

Study of Ionic Liquids UV-VIS and FTIR Spectra before and after Heating and Spruce Groundwood Dissolution

DOI: 10.5604/01.3001.0012.7515

Lodz University of Technology,
Institute of Papermaking and Printing,
Fibrous Papermaking Pulps Technology Division,
ul. Wolczanska 223, 90-924 Łódź, Poland;
* e-mail: magdalena.kmiotek@p.lodz.pl

Abstract

The absorption of 1-butyl-3-methylimidazolium chloride and acetate taken from commercial packaging was studied by means of UV-VIS and infrared spectroscopy with some differences observed. Further research showed that heating both 1-butyl-3-methylimidazolium chloride and acetate alone, as well as in the presence of wood pulp, causes the darkening of these ionic liquids. Changes in the colour of ionic liquids associated with a variation in the absorption characteristics of pure ionic liquids and wood solutions in these liquids in UV and visible light are expressed primarily in the widening of the absorption bands. The presence of coloured products formed during their heating, as well as dissolution of the chemical components of wood in ionic liquids, had relatively little effect on the position of individual absorption bands in the spectrum obtained by the FT-IR method. The small differences in the absorption of spruce groundwood solutions in ionic liquids in IR as compared to pure ionic liquids suggest that strong chromophore groups in ionic liquids are created without serious reconstruction of their structure.

Key words: *Ionic liquids, UV spectrum, IR spectrum, heating, groundwood, dissolution.*

in contrast to common organic solvents, have a number of advantages. These include, above all, better thermal and chemical stability, as well as low flammability and volatility [2-10].

The first ionic liquids that were synthesised were imidazolium ones. Their inventors were Wilkes and Zaworotko [11]. A sudden increase in interest in ionic liquids occurred after the test results of Swatloski et al., which indicated the ability of these compounds to dissolve fibrous cellulose [12]. The invention of ionic liquids able to dissolve fibrous cellulose has considerably expanded the number of the relatively small group of its solvents, whose different types have been presented by several authors [13-15].

Imidazolium ionic liquids are composed of an imidazolium residue (containing covalently linked side substituents) and a cation that neutralises the imidazolium residue. The chemical structure of imidazole ionic liquids has a significant influence on their ability to dissolve cellulose, as well as on their properties such as, the melting point, viscosity, thermal stability, miscibility with water and toxicity [10, 16].

Imidazolium ion liquids can be used not only to dissolve cellulose [1, 17-20] but also properly disintegrated lignocellulosic raw materials and other organic substances [21-28]. The dissolving of cellulose results from the ability of ionic

liquids to break hydrogen bonds forming a hydrogen bonding system in a cellulosic material [29, 30]. Hydrogen bonds also impart greater cohesiveness to lignin, because it also contains a large number of free hydroxyl groups capable of forming such bonds [31].

The ability of ionic liquids to dissolve cellulose can be used to develop more ecological methods of manufacturing products made of dissolved cellulose (artificial fibres, films, cellulose derivatives, aerogels). Moreover the ability of ionic liquids to liquefy lignocellulosic raw materials can be applied to the production of, for example, ecological adhesives, wood impregnates, and material composites with other substances, in particular polymers. The application of imidazolium ionic liquids as solvents of cellulose and lignocellulosic biomass has many advantages but also several disadvantages, among which the relatively high price, high viscosity at room temperature, and a tendency to darken during heating are the most important ones.

Taking into account the quite considerable changes in the colour of ionic liquids during their heating, as well as the even greater darkening of solutions of cellulose or lignocellulosic biomass in these liquids, research was undertaken to study this phenomenon using UV-VIS and FT-IR spectroscopy.

The results of this study are presented in this paper.

■ Introduction

Ionic liquids are salts made of a large organic cation and small inorganic or organic anion, characterised by a melting point below 100 °C [1]. They belong to the group of organic solvents which,

Experimental

Ionic liquids

1-butyl-3-methylimidazolium chloride (designated as BCl) and 1-butyl-3-methylimidazolium acetate (BOAc) were chosen as the objects of the research. These liquids were purchased from SIGMA-Aldrich. Their purity, according to the manufacturer, was $\geq 95\%$. Prior to testing, ionic liquids were dried in a desiccator over P_2O_5 for 16 hours.

Investigation of the absorption characteristics of ionic liquids in ultraviolet and visible light, as well as of the effect of heating of these liquids on these characteristics

The ionic liquids chosen for testing were heated in a laboratory dryer until they were liquefied at $110\text{ }^\circ\text{C}$. 2 ml of ionic liquid was placed in a spectrophotometer glass cuvette. The absorption of ionic liquids was measured in ultraviolet and visible light in the wavelength range 190 – 1100 nm. The measurement of light absorption by the ionic liquids was carried out on a UV-VIS T70 spectrophotometer (PG Instruments, United Kingdom). In order to investigate the effect of heating on the absorption characteristics of the ionic liquids in UV, they were heated in 5 ml vials in a laboratory dryer for 20 hours at $110\text{ }^\circ\text{C}$, after which they were poured into an absorption cuvette for absorption measurement on the UV-VIS spectrophotometer.

Preparation of groundwood for dissolution in the ionic liquid

The spruce groundwood used in the study was obtained from a Polish groundwood mill in Myszków. The air-dried spruce groundwood was fibred in a hammer mill to a form of fluff, followed by its drying in a laboratory dryer at $105\text{ }^\circ\text{C}$ for 16 hours.

Dissolution of pulp in ionic liquid

The spruce groundwood was weighed with an accuracy of 0.001 g on a laboratory scale in an amount corresponding to the pulp weight concentration in ionic liquid of 2% (by weight) and then placed in glass vials with a capacity of 2 ml, equipped with caps with a rubber gasket. The vials with the groundwood were then dried for 2 hours in a laboratory dryer at $105\text{ }^\circ\text{C}$. The ionic liquid (after it was preheated) was added to the groundwood in the vial using a glass pipette and then mixed. The samples were then heated in a laboratory drier for 20 hours at $110\text{ }^\circ\text{C}$.

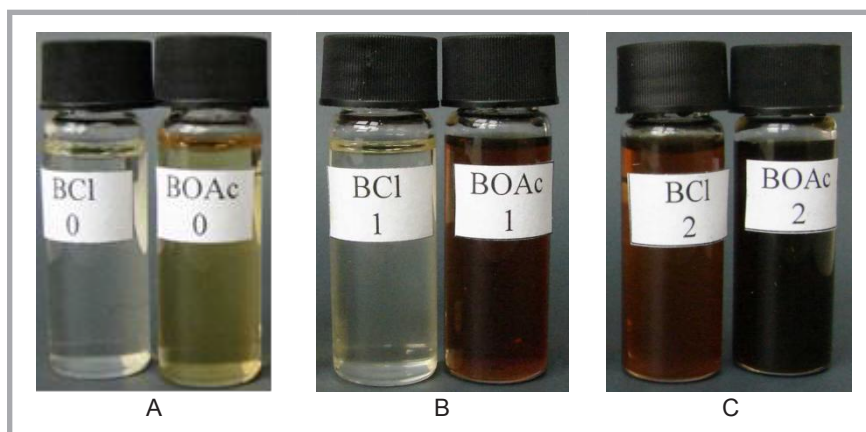


Figure 1. Visual changes in 1-butyl-3-methylimidazolium chloride and acetate before (A) and after heating at $110\text{ }^\circ\text{C}$ for 20 hours (B), and after heating with spruce groundwood (C).

Investigation of the absorption characteristics of ionic liquids and groundwood solution therein in UV light

Approximately 2 ml of the ionic liquid was poured into an absorbent cuvette, and its absorption in ultraviolet and visible light was measured in the wavelength range 190 – 1100 nm on a UV-VIS T70 spectrophotometer (PG Instruments, United Kingdom). The same procedure was performed in the case of groundwood solution in ionic liquids.

Investigation of the absorption characteristics of ionic liquids and groundwood solution therein in infrared light

Fourier transform infrared (FT-IR) studies were carried out on a Bio-Rad 175C spectrometer (Germany) with a Split-Pea (Harrick Scientific) as an internal reflec-

tion spectroscopy attachment. Samples of ionic liquids and solutions of groundwood in these liquids were placed directly on the measuring table under a source of radiation and scanned 16 times in the wave-number range between 400 and 4000 cm^{-1} at a resolution of 4 cm^{-1} .

Results and discussion

Examination of imidazolium chloride and acetate in ultraviolet, visible and infrared light

The absorption spectra of chloride and imidazolium acetate taken from commercial packaging (Figure 1.A) in UV-VIS and IR light are shown in Figures 2 & 3 and 4 & 5, respectively.

Figure 2 shows that in the range of 190–260 nm, the spectra of BCl and BOAc (taken from commercial packaging)

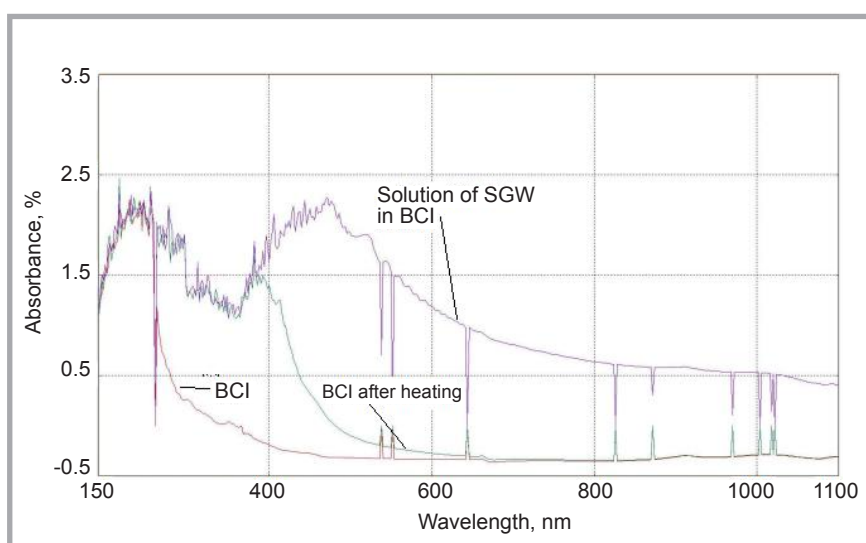


Figure 2. UV-VIS spectra of BCl, BCl after its heating, and the solution of spruce groundwood in BCl.

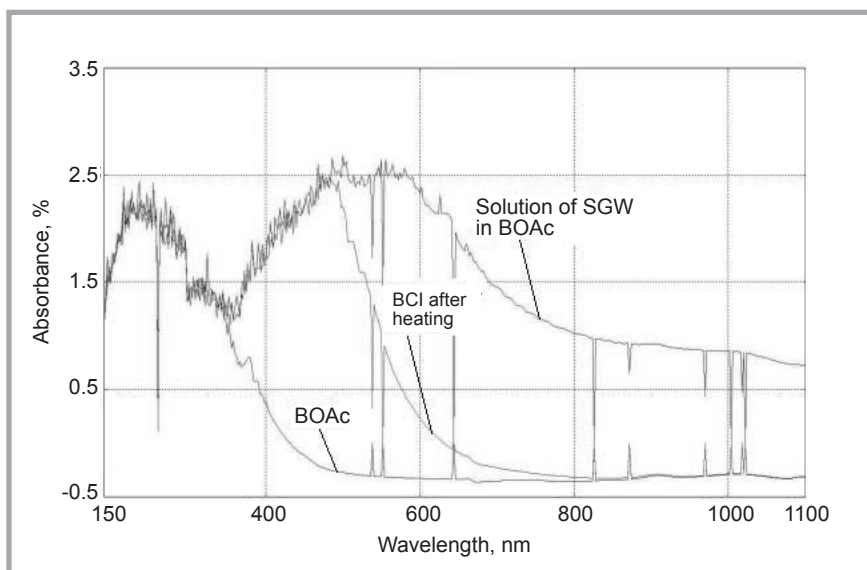


Figure 3. UV-VIS spectra of BOAc, BOAc after its heating, and spruce groundwood solution in BOAc.

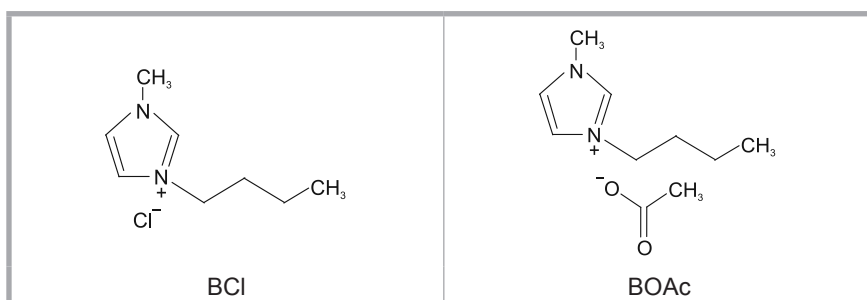


Figure 4. Chemical structure of 1-butyl-3-methylimidazolium chloride (BCI) and acetate (BOAc).

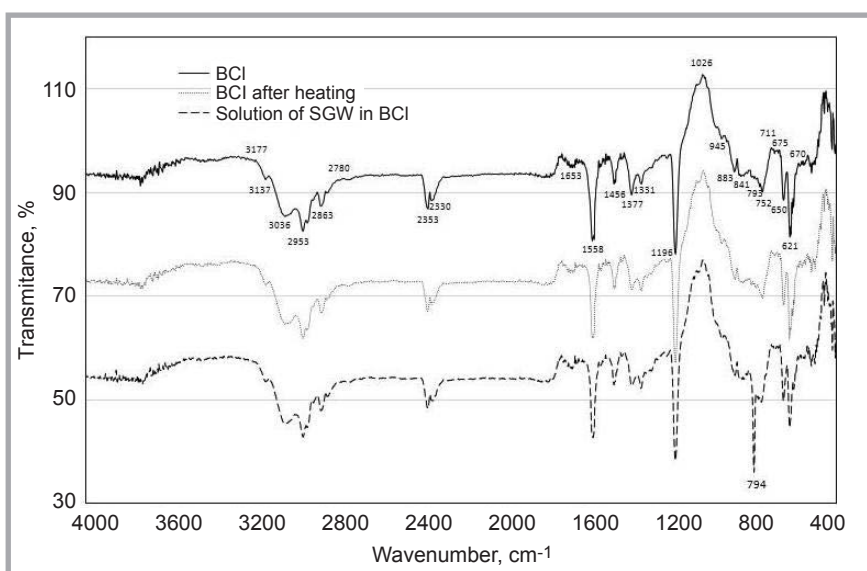


Figure 5. FT-IR spectra of BCI after its heating; and of the solution of groundwood (SGW) in this ionic liquid.

in UV-VIS do not differ substantially. The absorption in this wavenumber range with the maximum at about 235 nm can thus be attributed to the butyl-

methylimidazolium residue. BCI exhibits its maximum absorption at ca. 262 nm, after which its absorption in UV rapidly decreases. Together with an increase in

the wavelength, BOAc absorbs light in the wavelength range 262-300 nm and 300-600 nm (and therefore in UV and visible light). Then, similar to the case of BCI, along with an increase in the wavelength, absorption decreases. The difference in the absorption of pure chloride and imidazolium acetate in the wavelength range 262-600 nm can be attributed to the acetate residue. The chemical structure of BCI and BOAc is presented in **Figure 4**.

From the spectra of these ionic liquids in infrared light (**Figures 5** and **6**), it appears that in the wavelength range 3200-2800 cm^{-1} the imidazolium salts studied show maxima of absorbance at the same wave number. In the source literature, it is pointed out that it can be derived from methylene and methyl groups (stretching vibrations), as well as from primary, secondary and tertiary amine salts. The bands that can be seen in **Figures 5** and **6** can be attributed to the C-H stretching vibrations of the butyl residues and those of N-C atoms present in the imidazolium ring.

Another common element of the FT-IR spectra of the ionic liquids studied is a the weak band at 1650-1660 cm^{-1} and strong band with a maximum at 1560-1570 cm^{-1} . The first of these two may result from the presence of the C=C double bond system of the imidazolium moiety, and the second – from the primary ammonium salts or aromatic amines. As can be seen from the comparison of **Figures 5** and **6**, the absorption of BOAc in this region of the spectrum is much stronger than for BCI. This may result from the overlap of the absorption peak of ammonium salts with that of the carboxylate anion of acetate, which absorbs light at a wave number of about 1600 cm^{-1} [32].

Another distinct band extends from 1490 to 1230 cm^{-1} , which, both in the case of BCI and BOAc, consists of four maxima. In the case of the former ionic liquid, the intensity of the maxima at 1456, 1377 and 1331 cm^{-1} is significant, while the band at 1282 cm^{-1} is weak. In the case of the latter, only the absorbance peak of the third band is strong, i.e. at 1377 cm^{-1} , while the remaining bands are very weak. From the source literature it follows that infrared light between 1200 and 1500 cm^{-1} absorbs alkanes (range 1370-1500 cm^{-1}), alkenes (1400 cm^{-1}), aliphatic amines (1250-1350 cm^{-1}), as

well as ammonium ions (1400 cm^{-1}). The bands mentioned can thus be attributed to the vibrations of C-H and C = C groups of atoms and, above all, C-N and N-H ones. The peak at 1377 cm^{-1} , which is much stronger for BOAc than for BCl, may be attributed to the absorption of amine compounds and acetic carboxylate ions, which, according to the source literature, should also be absorbed between $1350\text{--}1450\text{ cm}^{-1}$ [32].

A strong BCl absorption band at 1196 cm^{-1} , which for BOAc is observed to be of much lower intensity at a similar wave number (1171 cm^{-1}), can be derived from the tertiary amine group presence. For the rest of the FT-IR spectrum, i.e. from 1026 to 670 cm^{-1} , it can be stated that the bands occur at the same wave-number values for both ionic liquids. From the source literature, it appears that absorption in this range of the spectrum can come from alkane and alkene groups.

Examination of BCl and BOAc after their heating at $110\text{ }^{\circ}\text{C}$ for 20 hours by UV-VIS and FT-IR spectroscopy

Ionic liquids are specific types of solvents of natural polymers. The process of dissolving these substances usually involves the long-term heating of samples, often at relatively high temperatures. The heating process can lead to changes in the chemical structure of ionic liquids, for example, due to oxidation. In order to determine the effect of the long-term heating of ionic liquids at high temperature on their structure, the salts were subjected to heating at $110\text{ }^{\circ}\text{C}$ for 20 hours, and then their spectra were analysed by UV-VIS and FT-IR spectroscopy. As can be seen from the comparison of photographs A and B in *Figure 1*, the heating of ionic liquids caused a slight yellowing

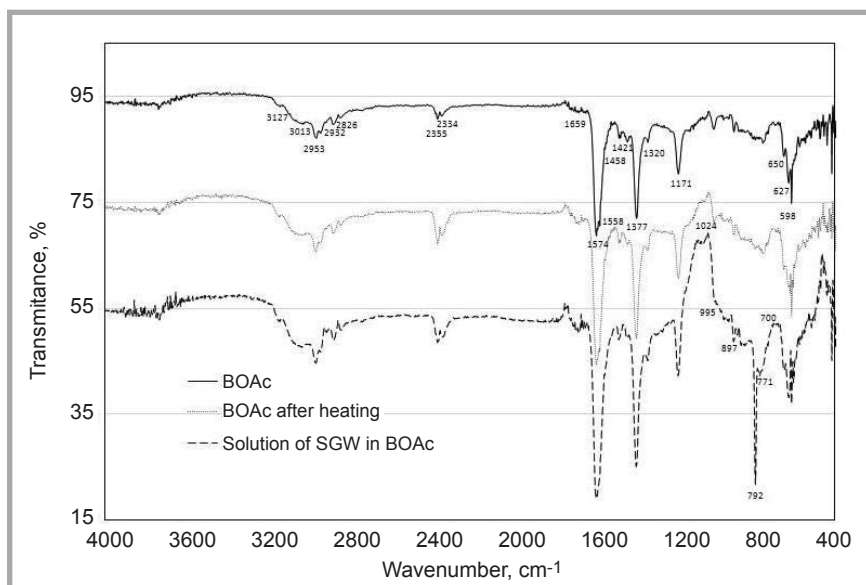


Figure 6. FT-IR spectra of BOAc after its heating, and of the solution of groundwood (SGW) in this ionic liquid.

of BCl and a change in colour of BOAc from light-yellow to dark amber.

The change in colour of ionic liquids caused the appearance of new absorption bands in the spectrum of these liquids under UV light, and also in the visible range of light. These are bands at $262\text{--}300$, $300\text{--}370$ and $370\text{--}650\text{ nm}$. The UV-VIS spectrum of BOAc subjected to heating reveals the appearance of a strong absorption band in the range of $370\text{--}800\text{ nm}$, with a clear maximum at 480 nm .

The presence of new absorption bands in the UV-VIS spectra of ionic liquids after their heating is accompanied by their various darkening (*Figure 1*), especially for BOAc, which colour changes drastically from yellow to dark amber. The darkening of BCl is minimal. Since the samples of ionic liquids used in the study did not contain any additives, the changes in colour observed must result from the vari-

ations in their chemical structure occurring under the influence of temperature or temperature and oxygen.

Interestingly, the colour changes found, as well as those in UV absorption, caused by long-term heating at high temperature, were not accompanied by changes in the distribution of absorption peaks in infrared light, but only by increased absorption intensities of these peaks, which were more visible in the imidazolium acetate spectrum (*Figures 5 and 6*). This indicates that the coloured compounds occurred as a result of thermal changes in the ionic liquids being formed without serious reconstruction of their structure; however, in the case of BOAc, they were responsible for the creation of strong chromophore groups. The reasons for these changes mentioned in the source literature may be the deprotonisation of ionic liquid cations under the influence

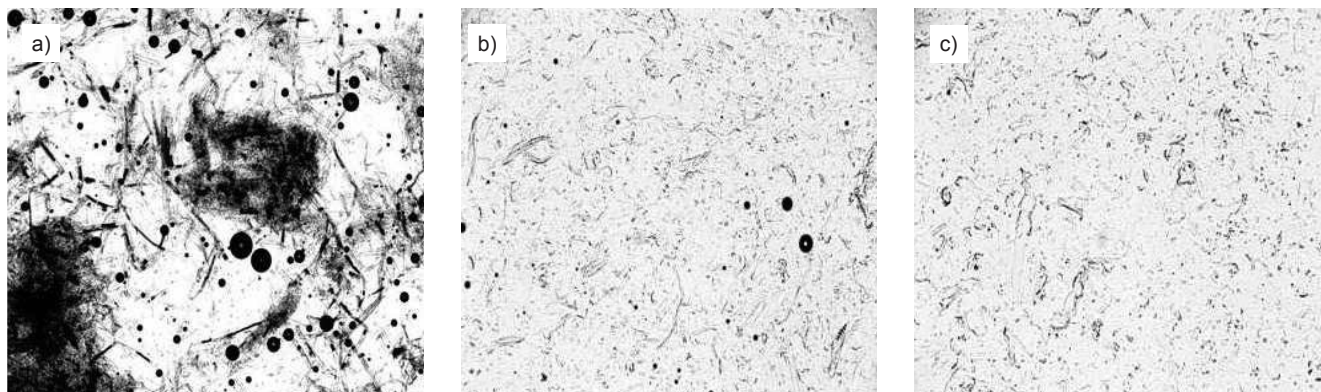


Figure 7. Microscopic images of groundwood after its dissolution in ionic liquids: a) SGW in BCl before heating, b) SGW in BCl after heating, c) SGW in BOAc after heating.

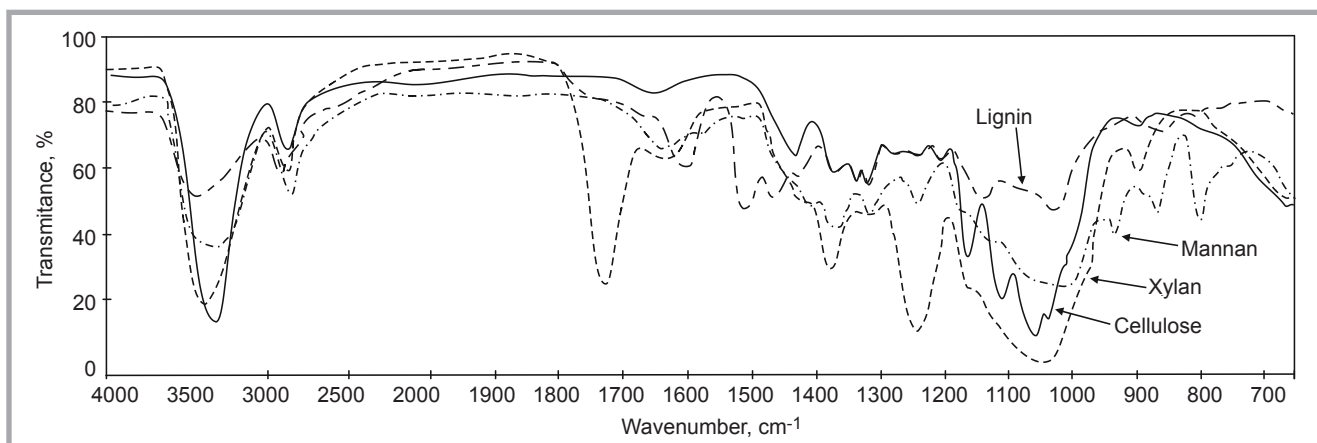


Figure 8. Infrared spectra of cellulose (solid curve), Klason lignin (dotted curve), 4-O-methylglucuronoxylan (small dotted curve) and mannan (pointed curve) [39].

of alkaline substrates used for their synthesis (e.g. imidazole), as well as the carbonation of side substituents attached to the ionic liquid cation [2, 3, 33, 34].

Examination of groundwood solutions in imidazolium chloride and acetate by UV-VIS and FT-IR spectroscopy

Microscopic images of 2 wt. % solutions of spruce groundwood in BCl and BOAc before and after heating are depicted in **Figures 7.a, 7.b** and **7.c**, respectively, whereas their UV-VIS and FT-IR spectra are shown in **Figures 2, 3, 5** and **6**, respectively.

Figures 2 and **3** show that in the case of BCl and BOAc, the process of dissolving the pulp leads to the extension of absorption bands in the light wavelength range 370–650 nm (**Figure 2**) and 370–800 nm (**Figure 3**), from 370 up to 1100 nm respectively. This is accompanied by their increasing intensity, especially in the case of BCl. The increase in the absorption of wood solutions in ionic liquids in visible light goes hand in hand with a clear strong darkening of both samples of groundwood solution in BOAc as well as in BCl (**Figure 1.c**).

A possible explanation for the strong darkening of groundwood solutions in ionic liquids observed may be the appearance of new strong chromophore groups derived from the chemical components of wood, especially lignin or carbohydrate components. Regarding possible known changes in lignin, the chromophore groups may result from structural changes in lignin aromatic rings, e.g. the transformation of the methoxide groups of lignin to quinone ones. The latter can also be converted to catechol

residues during heating in ionic liquids, which, according to studies by Imsgard et al. [35], as well as Ghosh and Mi [36], strongly absorb visible light.

From the comparison of FT-IR spectra of spruce groundwood solution in BCl (the lowest curve in **Figure 5**) with those of BCl from commercial packaging (the solid curve in **Figure 5**), it follows that there is no significant difference in the absorption of infrared light in the wavelength range 3200–1020 cm^{-1} . In fact, absorption peaks occur at the same values of the wave number and are characterised by the same intensity. A similar tendency in the range of wave numbers discussed can be found in the case of FT-IR spectra of groundwood in BOAc (**Figure 6**, lower and middle curves).

In contrast to BCl, in the spectrum of the groundwood solution in BOAc, higher intensity of the absorption bands in the range of 3200–1020 cm^{-1} is observed in comparison to that of the analogous bands in the pure BOAc spectrum. Differences in the intensity of the absorption peaks of these samples are particularly evident at around 1574 and 1377 cm^{-1} . The increase in the absorption peak at 1574 cm^{-1} could be attributed to the appearance of free lignin in the ionic liquid, as in the wavelength range of approx. 1500–1600 cm^{-1} absorbance area attributed to benzene ring bands appear. However, there is no second band characteristic for these rings at about 1510 cm^{-1} [37, 38].

The same is observed for the absorption band with a maximum at 1377 cm^{-1} . An increase in the intensity of absorption in the FT-IR spectrum at this

wavelength, noticed for the solution of groundwood in BOAc, can be attributed to the presence of free cellulose and hemicelluloses in the solution. This can also be confirmed by the increase in the intensity of the absorption bands in the range of 900–1000 cm^{-1} and at 792 cm^{-1} (the lowest spectrum in **Figure 6**), which can be assigned (according to literature data presented in **Figure 8**) to vibrations of the C-O groups of cellulose and hemicelluloses, respectively. The presence of strong and characteristic absorption bands of C-O-C groups at 1000–1200 cm^{-1} for cellulose and hemicelluloses confirms this.

Conclusions

- The spectra of 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate under UV light are different as a result of the different chemical structure of these liquids or/and the presence of different kinds or amounts of impurities in these liquids.
- The spectra of imidazolium chloride and acetate in infrared light are similar, but differ in the intensity of individual absorption bands.
- Heating imidazolium chloride and acetate at 110 °C causes their darkening. In the case of imidazolium acetate, this darkening is clearly stronger.
- Changes in the colour of ionic liquids caused by heating significantly affects the absorption characteristics of pure ionic liquids and wood solutions therein in UV-VIS light, mainly through significant widening of the absorption bands into the area of higher wavelengths of light.

■ In the FT-IR spectra of 2 wt. % ground-wood solutions in 1-butyl-3-methylimidazolium acetate, the growth of intensity of absorption peaks at 1574, 1377 and around 792-794 cm^{-1} is observed probably as a result of cellulose, lignin and hemicellulose introduction into the ionic liquids, originating in spruce groundwood.



References

- Plechkova NV, Seddon KR. Applications of ionic liquids in the chemical industry. *Chem Soc Rev*. 2008; 37: 123-150.
- Subbiah S, Venkatesan S, Ming-Chung T, Yen-Ho Ch. On the chemical stability of ionic liquids. *Molecules* 2009; 14:3780-3813.
- Ebner G, Schiehser S, Potthast A, Rosenau T. Side reaction of cellulose with common 1-alkyl-3-methylimidazolium-based ionic liquids. *Tetrahedron Lett*. 2008; 49: 7322-7324.
- Bonhote P, Dias AP, Papageorgiou N, Kalyanasundaram K, Gratzel M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg Chem*. 1996; 35: 1168-1178.
- McEwen AB, Ngo HL, LeCompte H, Goldman JL. Electrochemical properties of imidazolium salt electrolytes for electrochemical capacitor applications. *J Electrochem Soc*. 1999; 146: 1687-1695.
- Holbrey JD, Seddon KR. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates: ionic liquids and ionic liquid crystals. *J Chem Soc. Dalton Trans*. 1999; 2133-2139.
- Ngo HL, LeCompte H, Hargens L, McEwen AB. Thermal properties of imidazolium ionic liquids. *Thermochim Acta*. 2000; 357-358: 97-102.
- Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem*. 2001; 3: 156-164.
- Van Valkenburg ME, Vaughn RL, Williams M, Wilkes JS. Ionic liquid heat transfer fluids, *15th Symposium of Thermophysical Properties*; 2003 Jun 22-27; Boulder, CO.
- Pinkert A, Marsh KN, Pang S, Staiger MP. Ionic Liquids and their interaction with cellulose. *Chem Rev*. 2009; 109:6712-6728.
- Endres F, Zein El Abedin S. Air and water stable ionic liquids in physical chemistry. *Phys Chem Chem Physics* 2006; 8:2101-2116.
- Swatloski RP, Spear SK, Holbrey JD, Rogers SD. Dissolution of cellulose with ionic liquids. *J Am Chem Soc*. 2002; 124: 4974-4975.
- Heinze T, Liebert T. Unconventional methods in cellulose functionalization. *Progress Polym Sci*. 2001; 26: 689-1762.
- Heinze T, Koschella A. Solvents applied in the field of cellulose chemistry – a mini review. *Polimeros: Ciência e Tecnologia* 2005; 15:84-90.
- Fischer S, Leipner H, Thümmeler K, Brendler E, Peters J. Inorganic molten salts as solvents for cellulose. *Cellulose* 2003; 10:227-236.
- Huddleston JG, Visser AE, Reichert VM, Willauer HD, Broker GA, Rogers RD. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem*. 2001; 3:156-164.
- Hermanutz F, Gähr F, Uerdingen E, Meister F, Kosan B. New Developments in Dissolving and Processing of Cellulose in Ionic Liquids. *Macromol Symp*. 2008; 262: 23-27.
- Zhu S, Wu Y, Chen O, et al. Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chem*. 2006; 8: 325-327.
- Kuzmina O, Sashina E, Troshenkowa S, Wawro D. Dissolved state of cellulose in ionic liquids – the impact of water. *FIBRES & TEXTILES in Eastern Europe* 2010, 18, 3 (80): 32-37.
- Wawro D, Hummel M, Michud A, Sixta H. Strong cellulosic film cast from ionic liquid solutions. *FIBRES & TEXTILES in Eastern Europe* 2014; 22, 3(105): 35-42.
- Kilpeläinen S, Xie H, King A, Granstrom M, Heikkinen S, Argyropoulos DS. Dissolution of wood in ionic liquids. *J Agric Food Chem*. 2007; 55: 9141-9148.
- Han S, Li J, Zhu S, et al. Potential applications of ionic liquids in wood related industries. *BioResources* 2009; 4: 825-834.
- Zavrel M, Bross D, Funke M, Büchs J, Spiess AC. High-throughput for ionic liquids dissolving (ligno)-cellulose. *Biore-source Technol*. 2009; 100:2580-2587.
- Fort DA, Remsing RC, Swatloski RP, Moyna G, Rogers RD. Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. *Green Chem*. 2007; 9: 63-69.
- Sun N, Rahman M, Quin Y, Maxim ML, Rodriguez H, Rogers RD. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chem*. 2009; 11: 646-655.
- Surma-Ślusarska B, Danielewicz D. Solubility of various types of cellulose in ionic liquids. *Przegl Papiern*. 2012; 68: 43-48 (in Polish).
- Surma-Ślusarska B, Danielewicz D, Kaleta M. Comparison of properties of various types of cellulose before and after regeneration from ionic liquids. *Przegl Papiern*. 2012; 68: 99-103 (in Polish).
- Holnglu X, Wielun S. Wood liquefaction by ionic liquids. *Holtzforshung* 2006; 60: 509-512.
- Feng L, Chen Z. Research progress on dissolution and functional modification of cellulose in ionic liquids. *J Mol Liq*. 2008; 142:1-5.
- Heintze T, Dorn S, Schöbitz M, Liebert T, Köhler S, Meister F. Interaction of ionic liquids with polysaccharides – 2: Cellulose. *Macromol Symp*. 2008; 262:8-22.
- Miechell AJ. Hydrogen bonding in lignins and in related alcohols and phenols. *Cell Chem Technol*. 1982; 16: 87-101.
- Kosmulski M, Gustafsson J, Rosenholm JB. Thermal stability of low temperature ionic liquids revisited. *Thermochim Acta*. 2004; 412: 47-53.
- Almeida HF, Passos H, Lopes-da-Silva JA, Fernandes AM, Freire MG, Coutinho AP. Thermophysical properties of five acetate-based ionic liquids. *J Chem Eng*. 2012; 57: 3005-3013.
- Silverstein RM, Webster FX, Kiemle DJ. *Spectroscopic methods of identification of organic compounds*. Warszawa: Wydawnictwo Naukowe PWN; 2007.
- Ghosh A, Mi Y. Metal ion complexes and their relationship to pulp brightness. *J Pulp Paper Sci*. 1998; 24: 26-30.
- Imsgard F, Falkehag SI, Kringstad KP. On possible chromophoric structures in spruce wood. *TAPPI J*. 1971; 54: 1680-1694.
- Gosselink RJA, Abächerli A, Semke H, et al. Analytical protocol for characterization of sulphur-free lignin. *Ind. Crops Prod*. 2004; 19: 271-281.
- Tejado A, Peña Labidi J, Echeverria JM, Mondragon I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresource Technol*. 2007; 98: 1655-1663.
- Liang CY, Bassett KH, McGinnes EA, Marchessault RH. Infrared spectra of crystalline polysaccharides. VII. Thin wood sections. *TAPPI J*. 1960; 43: 1017-1021.

■ Received 13.07.2018 Reviewed 10.09.2018