a potential basis for clean separation processes, among them tenability, negligible vapor pressure, good thermal stability, and a wide liquid range. Although the first air and moisture stable ILs were described in 1992 by Wilkes and Zaworotko, it was not until several years later that their

potential as media in which to effect separations was first recognized. In the past several years, research publications and patent activity related to ionic-liquid-based separations have increased significantly [Depaoli, 2003].

The potential for the use of ILs in the energy sector is present across the board, from nuclear applications to the petroleum industry. ILs may be used to solve some of the outstanding issues in industry, from recovery of useful hydrocarbon fuels from refractory sources to the recycling and minimization of waste. Many of these concepts have been demonstrated on the laboratory scale, but scale up to industrial proportions has not yet been broadly accomplished or reported. The reasons for this are many. One is that the petroleum industry has already implemented measures to minimize waste in production and processing, driven by the economics of handling huge volumes of feedstock and waste. Hence, environmental issues that may drive implementation of technologies based on ILs in other chemical industries, such as pharmaceuticals and the production of fine chemicals, pose a greater challenge in the energy sector. Additionally, concerns about cost and toxicity are magnified when applied to the very large feedstock and waste streams in petroleum processing, and lead to a conservative approach to implementation of new processes. The energy sector, however, has a history of supporting research and development into new approaches to industry problems. This support is likely to continue as the investigations into applications of ILs deal with considerations such as high viscosities, moisture sensitivity, contamination and degradation/regeneration [Depaoli, 2003].

2 STARCH

Polysaccharides are widely distributed in nature and have been regarded as structural materials and as suppliers of water and energy. Natural polysaccharides such as cellulose, starch, chitin, and other many kinds of them have recently received much attention for use as resources of new green and sustainable materials because of their eco-friendly properties. However, the natural polysaccharides have often exhibited solubility, processability, and feasibility problems due to numerous hydrogen bonds in their polymeric chains, causing difficulty in employing them in a wide variety of materials [Kokorin, 2011].

Starch represents a link with the energy of the sun, which is partially captured during photosynthesis. It serves as a food reserve for plants and provides a mechanism by which non-photosynthesising organism, such as man, can utilize the energy supplied by the sun. The most important industrial sources of starch are corn, wheat, potato, tapioca and rice. Today, starch is inexpensive and is available annually from such crops, in excess of current market needs in the United States and Europe [Bastioli, 2005].

Corn production, has risen over time, as higher yields followed improvements in technology and in production practices. Besides starch, corn is also processed by wet millers into high-fructose corn syrup, glucose, dextrose, corn oil, beverage alcohol and fuel ethanol [Bastioli, 2005]. However, starches from different corn types differ widely with respect to the morphological, rheological, functional and thermal properties [Kaur et al., 2004].

Starches from different botanical sources, growing conditions, mutations, or maturity can vary in their chemical structures and physicochemical properties [Kuakpetoon & Wang, 2007]. Starch is the most abundant reserve carbohydrate in plants [Kaur et al., 2004]. Starch is mainly composed of a mixture of amylose and amylopectin [Kuakpetoon & Wang, 2007].

Starch varies greatly in form and functionality between and within botanical species, and even from the same plant cultivar grown under different conditions. This variability provides starches of diverse properties, but it can also cause problems in processing due to inconsistency of raw materials. As a result, chemically modified starches are used

extensively to overcome the variability of native starches and their lack of versatility over a wide range of processing conditions [Blazek et al., 2009].

In the last decade there was a significant decrease in the price of corn and potato starch (in the Europe and the USA); whereas in Europe during the period 1990-2001, the price of wheat starch remained almost unchanged [Bastioli, 2005].

The low price and the availability of starch associated with its very favourable environmental profile in the last 15 years aroused a renewed interest in starch-based polymers as an attractive alternative to polymers based on petrochemicals [Bastioli, 2005].

Starch is totally biodegradable in a wide variety of environments and permits the development of totally degradable products for specific market demands. Degradation or incineration of starch products recycles atmospheric carbon dioxide trapped by starch-producing plants and does not increase potential global warming [Bastioli, 2005].

The most relevant achievements in this sector are related to thermoplastic starch polymers resulting from the processing of native starch by chemical, thermal and mechanical means and to its complexation with other co-polymers: the resulting materials show properties ranging from the flexibility of polyethylene to the rigidity of polystyrene, and can be soluble or insoluble in water as well as insensitive to humidity. Such properties explain the leading position of starch-based materials in the bio-based polymers market [Bastioli, 2005].

2.1 Properties of starch

Starch is the main storage carbohydrate of plants. It is deposited as insoluble, semi-crystalline grains in storage tissues (grains, tubers, roots) and it also occurs to a lesser extent in most vegetative tissues of plants. Starch is made up of two polymers of D-glucose: amylose, an essentially unbranched α [1 \rightarrow 4] linked glucan, and amylopectin, which has chains of α [1 \rightarrow 6] branching links. Schematic representation amylose and amylopectin is shown in Figure 2. The moisture content of native starch grains is usually about 10 %. Amylose and amylopectin make up 98-99 % of the dry weight of native grains, with the remainder comprising small amounts of lipids, minerals, and phosphorus in the form of phosphates esterified to glucose hydroxyls. Starch grains range in size (from 1 to 100 μm diameter) and shape (polygonal, spherical, lenticular), and can vary greatly with

regard to content, structure and organization of the amylose and amylopectin molecules, the branching architecture of amylopectin, and the degree of crystallinity [Dabirmanesh et al., 2011].

Amylose has a molecular weight range of approximately 10^5 - 10^6 , corresponding to a degree of polymerization (DP) of 1000-10000 glucose units. Less than 0, 5 % of the glucoses in amylose are in α [1 \rightarrow 6] linkages, resulting in a low degree of branching, and a structure with 3-11 chains of approximately 200-700 glucose residues per molecule. Because of the low degree of branching, dissolved amylose has a tendency to form insoluble semi-crystalline aggregates, depending on the placement of the branches in the structure [Dabirmanesh et al., 2011].

Amylopectin is a much larger polymer, with molecular weight about 10^8 and a DP that may exceed one million. Most starches contain 60-90 % amylopectin, although high-amylose starches, with as little as 30 % amylopectin, and waxy starches with essentially 100 % amylopectin are well known. Amylopectin has about 5 % of its glucoses in α [1 \rightarrow 6] linkages, giving it a highly branched, tree-like structure and a complex molecular architecture that can vary substantially between different starches with regard to placement and length of branches. The amylopectin branches may be classified according to their pattern of substitution: A-chains are defined as unsubstituted, B-chains are substituted by other chains, and there is a single C-chain that carries the reducing glucose [Dabirmanesh et al., 2011].

Amylose and amylopectin have different structures and properties. Amylose is a relatively long, linear α -glucan containing around 99 % (1 \rightarrow 4)- α - and (1 \rightarrow 6)- α -linkages and differs in size and structure depending on botanical origin. Amylose has a molecular weight of approximately 1×10^5 – 1×10^6 , a degree of polymerization (DP) by number (DP_n) of 324-4920 with around 9-20 branch points equivalent to 3-11 chains per molecule. Each chain contains approximately 200-700 glucose residues equivalent to a molecular weight of 32,400-113,400 [Karkalas et al., 2004].

Amylopectin is a much larger molecule than amylose with a molecular weight of 1×10^7 - 1×10^9 and a heavily branched structure built from about 95 % (1 \rightarrow 4)- α - and 5 % (1 \rightarrow 6)- α - linkages. The DP_n is typically within the range 9600-15,900 but comprises three major species with DP_n 13,400-26,500, 4400-8400 and 700-2100. In common with amylose, the molecular size, shape, structure and polydispersity of the molecule varies with

botanical origin. Unlike amylose, however, there is great additional variation with respect to the unit chain lengths and branching patterns. Amylopectin unit chains are relatively short compared to amylose molecules with a broad distribution profile. They are typically ~ 18-25 units long on average although the range is extended if high-amylose starches are also included. The individual chains can be specifically classified in terms of their lengths (chain lengths) and consequently position within starch grains. Amylopectin molecules from high amylose starches contain relatively high proportions of very long chains [Karkalas et al., 2004].

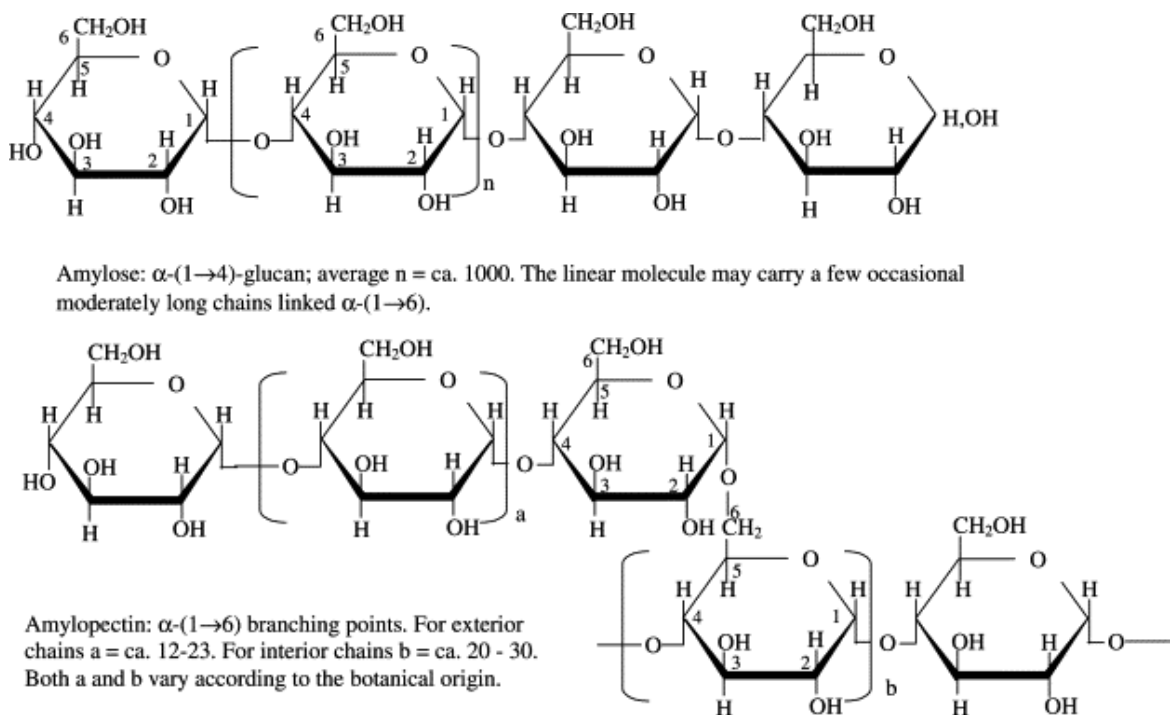


Figure 2. Schematic representation amylose and amylopectin [Karkalas et al., 2004].

The extent of crystallinity of native starch grains ranges from about 15 % for high-amylose starches to about 45-50 % for waxy starches. The grains have a hierarchical structure that can be observed readily by light and electron microscopy. Multiple concentric layers of so-called growth rings of increasing diameter extend from the hilum (the centre of growth) towards the surface of grains. The growth rings are typically 120-400 nm in thickness, and are considered to represent diurnal fluctuations in the deposition of starch in storage tissues. The concentric growth rings, in turn, contain alternating crystalline and amorphous regions of higher and lower density, respectively. The higher density regions have a

lamellar structure of alternating crystalline and amorphous layers with a repeat distance of 9-11 nm. Within these lamellae, the crystalline layers are considered to be formed mainly by amylopectin chains packed into a crystalline lattice, whereas the amorphous layers contain the amylopectin branching points and amylose and amylopectin molecules in a disordered conformation. Longer amylopectin chains are considered to pass from the crystalline region into the amorphous region of the lamellae. Amylopectin molecules near the surface of grains may have a different structure to those closer to the centre of the molecule. The ratio of long to short branch chains affect the shape of amylopectin, which influences their packing into grains. In this way, genetic and environmental factor that affect amylopectin biosynthesis can influence its molecular architecture, and in turn, grain morphology [Dabirmanesh et al., 2011].

Amylose is located in the low density layers of the growth rings, although amylose molecules are also considered to be interspersed between amylopectin in the crystalline layers, disrupting the crystal packing of amylopectin. In high-amylose starches, amylose helices may contribute to the crystallinity of grains. The organization of amylose and amylopectin in the growth rings, and the lamellar architecture of the crystalline layers within these rings, are still not fully understood. Nor is the distribution and role of water, which acts as a plasticiser and influences the crystallinity of the structure. Grains contain about 10 % water, which is probably not distributed uniformly. The concentric pattern of semi-crystalline layers is responsible for the birefringence of native starch grains when viewed under polarized light microscopy [Dabirmanesh et al., 2011].

Amylopectin chains with more than 10 glucose units are organized into double helices, which are arranged into either A- or B-crystalline forms that may be identified by characteristic X-ray diffraction spectral patterns. The double helical structures within the A- and B-type crystalline forms are essentially the same, but the packing of the helices in the A-type crystalline structure is more compact than in B-type crystallites, which have a more open structure with a hydrated core. The A-type crystal pattern has amylopectin molecules with shorter chains. Cereal starches tend to have the A-type pattern, whereas tuber starches and amylose-rich starches yield the B-type pattern, although both types may occur together. Legume, root and some fruit and stem starches yield an intermediate C-type pattern, but whether this is a mixture of the A- and B-type patterns or a distinct form is not clear [Dabirmanesh et al., 2011].

Starches from wheat (*Triticum aestivum* L.), barley, rye and triticale have a bimodal grain size distribution. Appearance of starch grains is shown in Figure 3. In wheat, there is one population of small spherical grains ranging in size from approximately 1 to 10 μm , which are referred to as B-grains, and another population of larger lenticular-shaped grains ranging from about 15 to 40 μm , known as A-grains. The biosynthesis of A- and B-grains differs during grain filling, resulting in differences in the molecular organization of the amylose and amylopectin fractions and molecular architecture of the amylopectin. The A-grains make up a much greater proportion of wheat starch by weight but are much fewer in number than B-grains. The A- and B-grains differ in structural and functional properties, including amylopectin of B-grains having more short chains and fewer medium and long chains than that of A-grains [Dabirmanesh et al., 2011].

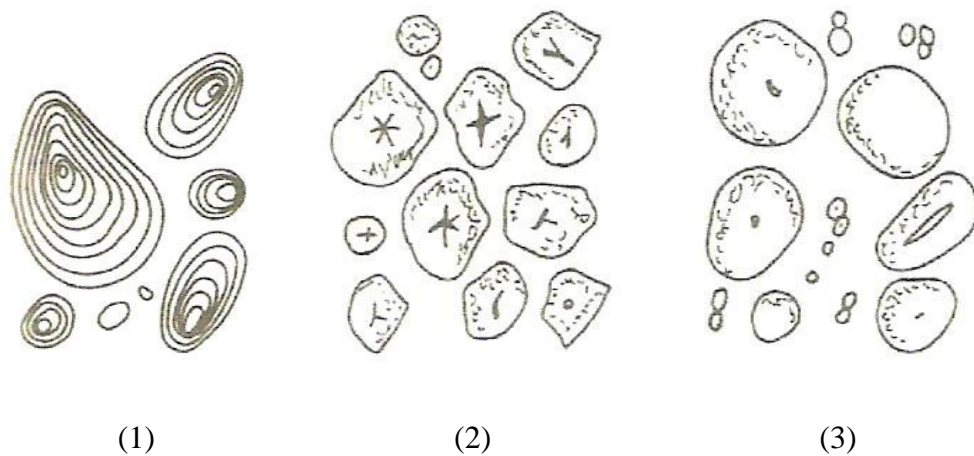


Figure 3. Appearance of starch grains. 1 – potato starch, 2 – corn starch, 3 – wheat starch [Chrvalová, 2009].

Most starch consumed by humans has undergone some form of processing, which usually involves rating in the presence of moisture under shear, and then cooling. During heat treatment, the starch grains are gelatinized, losing their crystallinity and structural organization. On cooling, the disaggregated starch molecules first form a gel and then retrograde gradually into semicrystalline aggregates that differ in form from the native grains. Starch-rich foods that have been cooked and cooled often contain substantial amounts of retrograded starch. Understanding the steps that occur during gelatinization and retrogradation of a particular starch are key steps to better predicting the functional properties of processed starch from knowledge of the structure of native grains [Dabirmanesh et al., 2011].

Gelatinization occurs when native starch is heated in the presence of sufficient moisture. The grains absorb water and swell, and the crystalline organization is irreversibly disrupted. Water first enters the amorphous growth rings, and at a certain degree of swelling, disruptive stress is transmitted through connecting molecules from the amorphous to the crystalline regions. Amylose molecules begin to leach from the grains as they are disrupted under shear and the viscosity of the point when the number of swollen but still intact starch grains is at a maximum. The maximum is followed by a decrease in paste viscosity, as the grains rupture and starch molecules are dispersed in the aqueous phase. The rate and extent of swelling and breakdown are dependent on the type and amount of starch, the temperature gradient, shear force and the composition of the mixture, for example the presence of lipids and proteins. The gelatinization temperature of most starches is between 60 and 80 °C. In general, there is a negative relationship between the amylose content of starch and the gelatinization temperature and peak viscosity [Dabirmanesh et al., 2011].

As the starch paste cools, the viscosity increases due to the formation of a gel held together by intermolecular interactions involving amylose and amylopectin molecules. In gels that contain about 25 % amylose, the starch molecules form a network resulting in a firm gel, in contrast to waxy starch gels, which are soft and contain aggregates but no network. On standing, starch gels retrograde and form insoluble B-type crystallites due to association of linear regions of α -[1→4] linked glucose units in the polymers. Retrogradation is an ongoing process occurring over an extended period. Amylose retrogrades over minutes to hours and amylopectin over hours to days, depending on the ability of the branched chains to form associations. The retrogradation of amylose in processed foods is considered to be important for properties relating to stickiness, ability to absorb water, and digestibility, whereas retrogradation of amylopectin is probably a more important determinant in the staling of bread and cakes. In rice, amylose contributes texture and stickiness, whereas gelatinization temperature, cooking and pasting properties are more closely related to amylopectin [Dabirmanesh et al., 2011].

Both amylose chains and exterior chains of amylopectin can form double helices which may in turn associate to form crystalline domains. In most starches these are confined to the amylopectin component [Karkalas et al., 2004].

The structure of amylose and amylopectin, and the form and crystallinity of starch grains, have been studied extensively using many complementary approaches. Amylose helices form inclusion complexes with polyiodide giving a blue color, which has long been used as a colorimetric test for starch. Although rapid and convenient, this method is subject to inaccuracies because the wavelength of maximum absorbance of amylose-iodine complexes varies with DP, and the formation of amylopectin-iodine complexes that can also absorb at interfering wavelengths. Separation of amylose from amylopectin by size exclusion chromatography or by using the lectin concanavalin A are alternative approaches to amylose measurement in starches but are less suited to high throughput analyses. The fine structure of amylopectin has been examined using highly purified amylolytic enzymes [Dabirmanesh et al., 2011].

A combination of techniques has been used to study the molecular organization within starch grains, to obtain estimates of the thickness of the crystalline regions, and explore how amylose affects amylopectin clusters in native starch grains. Small-angle scattering techniques measure differences in electron density distribution, whereas diffraction techniques are indicative of crystallinity of the material. Differential scanning calorimetry identifies melting and crystallization events as well as glass transition temperatures. Imaging techniques such as light microscopy, scanning and transmission electron microscopy, scanning probe techniques such as atomic force microscopy, spectroscopic methods such as nuclear magnetic resonance and Fourier transformed infra-red spectroscopy are other approaches that have been used to obtain structural information on starch grains and molecules [Dabirmanesh et al., 2011].

These analytical methods provide explicit information on the molecular constituents and their organization in starch grains. In comparison, functionality is usually assessed with tests that are relevant to a particular application and are based on measuring the collective properties of a material. Relating an observed functional effect to a physicochemical change in a specific molecular constituent is often difficult [Dabirmanesh et al., 2011].

2.2 Application of starch

Starch is a valuable ingredient to the food industry, being widely used as a thickener, gelling agent, bulking agent and water retention agent [Kaur et al., 2004].

Starch contributes 50-70 % of the energy in the human diet, providing a direct source of glucose, which is an essential substrate in brain and red blood cells for generating metabolic energy. Indeed, the availability of a reliable source of starch from agriculture is considered to have been an important factor in human development, although it now seems that the glycemic response to excessive consumption of rapidly digesting starch may be a factor in some diet-related illnesses. Starch is also an important industrial material. Approximately, 60 million tonnes are extracted annually worldwide from various cereal, tuber and root crops, of which roughly 60 % is used in foods (for example, bakery products, sauces, soups, confectionery, sugar syrups, ice cream, snack foods, meat products, baby foods, fat replacers, coffee whitener, beer, soft drinks) and 40 % in pharmaceuticals and non-edible purposes, such as fertilisers, seed coatings, paper, cardboard, packing material, adhesives, textiles, fabric, diapers, bioplastics, building materials, cement, and oil drilling. Starches with a wide range of functional properties are needed to ensure fitness-for-purpose for such a diverse range of end uses [Dabirmanesh et al., 2011].

In nature, starch is found as crystalline beads of about 15-100 μm in diameter, in three crystalline modifications designated A (cereal), B (tuber), and C (smooth pea and various beans). Crystalline starch beads in plastics can be used as fillers or can be transformed into thermoplastic starch which can be processed alone or in combination with specific synthetic polymers. To make starch thermoplastic, its crystalline structure has to be destroyed by pressure, heat, mechanical work or plasticisers such as water, glycerine or other polyols. Three main families of starch polymers can be used: pure starch, modified starch and partially fermented starch polymers [Bastioli, 2005].

Starch can be used as a natural filler in traditional plastics and particularly in polyolefins. When blended with starch beads, polyethylene (PE) films biodeteriorate on exposure to a soil environment. Starch-filled PE containing pro-oxidants are commonly used in agricultural mulch film, in bags and in six-pack yoke packaging [Bastioli, 2005].

3 SOLVATION OF STARCH

3.1 Solvation of starch in conventional solvents

Gelatinization, the process by which the internal structure of the grain is broken down and the whole grain disintegrates releasing the polysaccharide into the surrounding medium, is accompanied by a variety of changes. Being semi-crystalline, the grain exhibits birefringence when viewed between crossed polar. This birefringence is lost as the starch grains gelatinize and their structure is disrupted [Kaur et al., 2004].

The work carried out by Donovan in 1979 and by Colonna and Mercier in 1985 gave, however, a clear explanation of two different conditions for the loss of crystallinity of starch. Colonna reported that all starches exhibit a pure gelatinization phenomenon, which is the disorganization of the semicrystalline structure of the starch grains during heating in the presence of a water volume fraction > 0.9 . For normal genotypes, gelatinization occurs in two stages. The first step, at around 60-70 °C, corresponds mainly to swelling of the grains, with limited leaching. Loss of birefringence, demonstrating that macromolecules are not longer oriented, occurs prior to any appreciable increase in viscosity. By contrast, differential scanning calorimetry permits the determination of the gelatinization temperature more easily and precisely than microscopy and, additionally, the energy input needed to disorganize the crystalline structure of the grains. The second step, above 90 °C, implies the complete disappearance of granular integrity by excessive swelling and solubilisation. Nevertheless this last transition is not detectable by DSC. Only at this stage can the swollen grains be destroyed by shear. At high water volume fractions, melting of crystallites and swelling are co-operative processes [Bastioli, 2005].

3.2 Solvation of starch in ionic liquids

Some ILs are able to destroy the semicrystalline structure of native starch grains and disrupt hydrogen bonding between hydroxyl groups of polysaccharide. Starch solubility depends on both ionic liquid structure and temperature. The dissolution time depends on the starch origin – when corn, rice, wheat and barley starch is fully gelatinized, waxy corn and potato starch grains are still present. The molecular weight of starch polymers decreases with increasing time and temperature. The starch molecular weight reduction

might be an effect of the pH value determined by the ILs character: in acidic hydrolysis conditions, in alkaline oxidation conditions a breaking of glycosidic bonds might occur. A question of the most effective IL as starch solvent still seems to be open as is shown in [Smiglak, 2010]. Forty eight ILs composed of various cations and anions have been selected and their dissolution power tested toward three biopolymers: cellulose, lignin and starch (type of starch was not given). The following results have been obtained based on visual analysis of the vial contents: (a) for cellulose (10 wt %) – nine ILs dissolved cellulose completely, (b) almost all of the ILs tested dissolved lignin (5 wt %), whereas one IL did not dissolve lignin at all, (c) only one IL (non defined) was found to dissolve starch (5 wt %) completely. From the above data it is clear that the real solubility of cellulose in ILs (and lignin as well) is substantially better than that of starch [Spsychaj & Wilpiszewska, 2011].

It was published that IL 1-butyl-3-methylimidazolium chloride [BMIM] Cl is able effectively to dissolve starch [Biswas et al., 2007; Biswas et al., 2009; Joensuu et al., 2011]. The dissolution of barley and waxy starch in ILs based on imidazolium and ammonium was confirmed [Budtova & Liu, 2012; Karkkainen et al., 2012].

Dissolution of corn starch in ILs as [BMIM] Cl and 1-ethyl-3-methylimidazolium acetate ([EMIM] Ac) compared with dissolution in traditional organic solvent for starch dimethyl sulfoxide (DMSO) and the mixture of [BMIM] Cl - DMSO was studied. [EMIM] Ac was a better solvent for starch than [BMIM] Cl. The starch grains dispersed in [BMIM] Cl showed less crystallinity than native starch grains. The crystallinity disappeared when the starch grains were dispersed in [EMIM] Ac and DMSO. The addition of DMSO could increase the dissolubility of ILs, but too much DMSO could seriously destroy the structure of starch grains [Gao et al., 2012].

II. ANALYSIS

4 EXPERIMENT INTRODUCTION

Materials

In this study, six kinds of starch were used. Description of the starches is given in Table 4. Starches #1 to #5 were produced and kindly supplied by Limagrain, France. Starch #6 was purchased from Casino, France.

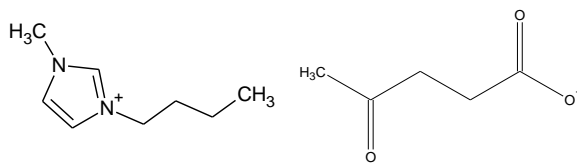
Prior to the experiments, the starches were dried in the oven at 70 °C for 12 h. Then the starches were stored in the oven at the same conditions within the experiments.

Ionic liquid, 1-butyl-3-methylimidazolium levulinate (BMIM LEV) was synthesized from Surface Organometallic Chemistry Team at the University in Lyon. Purity of this IL is 75 % as determined by ^1H NMR. A bottle of BMIM LEV was used as received without further purification.

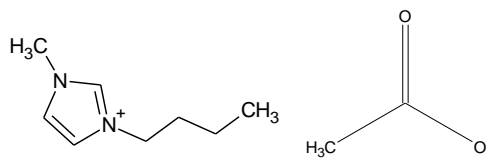
Ionic liquids, 1-butyl-3-methylimidazolium acetate (BMIM Ac), 1-butyl-3-methylimidazolium methylphosphite (BMIM $\text{CH}_3\text{OPO}_2\text{H}$), 1-butyl-3-methylimidazolium dimethylphosphate (BMIM $(\text{CH}_3\text{O})_2\text{PO}_2$), 1-butyl-3-methylimidazolium methylsulfate (BMIM CH_3SO_4), were synthesized from Surface Organometallic Chemistry Team at the University in Lyon. Their purity is 98 % as determined by ^1H NMR. Bottles of ionic liquids were used as received without further purification. For identification ILs by viscometer and densimeter, ILs were purified on vacuum line for minimum 12 hours. Purity of ionic liquids was tested by Karl-Fisher titration.

Ionic liquid, N, N – dimethyl – N - (2-hydroxyethyl) ammonium acetate ($\text{C}_4\text{H}_{11}\text{ONHCH}_3\text{COO}$) of purity 98 % was synthesized from IoLiTec (Germany). A bottle of IL was used as received without further purification for dissolution of starch. For identification IL by viscometer and densimeter, IL was purified on vacuum line for minimum 12 hours. Purity of ionic liquid was tested by Karl-Fisher titration.

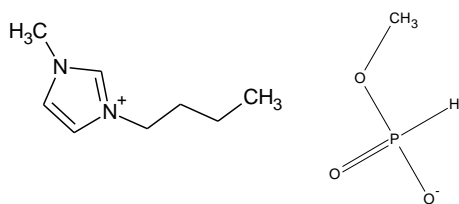
Ionic liquid, trihexyl (tetradecyl) phosphonium chloride ($\text{C}_{66614}\text{P Cl}$) of purity 98 % was synthesized from Belfast. A bottle of $\text{C}_{66614}\text{P Cl}$ was used as received without further purification.



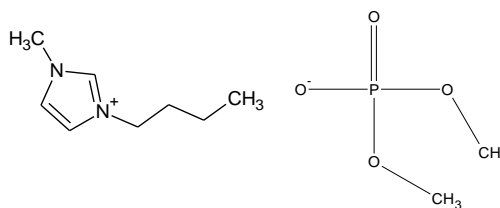
(1) [C₁C₄Im] [Levulinate]



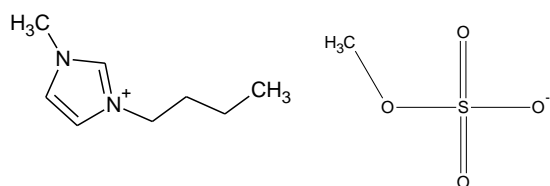
(2) [C₁C₄Im] [CH₃COO]



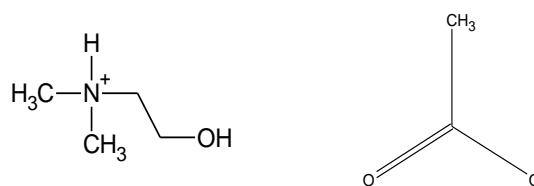
(3) [C₁C₄Im] [CH₃OPO₂H]



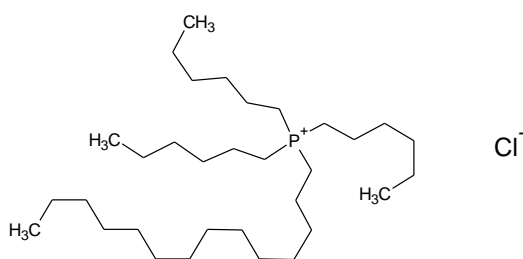
(4) [C₁C₄Im] [(MeO)₂PO₂]



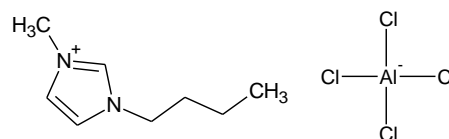
(5) [C₁C₄Im] [CH₃SO₄]



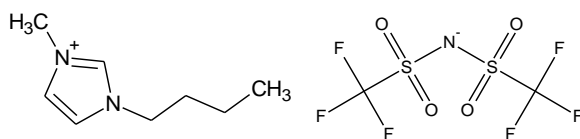
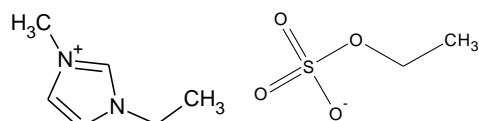
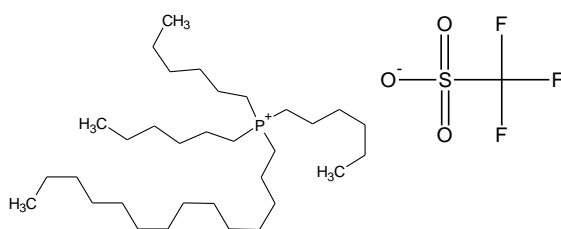
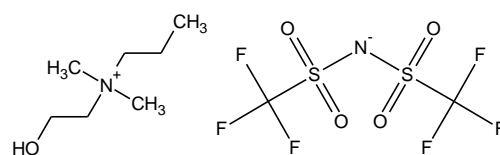
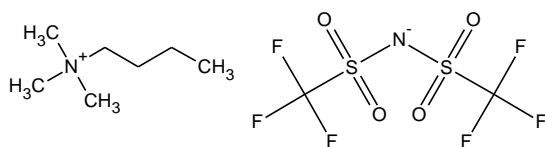
(6) [C₄H₁₁ONH] [CH₃COO]



(7) [C₆₆₆₁₄P] [Cl]



(8) [C₁C₄Im] [AlCl₄]

(9) [C₁C₄Im] [NTF₂](10) [C₁C₂Im] [C₂H₅OSO₃](11) [C₆₆₆₁₄P] [OTF](12) [Propylcholinium] [NTF₂](13) [N₄₁₁₁] [NTF₂]**Table 3.** Chemical structures and abbreviation of the examined ionic liquids.

1. 1-butyl-3-methylimidazolium levulinate.
2. 1-butyl-3-methylimidazolium acetate.
3. 1-butyl-3-methylimidazolium methyl phosphite.

4. 1-butyl-3-methylimidazolium dimethyl phosphate.
5. 1-butyl-3-methylimidazolium methyl sulfate.
6. N, N – dimethyl – N - (2-hydroxyethyl) ammonium acetate.
7. Trihexyl (tetradecyl) phosphonium chloride.
8. 1-butyl-3-methylimidazolium tetrachloroaluminate.
9. 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide.
10. 1-ethyl-3-methylimidazolium ethylsulfate.
11. Trihexyl (tetradecyl) phosphonium triflate.
12. Propylcholinium bis (trifluoromethanesulfonyl) imide.
13. Trimethylbutylammonium bis (trifluoromethanesulfonyl) imide.

Designation	Origin	Description	Producer
Starch #1	Corn starch	---	Limagrain, France
Starch #2	Other origin	---	Limagrain, France
Starch #3	Wheat starch	High content of amylose	Limagrain, France
Starch #4	Wheat waxy starch	High content of amylopectin	Limagrain, France
Starch #5	Wheat starch	Extra starch	Limagrain, France
Starch #6	Cassava starch	100 % manioc starch	Casino, France

Table 4. Description of the examined starches.

Methods

Optical microscopy

Optical microscope (Leica DM 2500 M, Germany) was used to observe and compare the behaviour of starch grains in IL and IL - tri-distilled water mixtures. For measurement 13 ILs and 6 kinds of starches were used. Dry starch was dispersed in each solvent to reach 5 wt% concentration. One drop of dispersion was placed between glass slides, quickly heated to 60 °C and then heated from 60 °C at 1 °C/min using Linkam hot stage with video recording. Experiment was terminated when all starch grains were dissolved. Each experiment was repeated two times for each system.

Densimetry

Densimeter Anton Paar DMA 512 P was used to determine the density of ionic liquids. Scheme of the Densimeter is shown in Figure 4.

Approx. 5 ml of ionic liquid was taken to the syringe. This ionic liquid was applied to densimeter system. Measurements were carried out in temperature range from 10 to 100 °C. After the calculation by the Eq. 1, density of ionic liquids was obtained:

$$\rho = A(T, p)\tau^2 + B(T, p) \quad (1)$$

ρ – density, [kg/m³]

A (T, p); B (T, p) – calibration constants characterizing the vibrating tube dependent on T and p

T – temperature, [K]

p – pressure, [MPa]

τ – period of oscillation of the tube, [s]

Density measurement

Working range: from 283 to 383 K, from 0.1 to 40 MPa

$$\rho = A(T,p) \tau^2 + B(T,p)$$

T : period of oscillation of the tube

A(T,p); B(T,p): Calibration constants characterizing the vibrating tube dependent on T and p.

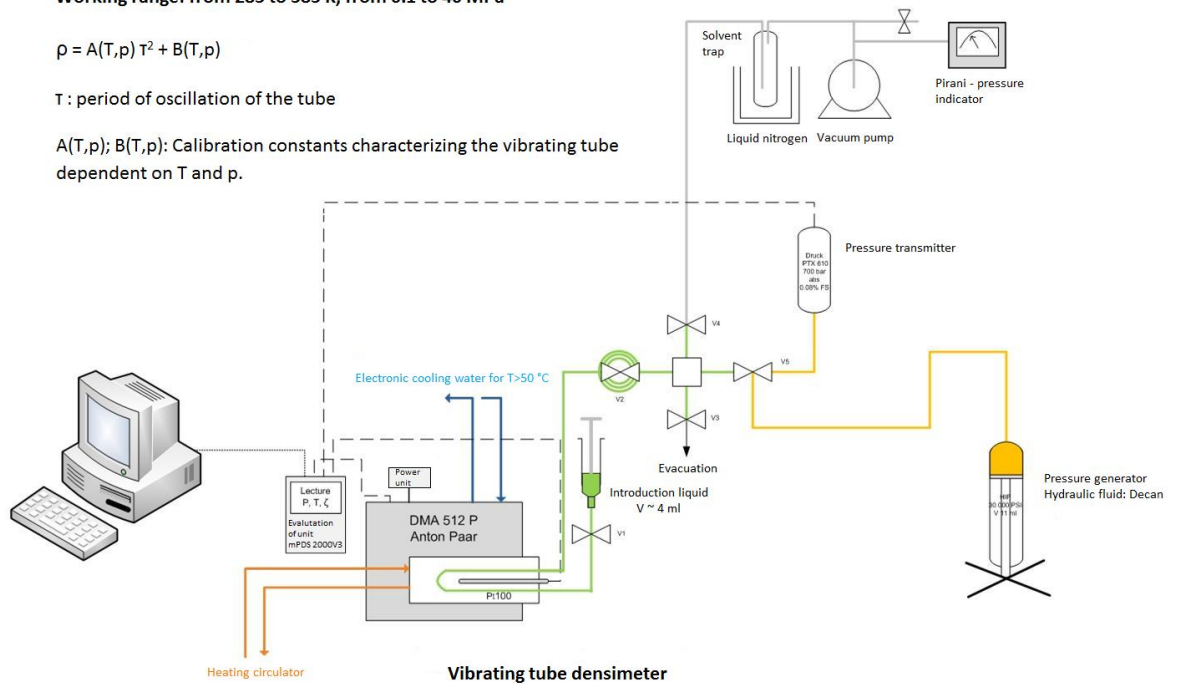


Figure 4. Scheme of the Densimeter [Laboratory data].

Viscometry

Automated Micro Viscometer Anton Paar AMVn was used to determine the viscosity of ionic liquids. Viscometer used, capillaries and measuring principle are shown in Figure 5.

Approx. 2 ml of ionic liquid was taken to the syringe. This ionic liquid was applied to capillary, small metal ball was inside capillary. Capillary was inserted into the viscometer, instrument was closed and measurement was started. Measurements were carried out in temperature range from 20 to 100 °C. After the calculation by the Eq. 2, it was obtain the viscosity of ionic liquids:

$$\eta = K_1(\rho_b - \rho_N)t \tag{2}$$

η – dynamic viscosity of sample, [Pa.s]

K_1 – calibration constant of the measuring system, [Pa.cm³/g]

ρ_b – density of ball, [g/cm³], (steel ball: $\rho_b = 7.85$ g/cm³)

ρ_N – density of the measured sample, [g/cm³]

t – ball rolling time, [s]

Where:

$$K_1 = \frac{\eta_N}{t_1(\rho_b - \rho_N)} \quad (3)$$

K_1 – calibration constant of the measuring system, [Pa.cm³/g]

η_N – dynamic viscosity of the viscosity standard fluid, [Pa.s]

t_1 – ball rolling time, [s]

ρ_b – density of ball, [g/cm³], (steel ball: $\rho_b = 7.85$ g/cm³)

ρ_N – density of the viscosity standard fluid, [g/cm³]

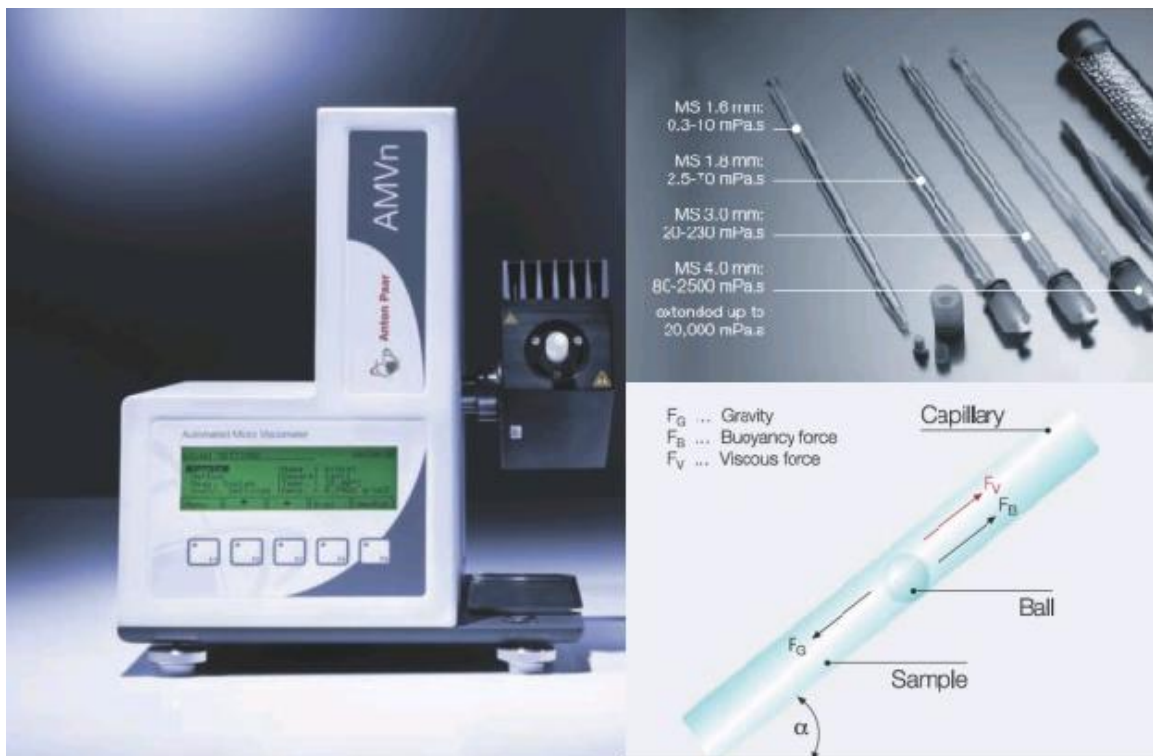


Figure 5. Viscometer used, capillaries and measuring principle [Laboratory data].

Karl Fischer Coulometry

Karl Fischer coulometer Mettler Toledo DL 32 was used for identification of purity of ionic liquids. Karl Fischer Coulometer is shown in Figure 6.

The Karl Fischer titration is a universally acknowledged method for measuring water content in all types of substances including chemicals, oils, pharmaceuticals and food.



Figure 6. Karl Fischer Coulometer [Laboratory data].

Differential scanning calorimetry

Thermal properties of ionic liquids were determined by using a differential scanning calorimeter (DSC 2920 modulated, TA Instruments, New Castle, DE).

For measurement, one drop of ionic liquid was precisely weighed in an aluminium pan and sealed. The sample was scanned at a rate of 1 °C/min over a temperature range of 25 °C to 725 °C. An empty pan was used as the reference. Every analysis of thermal properties was repeated two times for each system.

Micro differential scanning calorimetry

Heat of starch dissolution in ILs was determined by a micro calorimeter MICRO DSC III Setaram.

For measurement, ionic liquid was applied by syringe and precisely weighed in the reference batch mixing cell. To the sample batch mixing cell, precisely weighed ionic liquid with 5 wt% of starch was applied by syringe. Closed mixing cell is shown in Figure 7.

Batch mixing cells were inserted into the apparatus. Experiment was performed at a temperature range from 25 °C to 119 °C (maximum temperature of apparatus) at a rate 1 °C/min. Before and after the temperature rise the initial and final temperatures were stabilized for 15 minutes. At the beginning of the experiment, mixing of sample batch cell was triggered at a constant speed of 2.5 rotations per minute.

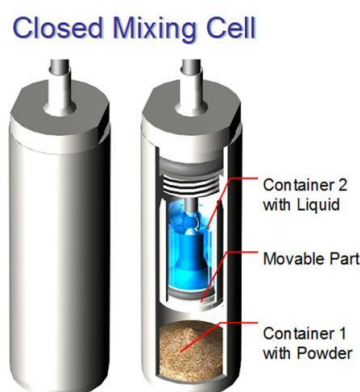


Figure 7. Closed mixing cell [Laboratory data].

Rheometry

The rheological properties were determined by an ARES (Rheometric Scientific) rotational rheometer with the plate-plate geometry. Diameter of plates was 25 mm, distance between the plates was set to 1 mm. Conditions of measurement were following: temperature 25 °C, angular frequency in the interval 0.1 – 100 rad/s.

5 RESULTS AND DISCUSSION

Natural starch exhibits grainy structure. Round particles possess the diameter in tens of micrometers and the overall appearance is dependent on the source. In Figure 8, the grain structure of all types of starches under study is documented. The smallest particles were found in the wheat starches (#3 to #5). Cassava starch #6 is formed from clusters of grains.

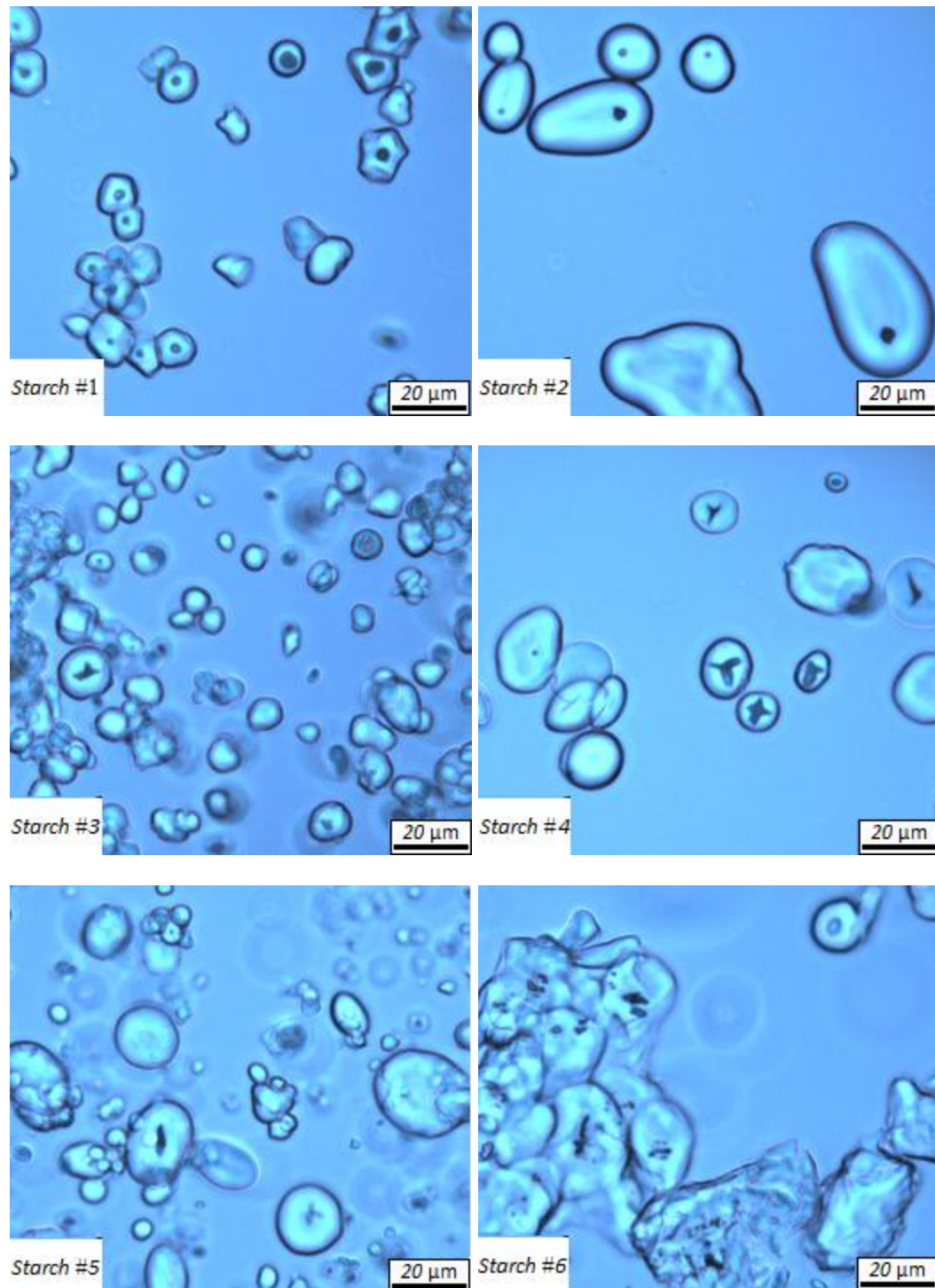


Figure 8. Appearance of starch grains.

It is generally known that the capability of ILs to dissolve organic polymers depends strongly on the cation and anion type. In this study, 13 ionic liquids covering a broad range of cation and anion types were selected and their capability to dissolve starch was tested. Table 5 gives the information on the capability of ILs under study to dissolve starch #1. As can be seen, the experiments performed on optical microscope showed the successful process of starch dissolution in 7 types of ILs. These 7 types of ILs were selected for further experiments and characterized from thermodynamics point of view. Density, viscosity and degradation temperature of selected ILs are summarized in Table 6. In Figures 9 and 10, an example of the dependence of density and viscosity of IL on temperature is given. As can be seen, the density is linearly dependent on temperature, while the viscosity exponentially decreases with temperature increase. Similar behaviour exhibited all the ILs under study.

Ionic liquid	Abbreviation	State at 25 °C	Capability to dissolve starch
1-butyl-3-methylimidazolium levulinate	[C ₁ C ₄ Im] [Levulinate]	Liquid, brown	YES
1-butyl-3-methylimidazolium acetate	[C ₁ C ₄ Im] [CH ₃ COO]	Liquid, slightly yellow	YES
1-butyl-3-methylimidazolium methyl phosphite	[C ₁ C ₄ Im] [CH ₃ OPO ₂ H]	liquid	YES
1-butyl-3-methylimidazolium dimethyl phosphate	[C ₁ C ₄ Im] [(CH ₃ O) ₂ PO ₂]	Liquid, light yellow	YES
1-butyl-3-methylimidazolium methyl sulfate	[C ₁ C ₄ Im] [CH ₃ SO ₄]	liquid	YES
N, N – dimethyl – N - (2-hydroxyethyl) ammonium acetate	[C ₄ H ₁₁ ONH][CH ₃ COO]	liquid	YES
Trihexyl (tetradecyl) phosphonium chloride	[C ₆₆₆₁₄ P] [Cl]	Liquid, slightly yellow	YES
1-butyl-3-methylimidazolium tetrachloroaluminate	[C ₁ C ₄ Im] [AlCl ₄]	liquid	NO

1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide	[C ₁ C ₄ Im] [NTF ₂]	liquid	NO
1-ethyl-3-methylimidazolium ethylsulfate	[C ₁ C ₂ Im][C ₂ H ₅ OSO ₃]	liquid	NO
Trihexyl (tetradecyl) phosphonium triflate	[C ₆₆₆₁₄ P] [OTF]	liquid	NO
Propylcholinium bis (trifluoromethanesulfonyl) imide	[Propylcholinium] [NTF ₂]	liquid	NO
Trimethylbutylammonium bis (trifluoromethanesulfonyl) imide	[N ₄₁₁₁] [NTF ₂]	liquid	NO

Table 5. General appearance of ILs and possibility of dissolution of starch.

ILs	Density ρ [kg.m ⁻³] (20 °C)	Viscosity η [mPa.s]	T _{degradation} [°C]
BMIM LEV (STE)	1102.5	1447.4 (30 °C)	250
BMIM OAc	1059.7	646.0 (20 °C)	Not detected
BMIM CH ₃ OPOH ₂	1149.3	605.2 (20 °C)	200
BMIM (CH ₃ O) ₂ PO ₂	1161.6	930.0 (20 °C)	300
BMIM CH ₃ SO ₄	1211.5	267.8 (20 °C)	Not detected
C ₄ H ₁₁ ONHCH ₃ COO	1047.2	44.4 (30 °C)	650
C ₆₆₆₁₄ P Cl	885.4	1824.0 (25 °C)	Not detected

Table 6. Density, viscosity and thermal properties of ILs.

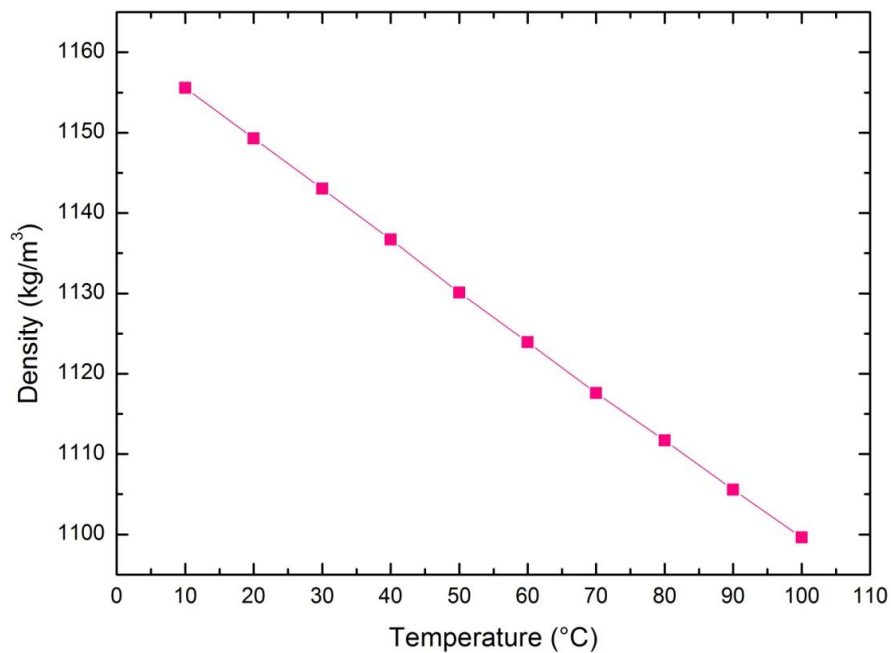


Figure 9. Linear temperature dependence on density of ionic liquid BMIM Methyl Phosphite.

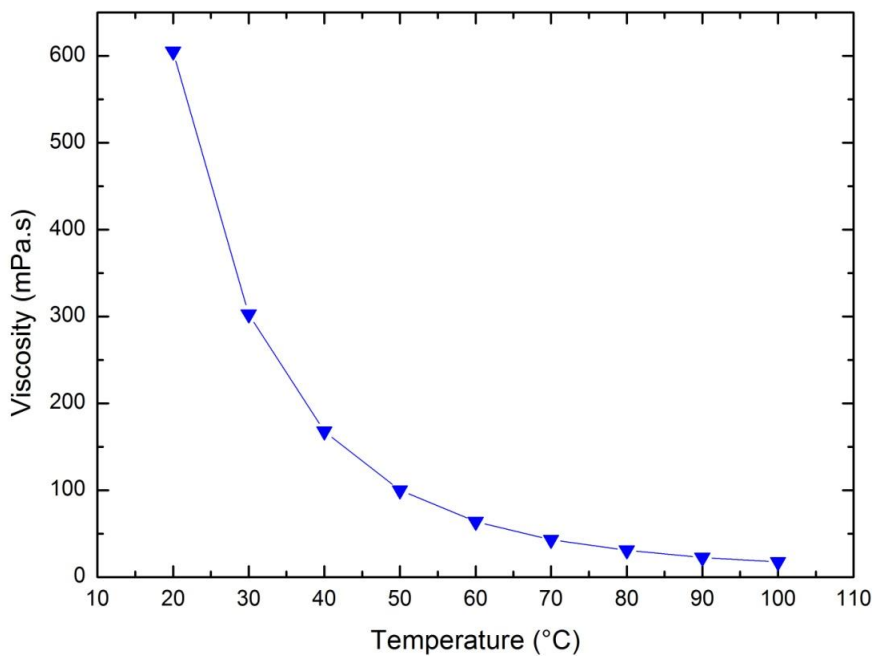
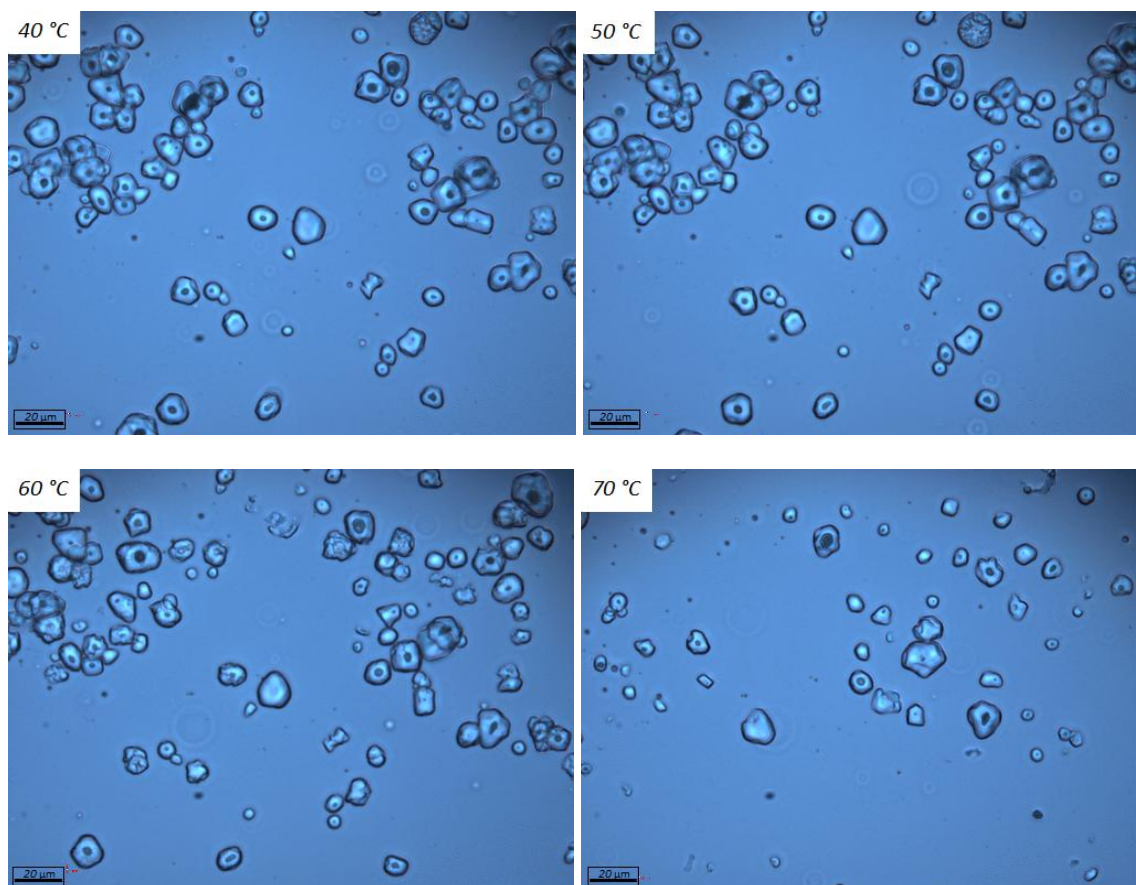


Figure 10. Exponential temperature dependence on viscosity of ionic liquid BMIM Methyl Phosphite.

Optical microscope equipped by the hot stage with precisely controlled temperature provided the possibility of documentation of entire process of starch dissolution in ILs. In Figure 11, the representative set of pictures taken within the dissolution process of starch #1 in $[C_1C_4Im][CH_3OPO_2H]$ is shown. Starch dissolution gradually proceeds with time and temperature. Solvent penetrates the grains, making outer layer slightly swollen. Most of the grains keeps their initial shape up to 60 °C. Above 60 °C grain diameter is dramatically decreased and quick dissolution occurs. Complete visual disappearance at 90 °C documents the total dissolution of starch. Similar behaviour was observed for all kinds of starch and ILs.



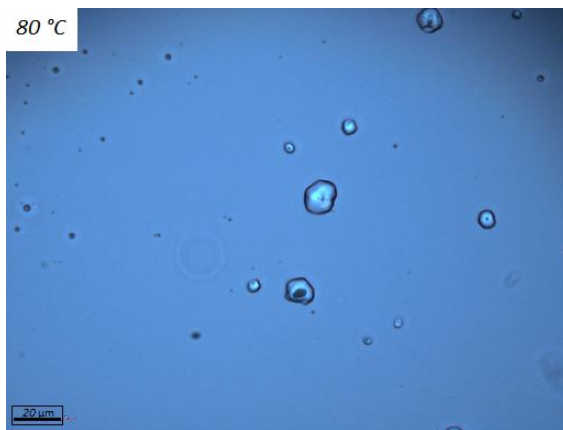


Figure 11. Evolution of 5 wt% starch #1 in BMIM Methyl Phosphite and during heating. The scale in all optical micrographs is 20 μm.

The process of starch #1 dissolution in water upon heating is documented in Figure 12. As can be seen, the behaviour of starch grains in water is entirely different, compared to starch - IL system. From 25 °C, gelatinisation process connected with water absorption starts. Water attacks starch grains, manifesting itself by grain swelling and cracking and gradual increase of grain diameter. At 70 °C the disintegrated grains begin to be dissolved. It has been reported [Budtova & Liu, 2012] that the grain size can even be increased 5 times, in dependence of starch origin.

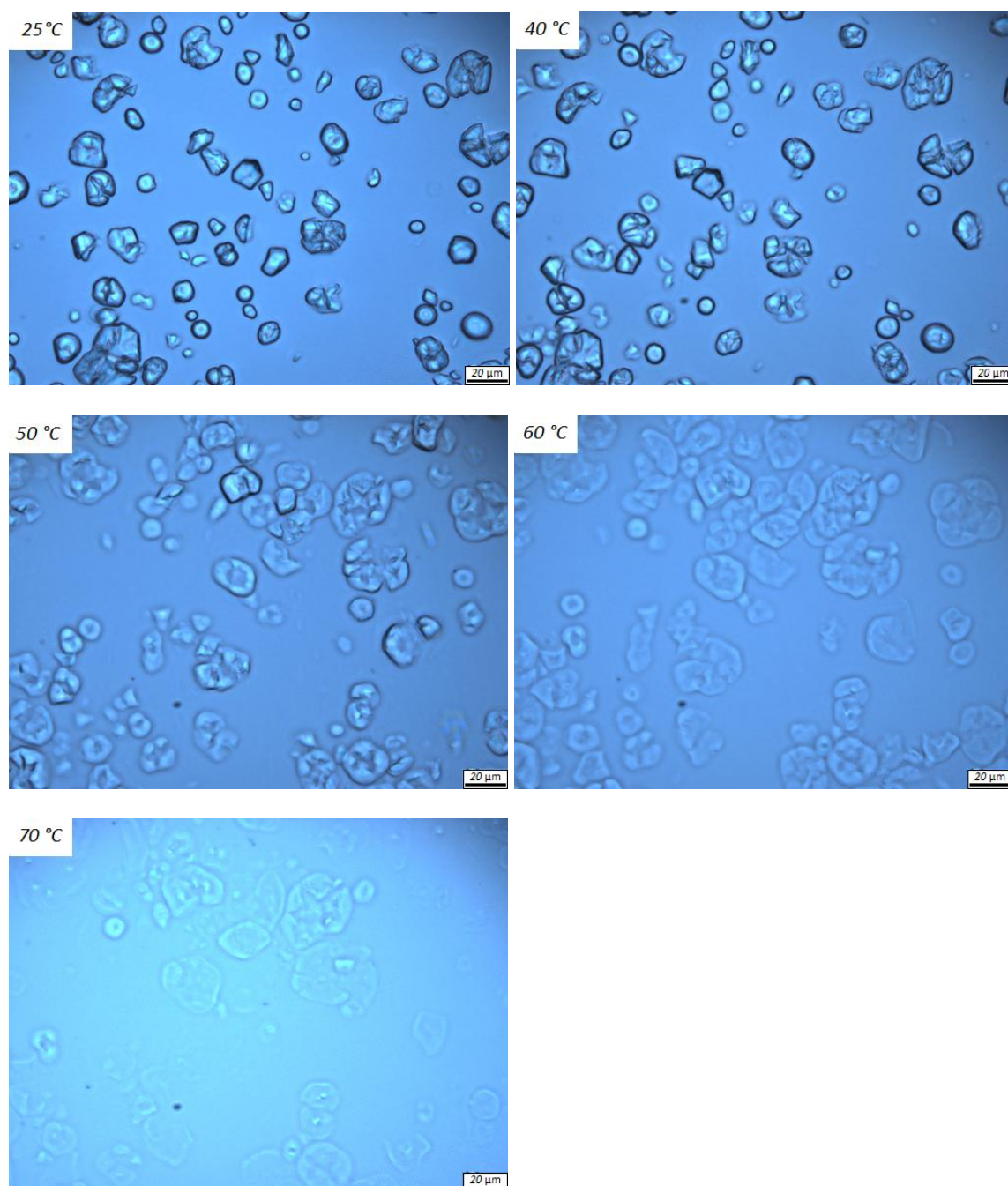


Figure 12. Evolution of 5 wt% starch #1 in water during heating. The scale in all optical micrographs is 20 μm .

It is interesting to demonstrate the behaviour of starch in the combination of IL and water. Figure 13 shows the process of starch dissolution in $[\text{C}_1\text{C}_4\text{Im}][\text{CH}_3\text{OPO}_2\text{H}]$ with 20 wt% of water. As can be seen the overall mechanism of starch dissolution is similar to the behaviour of the grains in pure IL. However, the presence of the water in the system accelerates the dissolution. In system IL – water the dissolution is visually completed

around 70 °C vs. 90 °C in pure IL. This phenomenon was observed for all ILs and starches under the study. Several reasons can be taken into account to explain these results:

- Water, being much less bulky than IL, penetrates the grain first, swells the outer layer and facilitates ionic liquid penetration and starch dissolution.
- The viscosity of system IL – water is lower than pure IL. The decrease in solvent viscosity increases polymer diffusion coefficient and allows faster homogenization of the whole system and thus quicker dissolution.
- Finally, IL and water are interacting and IL – water may become a more powerful solvent.

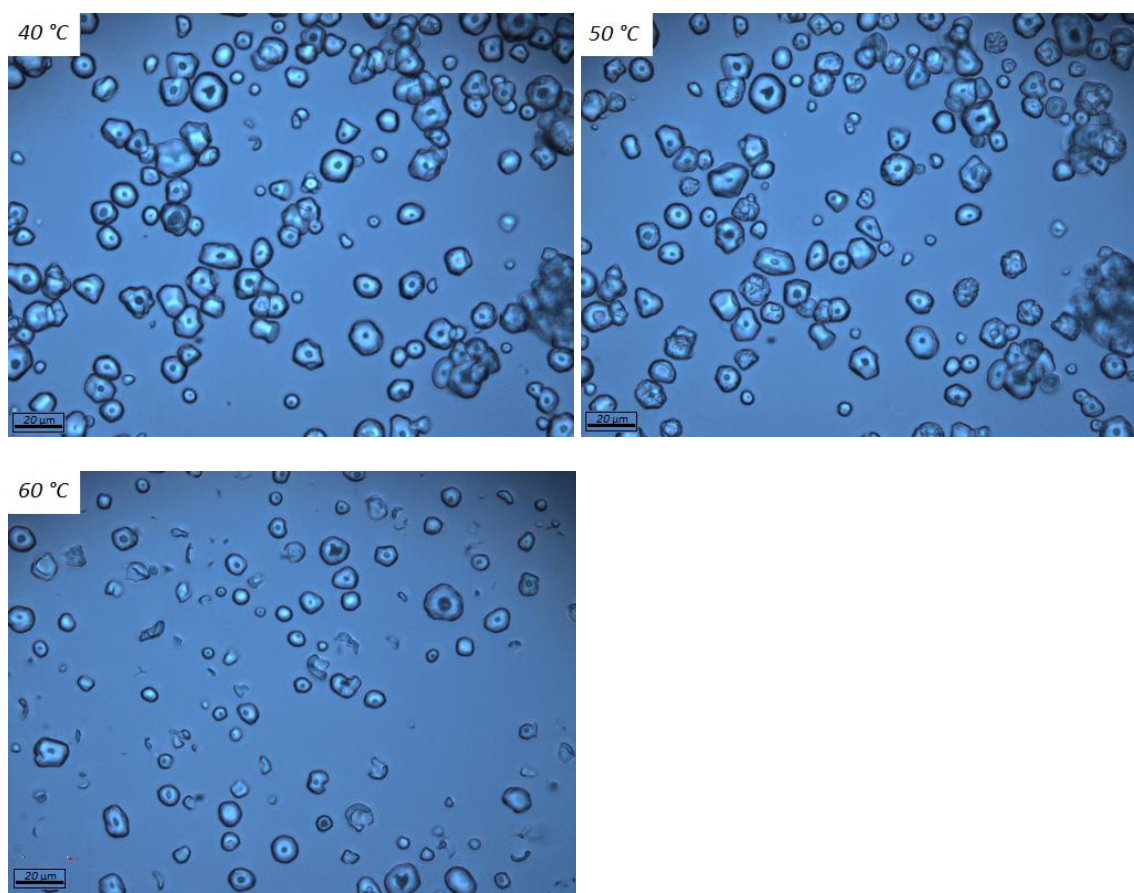


Figure 13. Evolution of 5 wt% starch #1 in BMIM Methyl Phosphite and 20 wt% water during heating. The scale in all optical micrographs is 20 μm .

Temperatures of dissolution onset and complete dissolution for individual IL are summarized in Table 7. As mentioned above, the presence of the water in IL generally accelerates the starch dissolution; dissolution onset and complete dissolution is shifted towards lower temperatures and, correspondingly, the temperature interval of starch dissolution is narrowed. It is worth mentioning that the cation and anion type has an impact on the starch dissolution. Within the ILs under study, $[\text{C}_1\text{C}_4\text{Im}][\text{CH}_3\text{OPO}_2\text{H}]$ was rated as the most powerful solvent for starch.

	Dissolution onset (°C)	Complete dissolution (°C)
100 % [C ₁ C ₄ Im] [Levulinate]	70	110-111
80 % [C ₁ C ₄ Im] [Levulinate] – 20 wt% water	45	74-75
100 % [C ₁ C ₄ Im] [CH ₃ COO]	70	110
80 % [C ₁ C ₄ Im] [CH ₃ COO] – 20 wt% water	55	83-85
100 % [C ₁ C ₄ Im] [CH ₃ OPO ₂ H]	60	90-95
80 % [C ₁ C ₄ Im] [CH ₃ OPO ₂ H] – 20 wt% water	50	64-65
100 % [C ₁ C ₄ Im] [(CH ₃ O) ₂ PO ₂]	70	115
80 % [C ₁ C ₄ Im] [(CH ₃ O) ₂ PO ₂] – 20 wt% water	53-55	85
100 % [C ₁ C ₄ Im] [CH ₃ SO ₄]	100	165
80 % [C ₁ C ₄ Im] [CH ₃ SO ₄] – 20 wt% water	100	145
100 % [C ₄ H ₁₁ ONH] [CH ₃ COO]	80	122-125
80 % [C ₄ H ₁₁ ONH] [CH ₃ COO] – 20 wt% water	55-56	80
100 % [C ₆₆₆₁₄ P] [Cl]	120	153-155
80 % [C ₆₆₆₁₄ P] [Cl] – 20 wt% water	110	153-155

Table 7. Parameters characterizing dissolution of corn starch #1 in used ILs and IL – water mixtures.

Parameters characterizing dissolution of 6 kinds of starches in the most powerful IL [C₁C₄Im] [CH₃OPO₂H] are shown in Table 8. Temperatures of dissolution onset and complete dissolution vary slightly with the kind of starch. The reason is the difference in size and shape of grains and content of amylose and amylopectin in starches. Dissolution starts first in starch # 4 (high contain of amylopectin) at 60 °C and, on the contrary, at the latest in starch # 3 at 70 °C (high contain of amylose).

	Beginning of dissolution (°C)	Temperature of complete dissolution (°C)
IL + 5 wt% starch # 1	60	90-95
IL + 5 wt% starch # 2	85	105-108
IL + 5 wt% starch # 3	70	95-96
IL + 5 wt% starch # 4	60	94-95
IL + 5 wt% starch # 5	60	95-98
IL + 5 wt% starch # 6	70	105-106

Table 8. Parameters characterizing dissolution of 6 kinds of starches in [C₁C₄Im] [CH₃OPO₂H].

The thermodynamics of starch dissolution in [C₁C₄Im] [CH₃OPO₂H] was studied using Micro DSC. In Figure 14, the thermograms of pure IL and IL with 5 wt% of starch are depicted. It can be seen that the process is exothermic and the specific heat of dissolution is -22.11 J.g⁻¹. The temperature interval of dissolution is in agreement with the dissolution interval derived from optical microscopy.

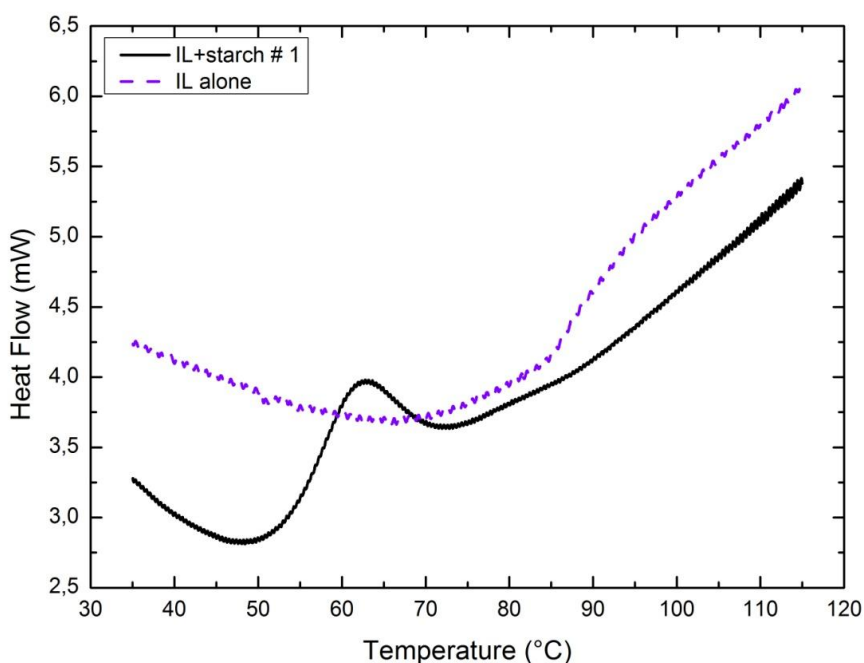


Figure 14. Heat flow dependence on temperature for BMIM Methyl Phosphite with 5 wt% starch #1 compare with pure BMIM Methyl Phosphite.

The rheological properties of systems IL - starch # 1, IL – water - starch # 1 and IL alone have been measured by rotational rheometer at temperature of 25 °C. BMIM Methyl Phosphite was used as ionic liquid. In Figure 15, the complex viscosity as a function of angular frequency is shown. It can be seen that all the systems exhibits Newtonian behaviour in the frequency interval used. Unexpectedly, the viscosity of the IL with dissolved starch is lower, compared to pure IL. For the understanding to this interesting phenomenon, further experimental study needs to be performed. Rheological experiment also supported the explanation of the higher effectiveness of the IL - water system to dissolve the starch based on the decrease of viscosity – from the Figure 15 is seen that the combination of IL – water - starch # 1 exhibited the lowest values of viscosity within the whole range of frequencies.

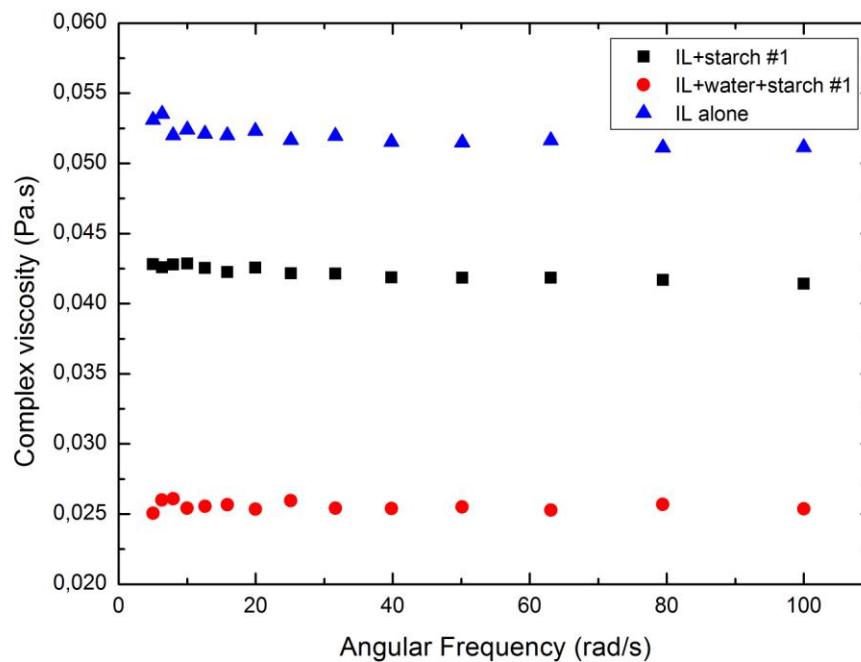


Figure 15. Complex viscosity dependence on the angular frequency of BMIM Methyl Phosphite in three systems.

CONCLUSION

The aim of the work was to broaden the use of ionic liquids as solvent for starch. For these purposes, 13 ILs differing in cations and anions, were applied on the starches from various natural sources.

The successful process of starch dissolution is demonstrated in [C₁C₄Im] [Levulinate], [C₁C₄Im] [CH₃COO], [C₁C₄Im] [CH₃OPO₂H], [C₁C₄Im] [(CH₃O)₂PO₂], [C₁C₄Im] [CH₃SO₄], [C₄H₁₁ONH] [CH₃COO], [C₆₆₆₁₄P] [Cl].

The dissolution process of starch in ionic liquids is different from starch gelatinization in water. While the water penetrates the starch and the grains are gradually swollen, ionic liquid dissolve the grains from outer to inner layers manifesting itself in continuous decrease of grain diameter. The presence of water in IL - starch system accelerates the dissolution due to partial swelling of grains in water and facilitation of ionic liquid diffusion.

BMIM Methyl Phosphite was rated as the most powerful solvent for starch and the thermodynamics of dissolution process was examined by Micro DSC. It was found that the starch dissolution process in ionic liquids is exothermic.

Rheological experiments revealed a peculiar behaviour of IL – starch system. As compared to pure BMIM Methyl Phosphite, the system of this ionic liquid with 5 wt% of dissolved starch exhibited lower values of complex viscosity. This finding needs further experimental description and theoretical explanation.

BIBLIOGRAPHY

Aslanov, L. A. Ionic liquids: Liquid structure. *Journal of Molecular Liquids*. **2011**, vol. 162, pp. 101-104.

Bastioli, C. *Handbook of biodegradable polymers* [online]. Shrewsbury: Rapra Technology, **2005**, pp. 534 [cit. 2012-03-12]. ISBN 9781859573891.

Biswas A., Inglett G. E., Jane J., Stevenson D. G. Changes in structures and properties of starch of four botanical sources dispersed in the ionic liquid, 1-butyl-3-methylimidazolium chloride. *Carbohydrate Polymers*. **2007**, vol. 67, pp. 21-31.

Biswas A., Shogren R. L., Willett J. L. Ionic liquid as a solvent and catalyst for acylation of maltodextrin. *Industrial Crops and Products*. **2009**, vol. 30, pp. 172-175.

Blanch H. W., Kim M., Padmanabhan S., Prausnitz J. M. Solubility and rate of dissolution for Miscanthus in hydrophilic ionic liquids. *Fluid Phase Equilibria*. **2011**, vol. 309, pp. 89-96.

Blazek, J.; Copeland, L.; Salman, H.; Tang, M. C. Form and functionality of starch. *Food Hydrocolloids*. **2009**, vol. 23, pp. 1527-1534.

Budtova T., Liu W. Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties. *Carbohydrate Polymers*. **2012**.

Carneiro A. P., Macedo E. A., Rodríguez O. Solubility of monosaccharides in ionic liquids – Experimental data and modeling. *Fluid Phase Equilibria*. **2012**, vol. 314, pp. 22-28.

Dabirmanesh B., Daneshjou S., Gill P., Heydari A., Khajeh K., Khavari-Nejad R. A., Rajnbar B., Sepahi A. A. Effect of ionic liquids on the structure, stability and activity of

two related α -amylases. *International Journal of Biological Macromolecules*. **2011**, vol. 48, pp. 93-97.

Depaoli, David, **2003**. *Technical Summaries on Ionic Liquids in Chemical Processing* [online]. New York [cit. 2012-02-13]. Available from: <http://chemicalvision2020.org/library.html>.

Gao J., Luo F., Luo Z. Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts. *Carbohydrate Polymers*. **2012**, vol. 89, pp. 1215-1221.

Chen Z., Feng L. Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids*. **2008**, vol. 142, pp. 1-5.

Chrvalová, L. *Výroba škrobů a jejich využití v průmyslu*. Zlín, **2009**. Bakalářská práce. Univerzita Tomáše Bati ve Zlíně, Fakulta technologická, Ústav potravinářského inženýrství. Vedoucí bakalářské práce Jana Rieglová.

Joensuu P., Karkkainen J., Lajunen M., Lappalainen K. HPLC – ELSD analysis of six starch species heat-dispersed in 1-butyl-3-methylimidazolium chloride ionic liquid. *Carbohydrate Polymers*. **2011**, vol. 84, pp. 509-516.

Karkalas, John; Tester, Richard F. and Xin Qi. Starch - composition, fine structure and architecture. *Journal of Cereal Science*. **2004**, vol. 39.

Karkkainen, J. *Preparation and characterization of some ionic liquids and their use in the dimerization reaction of 2-methylpropene* [online]. Oulu: University of Oulu, **2007**, pp. 145 [cit. 2012-03-12]. ISBN 978-951-4283-550.

Karkkainen J., Lajunen M., Lappalainen K. Dissolution and depolymerization of barley starch in selected ionic liquids. *Carbohydrate Polymers*. **2012**.

Kaur, M.; Sandhu, K. S.; Singh, N. Characteristics of the different corn types and their grain fractions. *Journal of Food Engineering*. **2004**, vol. 64, pp. 119-127.

Kokorin, Alexander, **2011**. *Ionic Liquids: Applications and Perspectives* [online]. [cit. 2012-03-12]. ISBN 978-953-307-248-7. Available from: <http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives>.

Kuakpetoon, Daris and Wang, Ya-Jane. Internal structure and physicochemical properties of corn starches. *Carbohydrate Research*. **2007**, vol. 342, pp. 2253-2263.

Lišková, Marcela. Syntézy za neklasických podmínek - E-Learningový kurs [online]. **2008** [cit. 2012-06-19]. Diplomová práce. Masarykova univerzita, Přírodovědecká fakulta. Vedoucí práce Pavel Pazdera. Dostupné z: http://is.muni.cz/th/77987/prif_m/>.

Smiglak, M. Ionic liquids as solvents for dissolution, fractioning, cracking and reprocessing of biomass and biopolymers. *Ionic Liquids Today*. **2010**, vol. 01–10, pp. 12–17. [Www.iolitec.com](http://www.iolitec.com).

Spychaj, T.; Wilpiszewska, K. Ionic liquids: Media for starch dissolution, plasticization and modification. *Carbohydrate Polymers*. **2011**, vol. 86, pp. 424-428.

LIST OF ABBREVIATIONS

DSC Differential scanning calorimeter

IL Ionic liquid

K_1 Calibration constant, [$\text{Pa}\cdot\text{cm}^3\cdot\text{g}^{-1}$]

p Pressure, [Pa]

T Temperature, [K], [$^{\circ}\text{C}$]

η Dynamic viscosity, [Pa.s]

ρ Density, [$\text{kg}\cdot\text{m}^{-3}$]

τ Period of oscillation, [s]

LIST OF FIGURES

Figure 1. Use of ILs [Lišková, 2008].	19
Figure 2. Schematic representation amylose and amylopectin [Karkalas et al., 2004].	24
Figure 3. Appearance of starch grains. 1 – potato starch, 2 – corn starch, 3 – wheat starch [Chrvalová, 2009].	26
Figure 4. Scheme of the Densimeter [Laboratory data].	38
Figure 5. Viscometer used, capillaries and measuring principle [Laboratory data].	39
Figure 6. Karl Fischer Coulometer [Laboratory data].	40
Figure 7. Closed mixing cell [Laboratory data].	41
Figure 8. Appearance of starch grains.	42
Figure 9. Linear temperature dependence on density of ionic liquid BMIM Methyl Phosphite.	45
Figure 10. Exponential temperature dependence on viscosity of ionic liquid BMIM Methyl Phosphite.	45
Figure 11. Evolution of 5 wt% starch #1 in BMIM Methyl Phosphite and during heating. The scale in all optical micrographs is 20 μm .	47
Figure 12. Evolution of 5 wt% starch #1 in water during heating. The scale in all optical micrographs is 20 μm .	48
Figure 13. Evolution of 5 wt% starch #1 in BMIM Methyl Phosphite and 20 wt% water during heating. The scale in all optical micrographs is 20 μm .	50
Figure 14. Heat flow dependence on temperature for BMIM Methyl Phosphite with 5 wt% starch #1 compare with pure BMIM Methyl Phosphite.	52
Figure 15. Complex viscosity dependence on the angular frequency of BMIM Methyl Phosphite in three systems.	53

LIST OF TABLES

Table 1. Commonly used cations in ILs [Karkkainen, 2007].	13
Table 2. Commonly used anions in ILs [Karkkainen, 2007].	14
Table 3. Chemical structures and abbreviation of the examined ionic liquids.	35
Table 4. Description of the examined starches.	36
Table 5. General appearance of ILs and possibility of dissolution of starch.....	44
Table 6. Density, viscosity and thermal properties of ILs.....	44
Table 7. Parameters characterizing dissolution of corn starch #1 in used ILs and IL – water mixtures.	51
Table 8. Parameters characterizing dissolution of 6 kinds of starches in [C ₁ C ₄ Im] [CH ₃ OPO ₂ H].	52