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

**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.

**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, 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.
## Experimental

### Ionic liquids

1-butyl-3-methylimidazolium chloride (designated as BCI) 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 ≥ 95%. Prior to testing, ionic liquids were dried in a desiccator over P₂O₅ for 16 hours.

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

The ionic liquids chosen for testing were heated in a laboratory dryer until they were liquefied at 110 °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 °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 fibreised in a hammer mill to a form of fluff, followed by its drying in a laboratory dryer at 105 °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 °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 °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.

### Results and discussion

#### Examination of imidazolium chloride and acetate in ultraviolet, visible and 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 reflection 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.

#### Figure 1. Visual changes in 1-butyl-3-methylimidazolium chloride and acetate before (A) and after heating at 110 °C for 20 hours (B), and after heating with spruce groundwood (C).

**Figure 2.** UV-VIS spectra of BCI, BCI after its heating, and the solution of spruce groundwood in BCI.
The absorption spectra of chloride and imidazolium acetate taken from commercial packaging in UV do not differ substantially. The absorption in this ionic liquid, which, both in the case of BCl, along 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 BCl, 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 BCl 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 BCl. 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 BCl 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\(^{-1}\)), and aliphatic amines (1250-1350 cm\(^{-1}\)), as 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. BCl exhibits its maximum absorption at ca. 262 nm, after which its absorption in UV rapidly decreases. Together with an increase in
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 BCI, may be attributed to the absorption of amine compounds and acetic carboxylate ions, which, according to the source literature, should also be absorbed between 1350-1450 cm\(^{-1}\) [32].

A strong BCI 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 BCI and BOAc after their heating at 110 °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 °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 of BCI 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 262-300, 300-370 and 370-650 nm. The UV-VIS spectrum of BOAc subjected to heating reveals the appearance of a strong absorption band in the range of 370-800 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 various darkening (Figure 1), especially for BOAc, which colour changes drastically from yellow to dark amber. The darkening of BCI 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 variations 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

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

**Figure 7.** Microscopic images of groundwood after its dissolution in ionic liquids: a) SGW in BOCI before heating, b) SGW in BOCI after heating, c) SGW in BOAc after heating.
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 BCI 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 BCI 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 BCI. 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 BCI (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 methoxyl 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 BCI (the lowest curve in Figure 5) with those of BCI 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 BCI, 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 appears. 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-C 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. % groundwood 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


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