

INFLUENCE OF IMIDASOLIUM RING SUBSTITUTION ON CHITIN DISSOLUTION IN IONIC LIQUIDS

Karolina A. Kopka, Małgorzata M. Jaworska

*Faculty of Chemical and Process Engineering,
Warsaw University of Technology
ul Waryńskiego 1, 00-645 Warszawa, Poland
e-mail: jaworska@ichip.pw.edu.pl*

Abstract

Presented paper discuss the influence of substitution of imidasolium ring on the solubility and structure of chitin. The 1-butyl-3-methyl imidazolium chloride (BMIM)(Cl) and the 1-butyl-2,3-dimethyl imidazolium chloride (BMMIM)(Cl) were used as solvents. These ionic liquids differ by the presence of the substituent in position 2 that causes differences in physical and chemical properties. The surface of chitin particle was observe under electron microscope and chitin IR spectra were compared to investigated polymer structure after regeneration with water. It was found that both IL are good solvents for chitin. Moreover after regeneration chitin structure was similar to native one but became more porous.

Key words: *chitin, ionic liquids, 1-butyl-3-methyl imidazolium chloride (BMIM)(Cl), 1-butyl-2,3-dimethyl imidazolium chloride (BMMIM)(Cl).*

1. Introduction

Chitin is a polysaccharide widely distributed in nature, but due to firm chain packing and the numerous of intermolecular hydrogen bonds it is insoluble in common solvents. There are only a few systems suitable for dissolution of this polymer: LiCl/N,N-dimethylacetamide, 1,2-chloroethanol + H₂SO₄. All of them are corrosive and harmful for environment.

Ionic liquids (IL) are new generation of solvents. They are called “green solvents” due to their properties: they are nonvolatile, thermal resistant (decompose above 300°C) and chemically stable. The term “ionic liquids” has very broad concept and it covers a group of liquid salts that compose of large-size, asymmetric organic cation and simple, usually inorganic anion. Some ionic liquids have been tested as solvents for chitin. The most promising were imidazolium-based IL: [BMIM], [AMIM], [EMIM] in the form of chloride, bromide or acetate salts [1,2]. All of them contain an imidazolium ring, which has different functional group at the R₁, R₂ and R₃ positions (**Figure 1**).

Changing functional groups at positions from R₁ to R₃, the physical/chemical properties of an ionic liquid can be changed. It can be easily observed when we compare the properties of 1-butyl-3-methyl imidazolium chloride, (BMIM)(Cl) and 1-butyl-2,3-dimethyl imidazolium chloride, (BMMIM)(Cl), (**Figure 1**). The cations differ in substitution at R₂ position while all other substitutions are the same. Above difference in cation structure causes changes in properties, (**Table 1**).

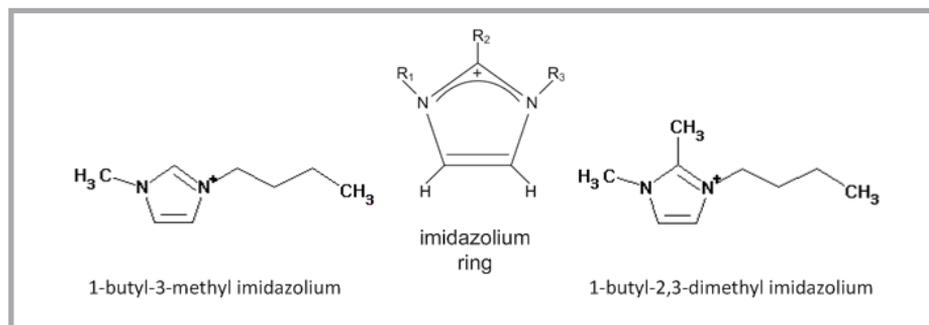


Figure 1. Imidazolium ring. R₁, R₂, R₃ – substituents. 1-butyl-3-methyl imidazolium, 1-butyl-2,3-dimethyl imidazolium –salts used in experiment.

Table 1. Properties of used ionic liquids; ¹⁾ at room temperature, in equilibrium with air

Property	BMIM	BMMIM
Molar mass, g/mol	175	189
Melting point °C	60	99
¹⁾ pH ¹	6.10	8.15

Various properties of the IL like 'pH' or structure also affect the chitin solubility. There is very few studies on chitin solubility in BMIM and BMMIM [2]. Using these two ionic liquids as solvents for chitin, the influence of substitution of imidazolium ring on solubility of chitin can be investigated.

The aim of presented work is to investigate the influence of the substitution of imidazolium ring on chitin structure after regeneration with water from solution of tested ionic liquids.

2. Materials and methods

2.1. Chitin

α -Chitin from shrimps with acetylation degree above 90% and high molecular weight was used in all experiments. Chitin particles have been ground, sieved and the fraction between 200-250 μ m was separated and used.

2.2. Ionic liquids

In the experiment, the 1-butyl-3-methyl imidazolium chloride (BMIM)(Cl) and the 1-butyl-2,3-dimethyl imidazolium chloride (BMMIM)(Cl) were used. Both of them are solids at room temperature in sealed vessel. The ionic liquids were purchase from Merck.

2.3. Experimental procedure

10 cm³ of an ionic liquid and 2.5 g of chitin were mixed together in oil bath at the temperature of 120 °C for 24 h with a mixing speed of 100 r.p.m. After that, received mixture was cooled down to room temperature and than 15 cm³ of water was added to regenerate the biopolymer. Chitin particles were filtrated out on a membrane filter with cut off of 0.45 μ m and IR measurements as well as electron microscopy study were performed.

2.4. Analytical method

IR spectrum was measured with a Thermo Scientific Nicolet 6700 Spectrometer. The microscopic observations were performed with FEI Phenom Scanning Electron Microscope.

3. Results and discussion

3.1. Dissolution of chitin in ionic liquids

The literature data [1, 2] showed that chitin dissolves in IL forming the transparent gels or a suspension of gelled chitin particles. These observations were confirmed in our investigations. A suspension of chitin particles was observed in BMIM chloride (**Figure 2**) at 120 °C. After cooling down to the room temperature, the ionic liquid become solid and some solid chitin particles could be seen at the bottom of a probe. The mixture was stored at room temperature (20 - 23 °C) during 24 hours and in that time gelation of chitin particles could be observed. Additionally it adsorbed some water as the increase in the volume of the mixture was noticed.

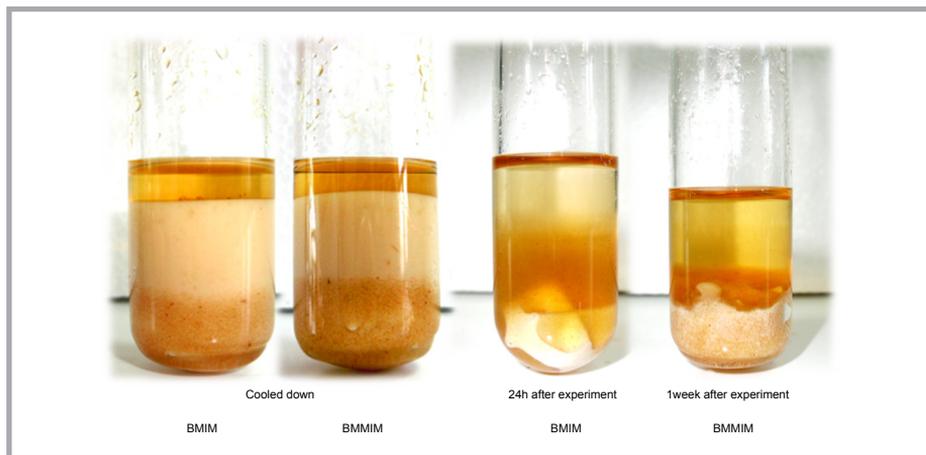


Figure 2. Ionic Liquids witch chitin after experiment.

Behavior of chitin in BMMIM chloride was different. Chitin was mixed with IL in 120°C for 24 h but contrary to previous experiment sedimentation appeared at once after an impeller was stopped (**Figure 2**). It can suggested that chitin doesn't dissolve in BMMIM completely. After cooling down of the chitin – IL mixture to the room temperature, we could easily observe that ionic liquids came back to solid state. This ionic liquid changed into a liquid after one week storage at room temperature, but the increase in the volume was not noticed. Contrary to previously used IL, only part of chitin particles turn in a gel form, while most of them stayed solid what was easily observed at the bottom of the probe.

Gelled chitin particles were observed under the light microscope (**Figure 3**). It can be seen that chitin particles in BMMIM are less translucent than that in BMIM. Connecting above phenomenon with chitin sedimentation in BMMIM, it can be assumed that chitin does not dissolve completely in BMMIM.

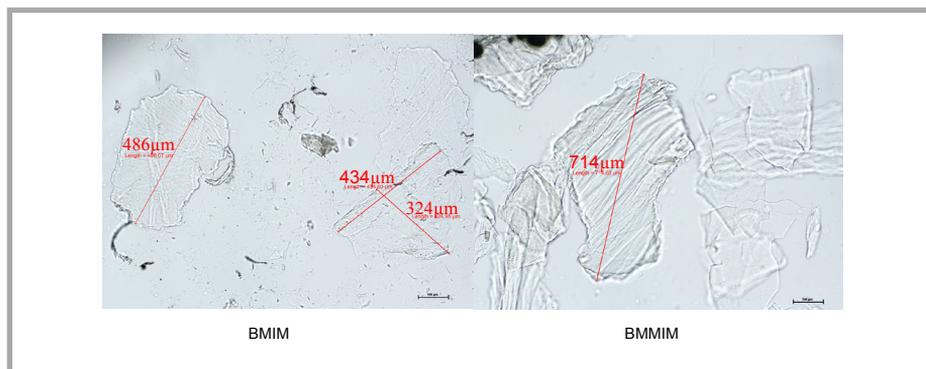


Figure 3. Optical microscope observations of chitin in ionic liquids after water absorption.

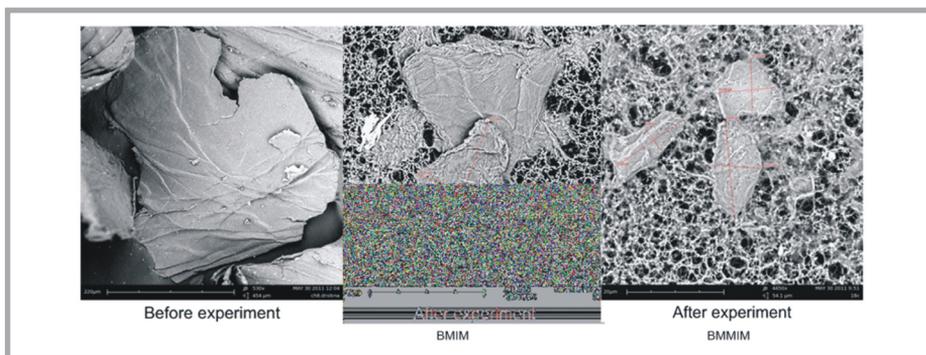


Figure 4. SEM microphotographs of regenerated chitin.

The mechanism of chitin dissolution in ionic liquids is not explained yet. It may be caused by hydrogen bonding ability of IL. Salts in experiments used contain delocalized charge (positive) in imidazolium ring and chloride anion. Moreover, in 1-butyl-3-methyl imidazolium chloride there is an ‘acidic hydrogen’ at R₂ position (**Figure 1**) which is able to form strong hydrogen bonds [4]. These facts may suggest that the stronger electron acceptors or donors can influence hydrogen bonds stabilizing the chitin structure and, these linkages can be destroyed resulting dissolution of chitin.

3.2. Regeneration of chitin

In the next part of experiments, chitin was regenerated from the solution by water. 15 cm³ of water was added to each sample and solid particles of chitin were precipitated. Physical structure of chitin before and after experiment were compared under electron microscope (**Figure 4**). The FTIR spectra of native and regenerated chitin were also compared.

The observation under electron microscope indicated that particles of native chitin used in experiment had smooth and uniform surface, while regenerated chitin become porous (**Figure 4**). Moreover, some insoluble chitin particles could be also observed.

Comparing the IR spectra of native chitin and regenerated from a BMIM chloride as well as from a BMMIM chloride no significant differences could be observed (**Figure 5** see page 42). All spectra are similar but native chitin spectrum is more intense than the spectrum of regenerated chitins. This may suggest the lack of changes in molecular network of the polymer.

After separation of precipitated chitin particles, both ionic liquids were filtered twice through nitrocellulose filter with cut-off of 0.45 μm and dried at 150 °C for 72 h and then stored at 40 °C.

4. Conclusions

Ionic liquids are promising solvents for chitin, but there are lack of systematic investigations focused on the identifications of the relationship between the structure of IL

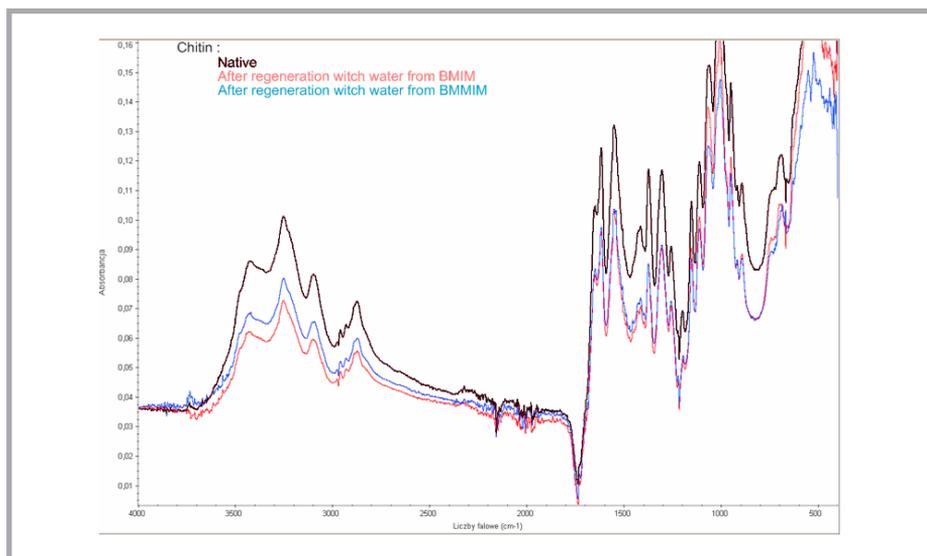


Figure 5. IR spectra of native chitin, regenerated chitin with water from BMIM and BMMIM.

and dissolution of chitin in it. The aim of presented preliminary research works was to investigate the influence of the substitution of imidazolium ring on solubility of chitin. In the experiment the 1-butyl-3-methyl imidazolium chloride and the 1-butyl-2,3-dimethyl imidazolium chloride were used. Both of the solvents are hydroscopic. It was observed that chitin gelled in the 1-butyl-3-methyl imidazolium chloride forming transparent suspension whereas chitin had only partial solubility in 1-butyl-2,3-dimethyl imidazolium chloride. Comparing FTIR spectra of native and regenerated chitin no significant changes were observed as well as the FTIR spectra of pure and purified ionic liquids showed no differences.

5. References

1. S. Mine, H. Izawa, Y. Kaneko, J. Kadokawa; (2009) Carbohydrate Research, 344, 2263-2265.
2. Y. Wu, T. Sasaki, S. Irie, K. Sakurai; (2008) Polymer, 49, 2321-232.
3. G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacka, H. Sixta; (2005) Langmuir Berichte, 84, 71-85.
4. H. Olivier-Bourbigou, L. Magna, D. Morvan; (2010) Applied Catalysis, 373, 1-56.