

Article

Alkylimidazolium Ionic Liquids Absorption and Diffusion in Wood

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Featured Application: Ionic liquids with alkylimidazolium cations represent a class of emerging wood additives with a swelling, plasticizing, and stabilizing character for wood-based materials. Their diffusion in wood depends on their structure and molecular weight, as well as their viscosity and surface tension.

Abstract: Ionic liquids represent a class of highly tunable organic compounds responsible for many applications in the domain of wood-based materials. It has often been emphasized that the use of ionic liquids derives from their high affinity for lignocellulose and their good penetration ability into wood structures. This paper discusses the sorption ability of different types of 1-alkyl-3-methylimidazolium ionic liquids with lateral alkyl chains, ranging from ethyl to hexyl into spruce and beech wood, as a function of their cation molecular mass, anion type (chloride, tetrafluoroborate, acetate), and intrinsic properties (surface tension and kinematic viscosity) at room temperature. All the studied ionic liquids present high relative uptake values at the equilibrium, ranging from 11.2% to 69.7%. The bulk diffusion coefficients of the ionic liquids into the wood range from 2×10^{-3} to 28×10^{-3} mm²/min, being higher in the longitudinal direction for both types of wood. The value of the diffusion coefficients for 1-ethyl-3-methylimidazolium chloride is only 25% lower than that for water, despite the obvious differences in viscosity and surface tension, demonstrating a good penetration ability and the potential for wood industry-related applications (as impregnation compound carriers and preservatives).

Keywords: wood; ionic liquids; wood preservatives; diffusion; swelling; lignocellulose



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1. Introduction

The uniform impregnation of wood materials is of great economic importance. Diffusion treatment with various chemicals can be viewed as a cost-efficient alternative to pressure impregnation, uniformly distributing water-borne preservatives (e.g., biocides, fire retardants, and moisture stabilizers) or resin precursors in wood, without the need for costly equipment [1,2]. In some instances, especially in hardwoods, diffusion treatment can be combined with pressure impregnation to improve the chemical distribution into the bulk of the material, ranging from green veneers to timber. Thus, a thorough understanding of various compounds' complex chemical transport phenomena into the wood matrix is critical for obtaining performant and durable materials [3–6].

Several factors generally influence diffusivity and permeability in wood-based materials, usually directly proportional to temperature and moisture content and inversely proportional to the density of the samples [7,8]. It has long been established that, generally, for green wood or wood above its fiber saturation point (~26% moisture), the diffusion of organic compounds such as glycerol, urea, or polysaccharides occurs through the cell wall polysaccharides, which, in the such moisture conditions, are likely to be in a rubbery, amorphous state. Diffusion generally obeys Fick's law of diffusion. Inorganic salts

which do not interact with lignocellulose (such as alkaline/alkaline earth metal halides) have a concentration-independent diffusion coefficient (0.2–0.4 cm²/day) [9,10], while for inorganic compounds which interact with lignocellulose (dichromates, copper salts, arsenic compounds, boric acid, and borates), substantial deviations are registered from the ideal Fickian behavior. Strong hydrogen bond-disruptors (usually compounds with large or aromatic side-chain constituents) present highly concentration-dependent diffusion coefficients values [11].

Ionic liquids (ILs) are a class of organic compounds with low melting points and negligible vapor pressures, linked since the late 1990s with various wood-related applications. Apart from their ability to dissolve wood, many ILs have been studied for their antifungal character, wood plasticizing effect, antistatic character, or thermal and UV stabilizers (especially those with long-chain alkylammonium and alkylimidazolium cations) [12–15]. They are reported to present good penetration into the bulk of the wood, swelling it, while at the same time presenting a low leaching ability [16]. Apart from their use as preservatives per se, they can be used in wood-related applications as carriers [16], or as a means for transporting antifungal agents [13].

Even if many studies report (bio)polymers (including wood lignocellulose) interaction, swelling, and dissolution in ILs [12,17], there are very few studies that report the dependence of wood swelling on the structure of the ionic liquid, and virtually none that report the diffusion coefficients of commercial alkylimidazolium ionic liquids (in pure liquid form or as aqueous solutions) in the wood [14,18]. This study, showing the potential of application, could provide the required encouragement for the application of ionic liquids in the wood industry. One can compile, for example, different information regarding the ILs sorption in wood from the reference literature. However, this information is not very useful, from a practical point of view, for comparison. Generally, the wood samples are prepared differently (only bulk sorption, or at most one or two sections, either tangential or radial, are taken into the discussion); expensive synthesized ILs with complex structures are discussed, or wood with questionable practical applications (tropical species) is used [19,20].

The scope of this paper is to determine the absorbed amount and diffusion coefficients of several types of alkylimidazolium ionic liquids at room temperature in two typical wood types: Norway spruce (*Picea* sp.) and beech (*Fagus* sp.). Due to the relatively high cost of ionic liquids, their practical industrial applications are yet to be utilized. This study could be potentially applicable to the encouragement of ionic liquids application in the wood industry, where the specific consumption of the chemical used for impregnation or other treatments is of paramount importance to determine the overall cost of the process.

2. Experimental Section

2.1. Materials

Two wood species were used for the experiments: Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*). Quarter-sawn samples from the two types of wood, with dimensions of 20 mm × 10 mm × 10 mm (longitudinal × radial × tangential), were used to determine ionic liquids uptake and diffusion coefficients. The bulk average density of the wood specimens used was 358 kg/m³ for spruce and 562 kg/m³ for beech.

The following water-soluble ionic liquids were used in the experiments: 1-ethyl-3-methylimidazolium chloride (EMIMCl, >95%, $M_w = 146.62$), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄, >98%, $M_w = 197.97$), 1-ethyl-3-methylimidazolium acetate (EMIMAc, 95%, $M_w = 170.21$), 1-butyl-3-methylimidazolium chloride (BMIMCl, 99%, $M_w = 174.67$), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄, 99%, $M_w = 226.02$), 1-butyl-3-methylimidazolium acetate (BMIMAc, >95%, $M_w = 198.26$), 1-hexyl-3-methylimidazolium chloride (HMIMCl, 99%, $M_w = 202.72$), and 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIMBF₄, 99%, $M_w = 254.08$). All ionic liquids were purchased from IoLiTec Ionic Liquids Technologies GmbH (Heilbronn, Germany).

These 1-alkyl-3-methylimidazolium ionic liquids were chosen for their relatively low price compared to other ionic liquids, wide commercial availability, ease of synthesis and good interaction with the wood components [21,22]. At room temperature, negligible dissolution of lignocellulose or wood extractives occurred [23], and several useful properties were imparted to the wood as demonstrated from both the authors' previous work and other independent studies [15,24,25].

To compare the different types of ILs in absorption and diffusion behavior, a concentration of 90% wt. was chosen in all instances, based on the authors' prior experimental parameters optimization. Considering that some ILs (EMIMCl and BMIMCl) were solids at room temperature, a solution (rather than a slurry) was satisfactorily obtained starting only with the specified concentration value.

After ILs sorption equilibrium was reached, the wood samples were dried in a CaCl₂-containing desiccator for 7 days and then analyzed by ATR-FTIR (Perkin-Elmer Spectrum BXII IR spectrometer) at a 4000–600 cm⁻¹ interval with a 4 cm⁻¹ resolution.

2.2. Methods

Before the ionic liquids sorption and diffusion experiments, the wood samples were weighed, oven-dried at 103 °C for 7 h, re-weighed (m_{od}), and conditioned in a desiccator over a supersaturated Mg(NO₃)₂ solution (54% relative humidity) for a week at 22 °C, to attain an average equilibrium moisture content (EMC) of 9.18% (spruce), respectively 8.75% (beech). The average densities of the two types of conditioned wood samples were 0.425 g/cm³ (Norway spruce) and 0.713 g/cm³ (beech), respectively.

The conditioned wood specimens were weighed ($m_{wood,0}$) and submerged in 50 mL of IL solutions in stoppered glass vials. Periodically, the wood samples were taken out from the IL solutions (from 10 to 10 min in the first 200 min, and from thereon hourly, from 3 to 3 h, or from 12 to 12 h until sorption equilibrium, depending on IL type and wood species), the superficial amount of liquid present on their surface was removed by blotting with filter paper, after which they were weighed ($m_{wood,IL,t}$). The weighing operation was performed until the absorption equilibrium was reached (on average between 500 and 6800 min). The relative amount of absorbed ILs ($w_{IL,t}$) was calculated with Equation (1) [16]:

$$w_{IL,t} = \frac{m_{wood,IL,t} - m_{wood,0}}{m_{wood,0}} \cdot 100 \quad (1)$$

After reaching the ILs' absorption equilibrium (corresponding to the value $w_{IL,eq}$), the wood samples were dried for 7 h until constant mass ($m_{wood,ILd}$). The drying was performed in a vacuum drying oven (Memmert, Germany) at 45 °C and 10 mbar to avoid the dissolution/leaching/degradation of wood components from the IL-loaded wood, which could occur under normal drying conditions.

The weight percent gain (WPG) of the IL-loaded wood at equilibrium was calculated with Equation (2) [26]:

$$WPG = \frac{m_{wood,ILd} - m_{od}}{m_{od}} \cdot 100 \quad (2)$$

The unidirectional (radial -R-, longitudinal -L-, or tangential -T-) ILs uptake were determined by coating the other sections of the wood samples apart from the two faces corresponding to the direction of interest through brushing with an epoxy resin [27,28] and immersion in the IL solutions, following the same protocol as described above. Prior experiments indicated that there was no detectable dissolution or swelling of the resin in the studied ILs.

The diffusion coefficients in the longitudinal, radial, and tangential direction (D_x , where $x = L, R$ or T) were determined from Neumann's form of Fick's law (Equation (3)) [9]:

$$D_x = \frac{\pi \cdot d^2 \cdot E^2}{16 \cdot w_{IL,eq}} \quad (3)$$

where d is the diffusional thickness of the specimen (i.e., the distance between the two uncoated faces of the sample for each unidirectional case), E is the slope of the IL uptake kinetic for the first 66% of the data, and $w_{IL,eq}$ is the relative IL uptake ratio at equilibrium.

Five parallel samples were used for each type of experiment, and the average values were presented in the paper.

3. Results and Discussion

For all the wood samples, the absorbed amount of ionic liquids is 30 to 85% higher than that corresponding to distilled water, demonstrating the wood matrix's high affinity for these compounds [14,15]. As an absorption trend, the uptake of ILs is strongly dependent on the molecular mass of the cation, i.e., $EMIM^+ > BMIM^+ > HMIM^+$ (Figure 1a–c). Chlorides are absorbed in a higher amount than acetates and tetrafluoroborates due to their higher interaction potential with the cellulose and lignin components of the wood, as found in the reference literature [29,30].

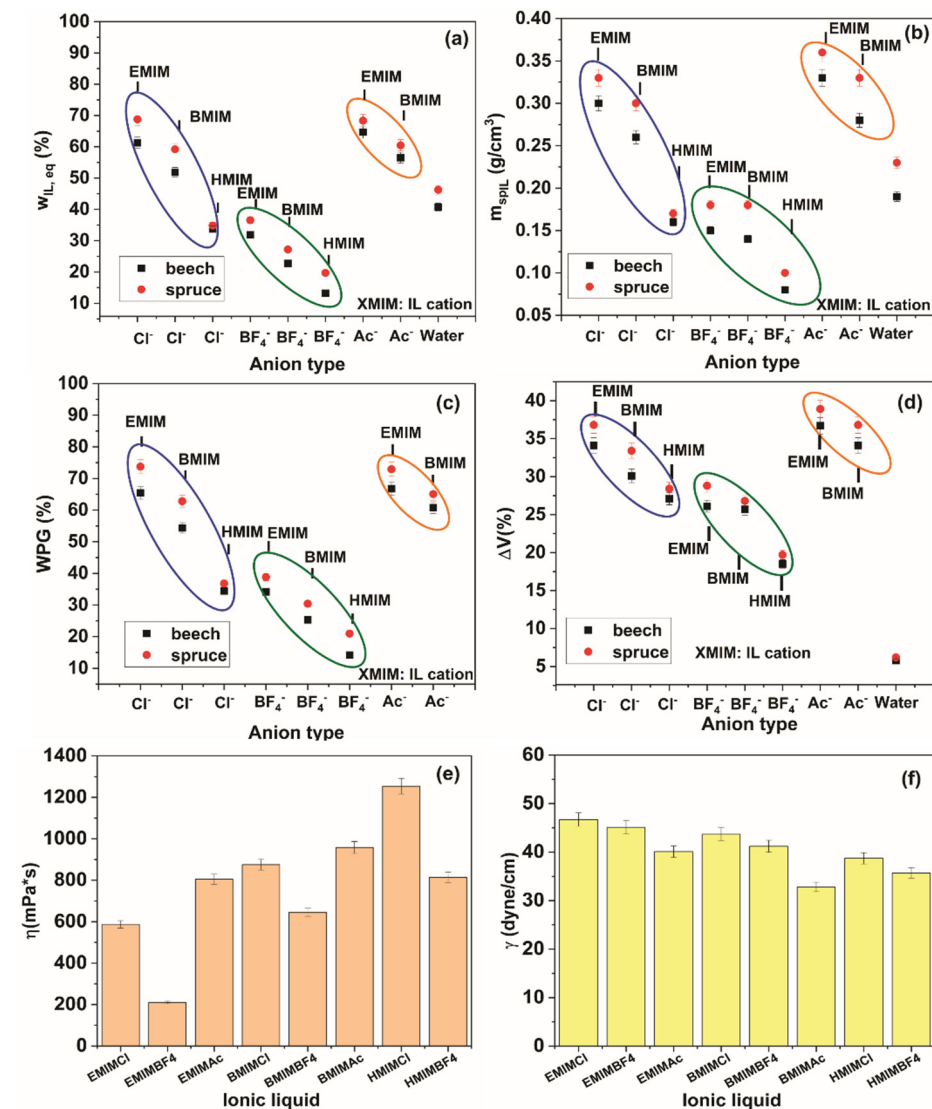


Figure 1. (a) Relative amount of ILs absorbed at equilibrium in spruce and beech wood; (b) specific mass of absorbed ILs at equilibrium for spruce and beech wood; (c); wood percent gain of spruce and beech wood swollen in ILs; (d) relative volumetric modifications of spruce and beech wood swollen in ILs; (e) kinematic viscosities of the ILs at 25 °C; and (f) surface tension of the ILs at 25 °C.

The uptake and swelling are marginally higher for spruce due to its looser microstructural packing than beech [31,32]. IL penetration into the wood determines much higher relative volume modifications (ΔV , %, Figure 1d) than in the case of water, which makes ILs useful as the transport media of various preservatives and impregnates (oligomeric resins, monomers) into the bulk of the wood.

The permeability of ILs into the wood structure is also influenced by their relative viscosity. For the same anion type, viscosity is dependent on the molar mass of the cation (Figure 1e), as lateral alkyl chains of higher dimensions promote van der Waals interactions which impede the sliding of the molecules past each other. All of the studied ionic liquids are tensioactive, which improves the wetting of the wood capillaries and aids adsorption and diffusion (Figure 1f).

An Anderson–Darling statistical analysis is performed to determine if the dependencies of the amount of ILs absorbed at the equilibrium ($w_{IL,eq}$), relative to the volume modification (ΔV , %) and surface tension (γ)/viscosity of the ILs (η), are normally distributed (Minitab 19 software). A correlation test is performed to test if there is a strong correlation between the variables at a 95% confidence level. The results are depicted in Table 1. From the available data, only the values of viscosity and surface tension for the ILs with EMIM, BMIM, HMIM cations, and Cl^- , BF_4^- anions are selected (not all the cations are paired with acetate anions).

Table 1. Statistical analysis of the dependence between selected wood-related properties (dependent variables) and ionic liquid-related properties (independent variables).

| IL-Related Properties (Independent Variable) | Statistical Analysis Parameters * | | Wood-Related Properties (Dependent Variable) | | | |
|---|-----------------------------------|-----|---|------------|-------------|------------|
| | | | Spruce | | Beech | |
| | | | $w_{IL,eq}$ | ΔV | $w_{IL,eq}$ | ΔV |
| γ | Normality | p | 0.140 | 0.365 | 0.261 | 0.554 |
| | Correlation | P | −0.031 | −0.258 | −0.118 | 0.017 |
| | | R | 0.953 | 0.621 | 0.824 | 0.890 |
| η | Normality | p | 0.145 | 0.332 | 0.282 | 0.483 |
| | Correlation | P | 0.099 | −0.306 | 0.018 | −0.368 |
| | | r | −0.851 | −0.555 | −0.729 | −0.473 |

* The meaning of the statistical parameters for the normality test: p - indicates the normal distribution of the data, if $p < 0.05$, the data do not follow a normal distribution (reject the null hypothesis), if $p > 0.05$, the data most likely follow a normal distribution (fail to reject the null hypothesis). For the correlation test, if p value ≤ 0.05 , the correlation is statistically significant, and if p value > 0.05 , the correlation is not statistically significant. The Pearson r coefficient expresses the linear relationship between variables. If $|r| \in [0.476; 0.93]$ then the relationship between variables is moderate; if $|r| > 0.93$, there is a strong relationship between variables [33].

As shown in Table 1, since the value of the p coefficient for normality testing is in all instances higher than 0.05, it can be assumed that the studied data are part of a normal distribution. With this assumption, the statistical correlation analysis indicates a strong positive correlation between the surface tension of the ILs (which is dependent on its structure) and their uptake for both types of wood. The higher the uptake of ILs, the higher the relative modifications in volume for the samples. Uptake and relative volume modifications seem to be moderately dependent on the viscosity of the ILs. The higher the viscosity, the lower the absorbed amount (hence the negative value for r). The correlations between the viscosity of ILs and their uptake in wood seem to be less positively correlated for beech, most likely due to its more complex anatomy. A higher ionic liquid viscosity can also mean that the IL is predominantly distributed near the surface of the wood, being less effective in promoting bulk volume modifications in general. For all the studied ILs and wood types, ILs penetration into the bulk of the wood and reaching of the sorption equilibrium occurs much faster than in the case of moisture, e.g., for all the ILs, the

equilibrium sorption is effectively reached after 8 to 10 h (Figure 2a), while for water it can take several days. In the case of water diffusion, generally, a two-step sorption kinetic can be observed, with the first step occurring at a higher rate, related to the filling and moisture saturation of capillaries and cavities near the surface of the wood, followed by a slow ongoing uptake related to water diffusion into the wood. As diffusion proceeds, the difference in chemical potential between the sorbed water and the water from the wood cellular walls decreases, and the water uptake rate also decreases [34,35].

Ionic liquids' high affinity for cellulose and lignin determines their high uptake rate, which remains unchanged in the diffusional step until the wood fiber saturation and the reaching of the sorption equilibrium. This high affinity is economically appealing, as wood is swollen and saturated with IL at room temperature at a higher rate than in the case of waterborne wood preservatives, despite their much higher viscosity.

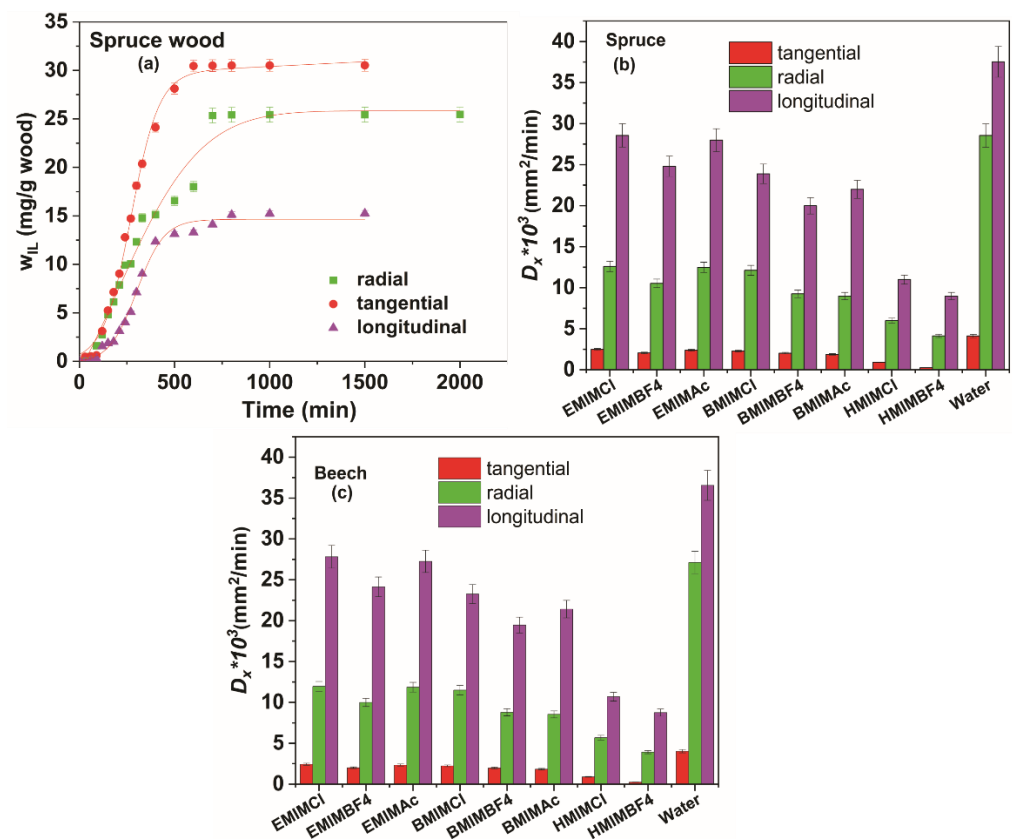


Figure 2. (a) Sorption kinetic of 1-butyl-3-methylimidazolium chloride IL into spruce wood; (b) diffusion coefficients for various ILs in spruce wood; and (c) diffusion coefficients for various ILs in beech wood.

The permeability of both spruce (softwood) and beech (hardwood) for the ILs was observed as reasonably similar (Figure 2b,c), as is the case in the reference literature for moisture diffusion [36–38]. The diffusion in the longitudinal direction is the highest, most likely due to the more significant number of pits (spruce) or wood vessels (beech) in this direction [37].

Figure 3a,c presents the ATR-FTIR spectra of beech wood and spruce wood treated with the alkylimidazolium chloride ILs, as these ILs promote the most significant interactions within the wood matrix. Since the IR absorption bands of the ILs can overlap with those of wood, the second derivative spectra were performed to discern the effect of ILs on the lignocellulose. Figure 3b,d represents the second derivative of the spectra from Figure 3a,c, respectively.

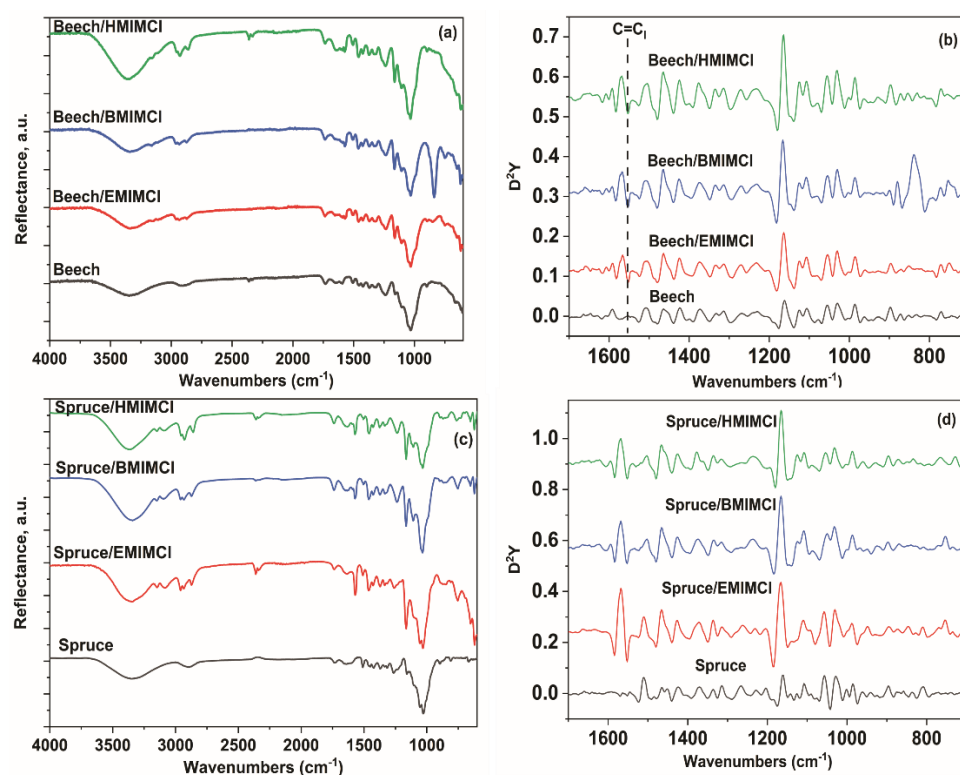


Figure 3. ATR-FTIR spectra of: (a) beech wood treated with alkylimidazolium chloride ILs; (b) second derivative spectra of beech treated with alkylimidazolium chloride ILs; (c) spruce wood treated with alkylimidazolium chloride ILs; (d) second derivative spectra of spruce treated with alkylimidazolium chloride ILs.

All the studied ILs promote physical interactions with the wood components (cellulose, hemicellulose, and lignin) [39], mainly related to intermolecular hydrogen bonds breaking and restructuring in both types of wood (shifting of the -OH stretching band centered at $\sim 3330\text{ cm}^{-1}$ to lower wavenumbers [40]). The -OH band maximum shifting is more pronounced as the length of the lateral alkyl chain of the cation increases, i.e., $\text{HMIM}^+ > \text{BMIM}^+ > \text{EMIM}^+$ and as the hydrophilicity of the anion increases and $\text{Cl}^- > \text{CH}_3\text{COO}^- > \text{BF}_4^-$ (Figure 3a,c). Additionally, the band ascribed to -C-O-C- vibration in cellulose and hemicellulose, which is strongly related to the crystallinity of wood [40,41], shifts to lower wavenumbers and decreases in intensity depending on the molar mass of the cation, i.e., $\text{HMIM}^+ > \text{BMIM}^+ > \text{EMIM}^+$, and the Lewis base character of the anion: $\text{Cl}^- > \text{CH}_3\text{COO}^- > \text{BF}_4^-$. The molecular restructuring also seems more evident through the increase in the intensity of the bands associated with lignin (δ (C=C) of aromatic lignin rings, $\sim 1520\text{ cm}^{-1}$ [42]) (Figure 3b,d).

4. Conclusions

Swelling and transport phenomena occurring in commercially relevant hardwoods and softwoods are essential for wood impregnation, plasticization, and preservative-treating applications. Although much information can be found in the reference literature regarding the interaction of cellulose with ionic liquids and the dissolution of lignocellulosic biomass in ionic liquids, there are very few studies regarding ionic liquids diffusion in wood. When it comes to this diffusion, alkylimidazolium ionic liquids (1-alkyl-3-methylimidazolium chlorides, acetates, and tetrafluoroborates) have significant swelling ability, for both hardwood (beech) and softwood (spruce), dependent on the molecular mass and surface tension of the cation, as well as on the hydrophilicity of the anion. Due to the high swelling ability, the difference between wood types is less relevant than in moisture or waterborne preservatives. The highest diffusion coefficient was observed

for the longitudinal direction, with a lesser contribution from the radial direction, and finally, the tangential one. In the long run, it will be necessary to investigate other potential properties regarding the use of ionic liquid-treated wood, such as mechanical properties, durability, and the leaching potential of the ionic liquids from the wood's structure.

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