Long alkyl chain quaternary ammonium-based ionic liquids and potential applications

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Due to the high interest in the applications of ionic liquids, new, cheaper, multifunctional ionic liquids which are easy to prepare are highly desired. Here, we present a new group of air- and moisture-stable, hydrophobic ammonium-based ionic liquids and their properties, including the single-crystal X-ray structure of benzethonium nitrate. These salts have utility as anti-bacterial, anti-fungal agents. Additionally, the potential application of these ionic liquids for wood preservation was tested with positive results. The toxicity of benzalkonium and didecyldimethylammonium nitrates were studied and are presented herein.

Introduction

Quaternary ammonium salts (quats) are quite well known and have widespread industrial utilization due to their surface activity and other useful properties. In 1890, Menschutkin synthesized quats by the nucleophilic substitution reaction of tertiary amines with an alkyl halide, and the 'Menschutkin reaction' is still regarded as the best method for the preparation of quat salts.[1]

Quats are generally known to be bioactive and have high anti-microbial activity, as has been shown for water-soluble compounds that contain alkyl chains of length C_8 to C_{16}. In alkylbenzyldimethylammonium chloride, for example, the optimum alkyl chain length to kill *Pseudomonas aeruginosa* was found to be 14 carbon atoms.[2] One of the most thoroughly investigated anti-microbial quat salts is benzalkonium chloride, [BA][Cl], which is a mixture of homologues of alkylbenzyldimethylammonium chlorides, with alkyl groups ranging between *n*-C_8H_{17} and *n*-$C_{18}H_{37}$.

Recently, new applications for quats have been found in forming ionic liquids (ILs, salts that melt below 100 °C).[3] The synthesis and properties of a group of hydrophobic ILs, based on relatively small aliphatic quaternary ammonium cations, $[Me_3NR]^+$ or $[Et_3NR]^+$ (R = C_3H_7, *n*-C_4H_9 or $CH_2CH_2OCH_3$), and on perfluoroalkyltrifluoroborate anions have been reported.[4] Here, we report a novel, economic class of quat-based ILs, derived from common, ammonium-based halide cations with nitrate, nitrite, tetrafluoroborate, and bis(trifluoromethylsulfonyl)imide anions, along with their properties and potential applications.

Results and discussion

Synthesis and characterization

Quats, containing large cationic structures, such as didecyldimethylammonium $[DDA]^+$, benzalkonium $[BA]^+$, and Hyamine 1622 (benzethonium) $[HA1622]^+$ (Fig. 1), were synthesized by anion exchange reactions (at room temperature, in water) of the commercially inexpensive and broadly used quats: [DDA][Cl], [DDA][Br], [BA][Cl], and [HA1622][Cl], with inorganic and acidic sources of $[NO_3]^-$, $[NO_2]^-$, $[BF_4]^-$, and $[Tf_2N]^-$, with an efficiency of over 95%. All of the synthesized salts, $[BA][NO_3]$, $[DDA][NO_3]$, $[HA1622][NO_3]$, $[BA][BF_4]$, $[DDA][Tf_2N]$, $[DDA][NO_2]$, $[BA][NO_2]$, and $[BA][Tf_2N]$, are reported here for the first time. The only known example of a similar product was noted in the patent literature for $[DDA][BF_4]$.[5–12] That salt showed significant activity against bacteria and fungi[6,9–12] and can form an emulsion with polyoxyethylene, exhibiting termite repellency comparable to that of pentachlorophenol.[5]

The prepared salts are all hydrophobic, except for the $[NO_2]^-$ salts, which were partially water-soluble (which also explains the low efficiency (75–85% yields) of the synthesis of

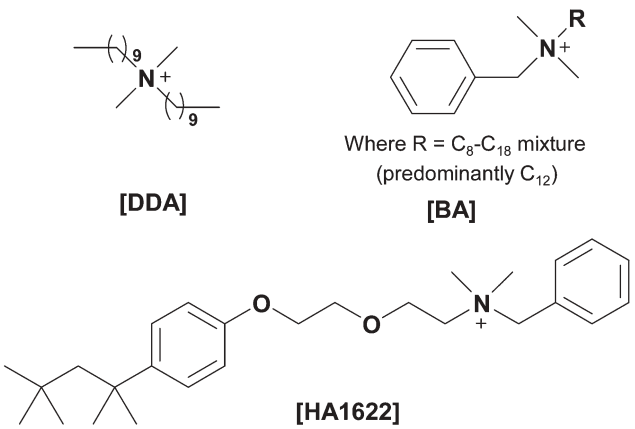

Fig. 1 Structures of the cations

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the nitrite salts). The concentration of water in the obtained salts was found to be temperature dependant. For example, [DDA][NO_3] at 20 °C was found to contain 0.4 g L^{-1} water, with a decrease to 0.2 g L^{-1} at 10 °C.

In the anion exchange reactions we report, both salts and acids can be used to supply the required anion. For example, in the production of [BA][NO_3], we have used $NaNO_3$, KNO_3, as well as 60% HNO_3. The efficiencies of the reactions proved to be independent of the applied salt or acid. When inorganic salts were used for the ion exchange reaction, the organic phase was washed with water until no chloride ions were detected using $AgNO_3$. When 60% HNO_3 was used, the product was easily purified by extraction of byproducts with distilled water.

[DDA][NO_3], [BA][Tf_2N], [DDA][Tf_2N], [BA][NO_2] were isolated as room temperature ionic liquids, while [BA][BF_4], [DDA][BF_4], and [DDA][NO_2] were waxes, and [HA1622][NO_3] was a solid. All isolated salts are nonvolatile, nonflammable, soluble in chloroform and ethyl acetate, and insoluble in hexane. Separation of phases using chloroform progressed rapidly and emulsification of the reaction mixture was avoided. After separation, the chloroform phase was transferred to a round-bottomed flask and rotovapped to remove the solvent. The product was dried under vacuum, at 80 °C for 12 h, and then stored over P_4O_{10}. The water content, determined by Karl–Fischer measurements, was found to be less than 500 ppm for all analyzed salts.

The prepared salts were characterized by ^1H and ^{13}C NMR and elemental analysis. Only in the case of $[BA]^+$ salts were slight shifts in proton spectra observed. These shifts pertained to the benzyl group and were determined to be related to anion interactions. The ^1H NMR spectra of [BA][Cl] showed two multiplets at 7.61 and 7.50 ppm for five aromatic protons and a singlet at 4.68 ppm for the CH_2 group. However, the spectra of the $[BA]^+$ salts had a single multiplet at 7.52 and a singlet at 4.54 ppm. Reports indicate that even more distinct shifts in the spectra have been previously observed. In choline derivates, *e.g.*, for butoxymethyl(2-hydroxyethyl)dimethylammonium, the substitution of a small anion such as $[Cl]^-$ for a large one $[Tf_2N]^-$ resulted in proton signal shifts as much as 0.53 ppm.[13]

The thermal properties for the reported compounds were determined using DSC and TGA analyses (Table 1). The salts formed stable super-cooled phases. The best example of this was observed for [DDA][Tf_2N], with a glass transition temperature (T_g) of −85.5 °C and an onset for thermal decomposition temperature (T_{onset}) of 376 °C. Melting points for [BA][NO_3] and [DDA][NO_3] were observed to be 36.3 °C and 18.8 °C, respectively.

The least thermally stable compounds proved to be the $[NO_2]^-$-based salts, with T_{onset} of 160–190 °C. The decomposition temperatures of $[NO_3]^-$ salts were higher and ranged between 215–230 °C. As compared to [BA][BF_4], which was stable up to 300 °C, [DDA][BF_4] underwent decomposition at 200 °C, losing 20% of its mass while the remaining product was stable until T_{onset} = 358 °C.

Literature data[14] indicate that compounds based on the $[Tf_2N]^-$ anion generally show high thermal stability. Our analyses confirmed this observation. [BA][Tf_2N] was stable up to 298 °C, while [DDA][Tf_2N] was stable up to 330 °C.

Additionally, we found that the melting point for [HA1622][NO_3], which was determined by DSC on heating, to be 85 °C, was lower than the melting point of the crystalline form of the product (92–94 °C) obtained by crystallization from the THF/anhydrous acetone/ethyl ether system.

The crystal structure of [HA1622][NO_3][15] was determined at −100 °C and is shown in Fig. 2. The $[HA1622]^+$ cations pack in 2-dimensional layers which stack in alternating directions. Cations of the same orientation pack head-to-tail along the long (*c*) axis and stack down the short (*a*) axis. These stacks of like-oriented cations form columns of alternating cations and anions which are slightly offset from each other, creating hydrophobic and hydrophilic regimes. Layers of the same orientation of cations alternate with layers of the opposite orientation along the *b* direction. In Fig. 2, layers of the same orientation are seen to overlay, in a canted fashion, layers of the opposite orientation below when viewed in the *bc* plane.

CCDC reference number 602689. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604353d

As shown in Table 1, all the synthesized salts can be assigned to the class 'ionic liquids' (as defined by a melting point <100 °C). These ILs are stable in air, and while in contact with water and commonly used organic solvents. The densities of [DDA][NO_3] at 20 °C, [DDA][NO_2] at 20 °C, and [BA][BF_4] and [DDA][BF_4] at 80 °C are lower than that of water while all other salts are more dense than water. All of the prepared ILs are viscous, but become significantly less so upon modest heating or with the addition of water or organic solvents. Additionally, it was found that these salts, even

Table 1 Thermal properties of the prepared quaternary ammonium-based ILs

IL	T_g[a]	T_{l-l}[b]	T_c[c]	T_{s-s}[d]	T_m[e]	$T_{onset(5\%)}$[f]	T_{onset}[g]
[BA][NO_3]	−56.8	—	6.1	—	36.3	173	215
[DDA][NO_3]	—	−19.8	—	—	18.8	189	234
[HA1622][NO_3]	—	—	—	—	85.0[h]	180	216
[BA][NO_2]	−48.2	—	—	—	—	131	163
[DDA][NO_2]	−93.3	—	−30.2	37.6; 67.2	−2.4	150	192
[BA][BF_4]	−43.2	—	−21.8	—	56	251	305
[DDA][BF_4]	—	−26.4	−3.0	55.5	27.5	183	(197) 358
[BA][Tf_2N]	−54.6	36.1; 71.8	—	—	—	298	346
[DDA][Tf_2N]	−85.5	—	—	—	—	330	376

[a] Glass transition temperature determined by DSC on heating. [b] Liquid–liquid transition temperature determined by DSC on heating. [c] Crystallization temperature determined by DSC on heating. [d] Solid–solid transition temperature determined by DSC on heating. [e] Melting point determined by DSC on heating. [f] $T_{5\%dec}$, decomposition temperatures determined from onset to 5 wt% mass loss. [g] T_{onset}, decomposition temperatures determined from onset to 50 wt% mass loss. [h] mp 92–94 °C from THF/anhydrous acetone/ethyl ether.

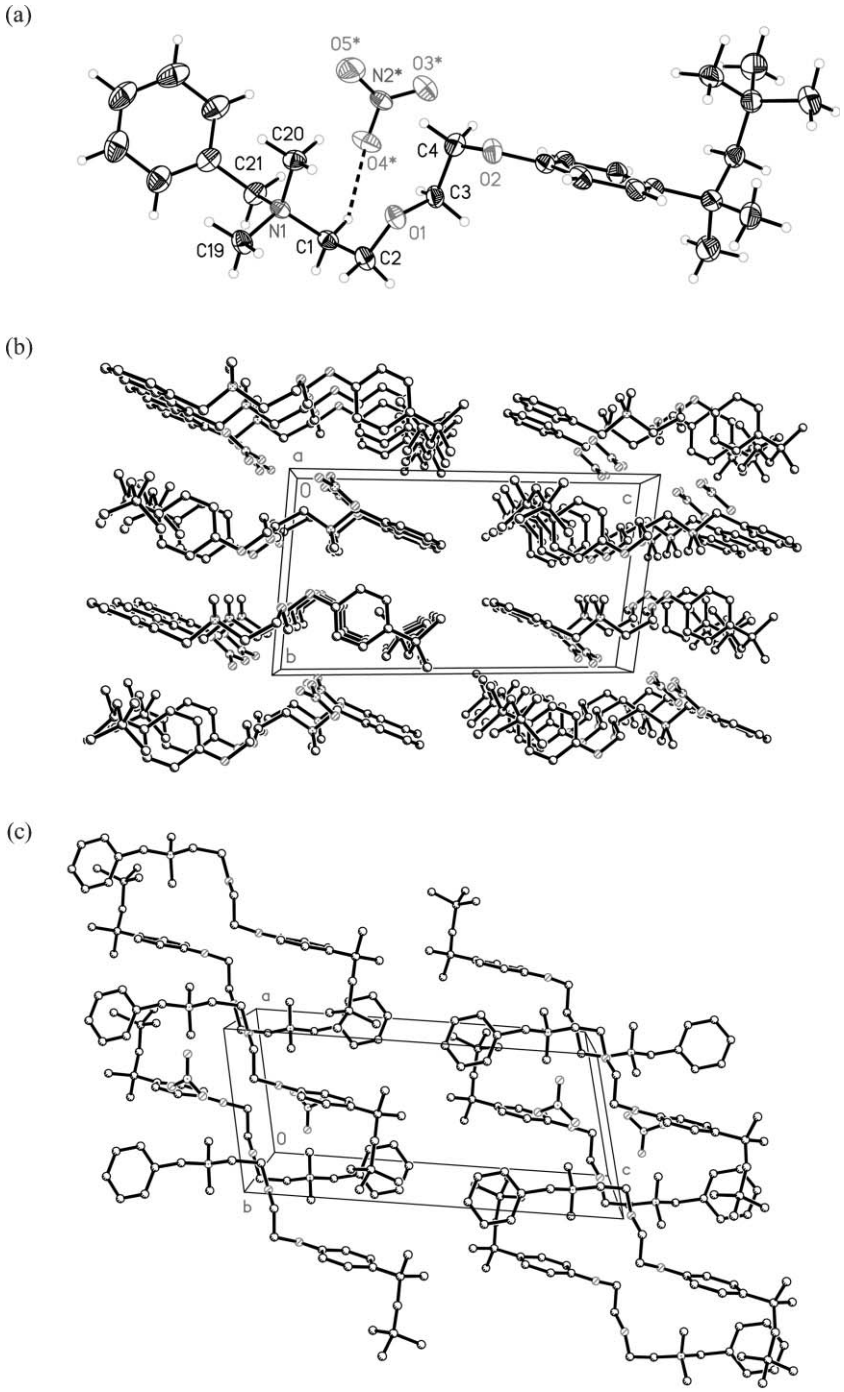

Fig. 2 (a) ORTEP illustration (50% probability ellipsoids) of [HA1622][NO_3] showing connectivity, conformation, and partial atom numbering scheme of the ions present in the asymmetric unit emphasizing the intermolecular contact with the largest negative difference from van der Waals separation (symmetry code for atoms labeled with * is $1 - x$, $1 - y$, $-z$); (b) packing diagram showing alternating orientations of the 2-dimensional layers of $[HA1622]^+$ cations packing in the *ac* direction; and (c) the overlay of oppositely orientated cations viewed down the *b* axis.

though highly hydrophobic, absorb small amounts (<2 wt%) of moisture from the atmosphere.

Biological activity

The biological activity of all of the prepared ILs was estimated and the minimum inhibitory concentration (MIC), and minimum bactericidal or fungicidal concentration (MBC) were established. The studies were conducted on three strains of bacteria and one strain of fungi. MIC and MBC values for 4 strains of the prepared salts and the commercially available [DDA][Cl], [BA][Cl], and [HA1622][Cl] are compared in Tables 2 and 3.

The results demonstrate that the $[NO_3]^-$ and $[NO_2]^-$ salts are very effective agents against bacteria and fungi. Their activities are comparable to that of the original chlorides.

Table 2 MIC[a] values of the studied ILs

Salts	*S. aureus*	*E. faecium*	*E. coli*	*C. albicans*
$[BA][NO_3]$	4	4	16	16
$[DDA][NO_3]$	2	4	8	8
$[HA1622][NO_3]$	4	8	31.2	8
$[BA][NO_2]$	4	8	16	16
$[DDA][NO_2]$	4	4	8	16
$[BA][BF_4]$	4	8	16	31.2
$[DDA][BF_4]$	8	8	16	31.2
$[DDA][Tf_2N]$	31.2	31.2	62.5	62.5
[BA][Cl]	2	4	8	8
[DDA][Cl]	2	4	8	8
[HA1622][Cl]	2	2	16	8

[a] MIC in μg mL^{-1}.

Table 3 MBC[a] values of the studied ILs

Salts	*S. aureus*	*E. faecium*	*E. coli*	*C. albicans*
$[BA][NO_3]$	16	62.5	62.5	31.2
$[DDA][NO_3]$	16	31.2	31.2	16
$[HA1622][NO_3]$	31.2	31.2	125	31.2
$[BA][NO_2]$	31.2	31.2	31.2	31.2
$[DDA][NO_2]$	31.2	31.2	62.5	16
$[BA][BF_4]$	125	125	62.5	62.5
$[DDA][BF_4]$	31.2	125	62.5	31.2
$[DDA][Tf_2N]$	>1000	>1000	>1000	>1000
[BA][Cl]	62.5	31.2	62.5	16
[DDA][Cl]	31.2	31.2	31.2	16
[HA1622][Cl]	16	62.5	125	31.2

[a] MBC in μg mL^{-1}.

The $[BF_4]^-$ salts proved to be slightly less effective, while $[Tf_2N]^-$ salts exerted no anti-bacterial or anti-fungal effect. The $[BA]^+$, $[DDA]^+$, and $[HA1622]^+$ salts were effective antimicrobial agents at concentrations below 100 μg mL^{-1}, with the solubility of the ILs in water playing a significant role. The $[Tf_2N]^-$-based ILs were not soluble in water to concentrations higher than that of the lowest recorded MBC level (16 μg mL^{-1}) and thus, no real values of MBC could be established for these compounds. However, we conclude that all of the other synthesized salts of $[NO_3]^-$, $[NO_2]^-$, and $[BF_4]^-$ anions can be successfully utilized for disinfection. When considering practical application and production costs, the $[BA][NO_3]$ and $[DDA][NO_3]$ salts are the most promising, and they may be regarded as cheap, hydrophobic, multifunctional ILs.

Wood preservation

Recently, ILs have also been studied for wood preservation[16,17] and as effective anti-electrostatic agents for pine maple.[18] Application of $[BA][NO_3]$ and $[DDA][NO_3]$ as a wood preservative proved to be effective. The effective dose (ED_{50} and ED_{100}) and lethal dose (LD) values were established for the two $[NO_3]^-$ salts, targeted for:

1. *Sclerophoma pityophila* fungus, belonging to imperfect fungi (*Deuteromycotina*), which causes blue discoloration of wood (Fig. 3),
2. *Trametes versicolor* fungus, causing white rot,
3. *Coniophora puteana* fungus, causing brown rot (Fig. 5), both belonging to the *Basidiomycotina* class which usually shows higher tolerance to fungicidal chemicals in biological reactions (Fig. 4).

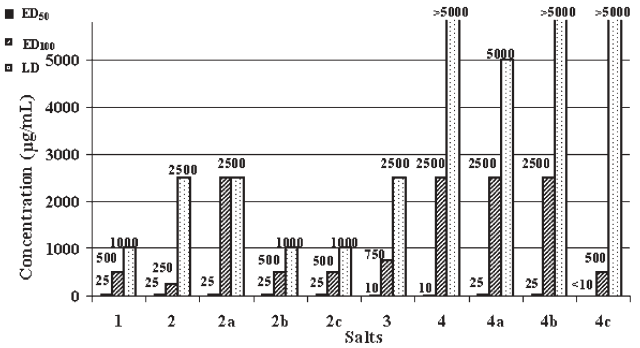

Fig. 3 The effective dose ED and the lethal dose LD of: **1** – [BA][Cl], **2** – $[BA][NO_3]$, **2a** – 60% w/w $[BA][NO_3]$ and 40% w/w PEG-400, **2b** – 60% w/w $[BA][NO_3]$ and 40% w/w PEG-600, **2c** – 60% w/w $[BA][NO_3]$ and 40% w/w PPG-425, **3** – [DDA][Cl], **4** – $[DDA][NO_3]$, **4a** – 60% w/w $[DDA][NO_3]$ and 40% w/w PEG-400, **4b** – 60% w/w $[DDA][NO_3]$ and 40% w/w PEG-600, **4c** – 60% w/w $[DDA][NO_3]$ and 40% w/w PPG-425, tested for *Sclerophoma pityophila.*

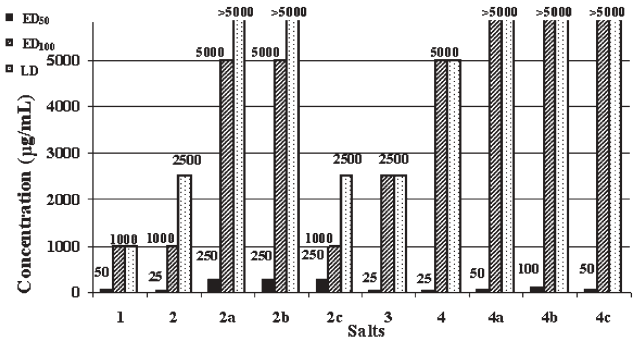

Fig. 4 The effective dose ED and the lethal dose LD of: **1** – [BA][Cl], **2** – $[BA][NO_3]$, **2a** – 60% w/w $[BA][NO_3]$ and 40% w/w PEG-400, **2b** – 60% w/w $[BA][NO_3]$ and 40% w/w PEG-600, **2c** – 60% w/w $[BA][NO_3]$ and 40% w/w PPG-425, **3** – [DDA][Cl], **4** – $[DDA][NO_3]$, **4a** – 60% w/w $[DDA][NO_3]$ and 40% w/w PEG-400, **4b** – 60% w/w $[DDA][NO_3]$ and 40% w/w PEG-600, **4c** – 60% w/w $[DDA][NO_3]$ and 40% w/w PPG-425, tested for *Trametes versicolor.*

The tested nitrate ILs showed the highest anti-fungal–fungistatic action and also exhibited a fungicidal action against wood attacking fungi. The activity of $[BA][NO_3]$ against the fungi tested was more pronounced than that of $[DDA][NO_3]$. However, the action of the quaternary ammonium $[NO_3]^-$ salts was less effective than that of the $[Cl]^-$ salts which have been successfully used in wood preservation (Figs. 3–5).[19]

The nitrate-based ILs were mixed with polyethylene glycol of average molecular weight 400 (PEG-400) and 600 (PEG-600), as well as, polypropylene glycol of average molecular weight 425 (PPG-425), yielding stable solutions of 60% w/w IL and 40% w/w polyether. Figs. 3–5 show the anti-fungal activities of these mixtures (**2a–c** and **4a–c**). The most effective mixture proved to be **2c** (60% w/w $[BA][NO_3]$/40% w/w PPG-425). The values of ED_{50}, ED_{100}, and LD obtained for this salt were comparable to those of [BA][Cl] and were lowered by half in the case of *Sclerophoma pityophila*. In the latter case, addition of PPG-425 improved the effectiveness of $[BA][NO_3]$ in contact with the mycelium. These results show that quaternary ammonium nitrate-based ILs are potentially applicable for wood preservation.

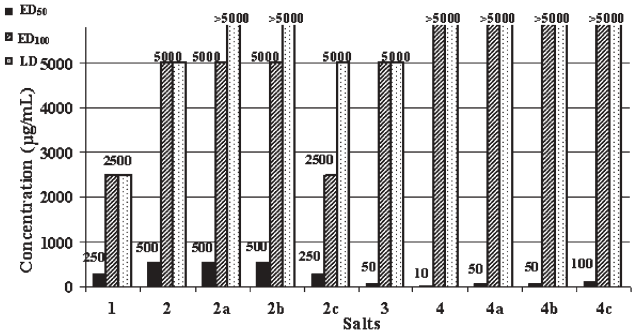

Fig. 5 The effective dose ED and the lethal dose LD of: **1** – [BA][Cl], **2** – [BA][NO_3], **2a** – 60% w/w [BA][NO_3] and 40% w/w PEG-400, **2b** – 60% w/w [BA][NO_3] and 40% w/w PEG-600, **2c** – 60% w/w [BA][NO_3] and 40% w/w PPG-425, **3** – [DDA][Cl], **4** – [DDA][NO_3], **4a** – 60% w/w [DDA][NO_3] and 40% w/w PEG-400, **4b** – 60% w/w [DDA][NO_3] and 40% w/w PEG-600, **4c** – 60% w/w [DDA][NO_3] and 40% w/w PPG-425, tested for *Coniophora puteana.*

Wood penetration

The penetration depth of [DDA][NO_3] and [BA][NO_3] in mixtures with PEG and PPG was tested in Scots pine wood (Fig. 6). In general, it is known that quats poorly penetrate wood, *e.g.*, for [BA][Cl], the penetration depth into dry Scots pine was 3.7 mm and, in the case of wet wood, 2.9 mm.[16] [DDA][NO_3] and [BA][NO_3] penetrated to depths of 3.8 and 3.5 mm, respectively. [BA][NO_3] penetrated faster than [DDA][NO_3], which reflects the different densities of the two salts: [DDA][NO_3] is less dense than water while [BA][NO_3] is more dense than water. Adding PEG or PPG improved the penetration of wood by the ILs to depths of more than 6 mm (**4c** and **2c** in Fig. 6).

Leaching from wood

Resistance to water leaching is significant for wood impregnation agents. To test this aspect of the prepared ILs, the procedures of Zhang and Kamdem[20] were used. The results

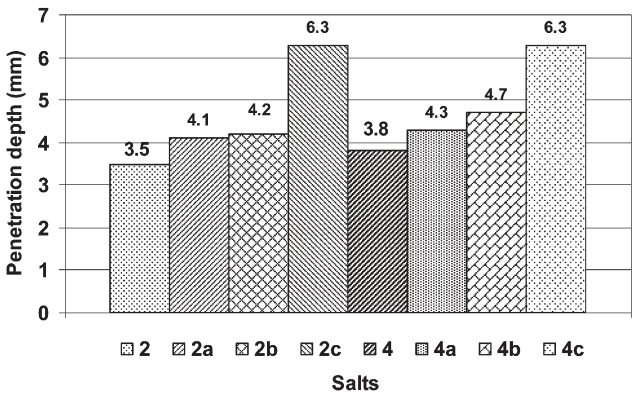

Fig. 6 Penetration depth into Scots pine wood of: **2** – [BA][NO_3], **2a** – 60% w/w [BA][NO_3] and 40% w/w PEG-400, **2b** – 60% w/w [BA][NO_3] and 40% w/w PEG-600, **2c** – 60% w/w [BA][NO_3] and 40% w/w PPG-425, **4** – [DDA][NO_3], **4a** – 60% w/w [DDA][NO_3] and 40% w/w PEG-400, **4b** – 60% w/w [DDA][NO_3] and 40% w/w PEG-600, **4c** – 60% w/w [DDA][NO_3] and 40% w/w PPG-425.

Table 4 Leaching of ILs from treated Scots pine wood after an 8 day shaking cycle

Salts	Treating solution concentration (%)	IL content in treated wood/kg m^{-3}	Degree of leaching (%)
[BA][NO_3]	1.0	3.87	1.05
	1.6	6.17	2.05
[DDA][NO_3]	1.0	3.95	0.85
	1.6	6.35	1.00
60% [BA][NO_3] and 40% PPG-425	1.0	2.34	0.71
	1.6	3.34	1.17
60% [DDA][NO_3] and 40% PPG-425	1.0	2.11	0.91
	1.6	3.47	1.08
[BA][Cl]	1.0	5.22	5.03
	1.6	8.37	9.66
[DDA][Cl]	1.0	5.25	3.65
	1.6	8.51	7.80

obtained for the $[NO_3]^-$ and $[Cl]^-$ salts, as well as for the mixtures of ILs with PPG, are listed in Table 4. As compared to the hydrophilic $[Cl]^-$ salts, for which the degree of leaching ranged between 3.7 and 9.7%, the hydrophobic $[NO_3]^-$ salts might be expected to undergo significantly less leaching. The degrees of leaching for [DDA][NO_3] ranged between 0.9 and 1.0%, and were markedly lower than those for [BA][NO_3] (1.0–2.1%). Mixtures of IL with PPG, which penetrated wood most effectively, showed an insignificant extent of leaching (0.7–1.2%).

These studies indicated that wood was most effectively preserved by the use of the mixture of 60% w/w [BA][NO_3] and 40% w/w PPG-425, which (i) attacked fungi, (ii) penetrated wood to the depth of 6.3 mm, and (iii) was resistant to water leaching (the degree of leaching was approximately 1%). The mixture of 60% w/w [DDA][NO_3] and 40% w/w PPG-425 should be regarded as an effective preparation for wood preservation.

Toxicity

Acute oral toxicity studies of [BA][NO_3] and [DDA][NO_3] were performed with rats, in compliance with the OECD Guideline for Testing of Chemicals No 420 (Fixed Dose Method).[21] The results reported below allow the conclusion that the oral median lethal dose (LD_{50}) of [BA][NO_3] exceeds 50 mg kg^{-1} body weight (b.w.) and is lower than 500 mg kg^{-1} b.w., while for [DDA][NO_3] the dose exceeds 500 mg kg^{-1} b.w.

Clinical signs. In preliminary experiments [BA][NO_3] was administered at the dose of 2000 mg kg^{-1} b.w. Ten minutes later the rat developed salivation and the female died after 24 h. The dose of 500 mg kg^{-1} b.w. induced, after 1–2 h, dejection, restricted motility, staggering gate, and bristled hair in females. None of the females survived six days. On the other hand, administration of [BA][NO_3] at the dose of 50 mg kg^{-1} b.w. was followed by no toxic symptoms in the course of 14 days observation. Individual results on weight gain in the animals are listed in Table 5.

The dose of 2000 mg [DDA][NO_3] per kg b.w. proved excessively high. Subsequent administration of the $[NO_3]^-$ compound to four females at a dose of 500 mg kg^{-1} b.w. was followed in the same day of application by dejection and

Table 5 Tests of acute oral toxicity of [BA][NO_3] in rats

Dose/ mg kg^{-1} b.w.	Rat no.	Animal body weight/g Original	Following 7 days	Following 14 days	Difference between day 0 and day 14
2000	1[a]	188	—	—	—
500	1[a]	184	—	—	—
	2	176	—	—	—
	3	188	—	—	—
	4	185	—		
	5	184	—	—	—
50	1[a]	202	231	244	42
	2	194	222	224	30
	3	187	221	226	39
	4	197	222	226	29
	5	191	213	222	31

[a] Females in the preliminary experiment.

restricted motility in two females (no. 2 and 5) and by dejection and salivation in a single female (no. 3). The signs developed within 0.5–1 h after administration. The female No. 3 died before the second hour and the female No. 2 before the 24th hour. In the first day after administration, the female No. 5 continued to demonstrate restricted motility, but between the second day and the end of observation period no signs of toxicity were observed and the female survived the observation period. In the female no. 4, no signs of toxicity were observed in the course of the 14 day observation period; the female survived the observation period.

The individual data on body weight in the animals are listed in Table 6. In three females given the studied material at the dose of 500 mg kg^{-1} b.w., the 14-day observation period was accompanied by less intense growth in body weight (no. 1) or by a decrease in body weight (females no. 4 and 5).

Pathology. In the female which died after being administered the dose of 2000 mg kg^{-1} b.w., cyanosis was disclosed macroscopically. This was also noted in the four females which died following the dose of 500 mg kg^{-1} b.w. Moreover, in three of the females, softening of intestinal wall, and in a single one, softening of the gastric wall was disclosed. In five females given the dose of 50 mg kg^{-1} b.w., which were sacrificed following 14 days of observation, no lesions were noted upon macroscopical examination of the internal organs and they did not show any pathological changes in macroscopic study. In control females given dimethylsulfoxide (DMSO), no lesions could be noted upon macroscopic examination.

Table 6 Tests of acute oral toxicity of [DDA][NO_3] in rats

Dose mg kg^{-1} b.w.	Rat no.	Animal body weight/g Original	Following 7 days	Following 14 days	Difference between day 0 and day 14
2000	1[a]	170	—	—	—
500	1[a]	204	173	209	5
	2	195	—	—	—
	3	195	—	—	—
	4	203	166	192	−11
	5	202	163	199	−3
50	1	205	233	236	31
	2	198	219	217	19
	3	202	229	235	33
	4	198	217	221	23
	5	209	232	235	26

[a] Females in the preliminary experiment.

Experimental

Synthesis

All reagents were purchased from a commercial source (Sigma–Aldrich) and were used as received.

General. NMR spectra were obtained in DMSO-d_6 with TMS as the internal standard. Elemental analyses were performed at the A. Mickiewicz University, Poznań. Melting points were determined on a hot-stage apparatus and DSC instrument.

General procedure for preparation of nitrates and nitrites. 0.03 mol of quaternary ammonium halide was dissolved in 40 mL distilled water and then 0.03 mol of nitric acid (60%) was added. The solution was stirred at room temperature for 1 h. Chloroform (40 mL) was added to the reaction mixture and then shaken. The mixture was stirred for an additional 1 h. After separation of the phases, the organic phase was washed with 40 mL distilled, cold water until chloride ion was no longer detected using $AgNO_3$. Chloroform was removed and the residue was dried at 50 °C in vacuum.

Benzalkonium nitrate ([BA][NO_3]) was obtained in 94% yield (10.3 g, 28.1 mmol). Mp = 36.3 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.52 (m, 5H), (m, 5H), 4.54 (s, 2H), 3.25 (m, 2H), 2.98 (s, 6H), 1.78 (m, 2H), 1.25 (m, 20H), 0.85 (t, J = 7 Hz, 3H); ^{13}C NMR 132.8, 130.1, 128.8, 128.1, 66.1, 63.4, 49.0, 31.2, 29.0, 28.96, 28.88, 28.7, 28.65, 28.4, 25.8, 22.0, 21.7, 13.8.

Didecyldimethylammonium nitrate ([DDA][NO_3]) was obtained in 90% yield (10.5 g, 27.0 mmol. Mp = 18.8 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 3.24 (m, 4H), 2.99 (s, 6H), 1.62 (m, 4H), 1.26 (m, 28H), 0.86 (t, J = 7 Hz, 6H); ^{13}C NMR 62.7, 49.9, 31.2, 28.8, 28.7, 28.6, 28.4, 25.7, 22.0, 21.6, 13.9. Elemental analysis: Found: C 68.12, H 12.71, N 7.03. Calc. for $C_{22}H_{48}N_2O_3$ (388.6): C 67.99, H 12.45, N 7.21%.

Benzethonium nitrate ([HA1622][NO_3]) was obtained in 93% yield (13.2 g, 27.8 mmol). The wax was obtained from an anhydrous acetone/THF mixture (1 : 1 v/v). The final product was obtained as white crystals with mp = 92–94 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.53 (m, 5H), 7.25 (d, J = 9 Hz, 2H), 6.83 (d, J = 9 Hz, 2H), 4.61 (s, 2H), 4.12 (d, J = 5 Hz, 2H), 4.00 (s, 2H), 3.83 (t, J = 5 Hz, 2H), 3.55 (t, J = 4Hz, 2H), 3.02 (s, 6H), 1.67 (s, 2H), 1.28 (s, 6H), 0.66 (s, 9H); ^{13}C NMR 155.8, 141.4, 133.0, 130.1, 128.7, 127.9, 126.8, 113.5, 68.7, 67.4, 66.5, 63.8, 62.5, 56.2, 49.7, 37.4, 31.9, 31.41, 31.38. Elemental analysis: Found: C 73.57, H 9.71, N 6.03. Calc. for $C_{27}H_{42}N_2O_5$ (474.63): C 68.33, H 8.91, N 5.90%.

Benzalkonium nitrite ([BA][NO_2]) was obtained as a yellow oil in 75% yield (7.9 g, 22.5 mmol). ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.52 (m, 5H), 4.58 (s, 2H), 3.27 (m, 2H), 2.97 (s, 6H), 1.78 (m, 2H), 1.25 (m, 20H), 0.85 (t, J = 7 Hz, 3H); ^{13}C

NMR 132.9, 130.1, 128.8, 128.2, 65.9, 63.3, 48.9, 31.2, 28.95, 28.87, 28.7, 28.6, 28.5, 25.8, 22.0, 21.7, 13.9.

Didecyldimethylammonium nitrite ([DDA][NO_2]) was obtained as a yellow wax in 85% yield (9.5 g, 25.5 mmol). Mp = −2.4 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 3.25 (m, 4H), 3.00 (s, 6H), 1.62 (m, 4H), 1.26 (m, 28H), 0.85 (t, J = 7 Hz, 6H); ^{13}C NMR 62.6, 49.8, 31.2, 28.8, 28.7, 28.6, 28.4, 25.7, 22.0, 21.6, 13.8. Elemental analysis: Found: C 71.12 H 13.15, N 7.43. Calc. for $C_{22}H_{48}N_2O_2$ (372.6): C 70.91, H 12.98, N 7.52%.

Preparation of benzalkonium tetrafluoroborate ([BA][BF_4]). Equal molar amounts (0.03 mol) of [BA][Cl] and $NaBF_4$ were dissolved in distilled water and stirred at room temperature for 0.5 h. The addition of chloroform was followed by thorough mixing and then the solution was transferred to a separating funnel where the organic phase was the lower phase. The organic phase was extracted by distilled water until chloride ions were no longer detected using $AgNO_3$. The chloroform phase was then transferred in a round-bottomed flask to a rotovap at 80 °C under a vacuum to remove any residual chloroform. The wax, prepared in 90% yield (10.6 g, 27.1 mmol), was dried for several hours in vacuum. Mp = 56.0 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.53 (m, 5H), 4.52 (s, 2H), 3.24 (m, 2H), 2.95 (s, 6H), 1.78 (m, 2H), 1.25 (m, 20H), 0.86 (t, J = 7 Hz, 3H); ^{13}C NMR 132.8, 130.1, 128.8, 128.0, 66.1, 63.4, 49.0, 31.2, 29.0, 28.89, 28.74, 28.67, 28.5, 25.8, 22.0, 21.7, 13.9.

Preparation of didecyldimethylammonium tetrafluoroborate ([DDA][BF_4]). A saturated aqueous solution of $NaBF_4$ was added to a stoichiometric amount (0.03 mol) of a hot 75% [DDA][Br] aqueous gel. The reaction mixture was stirred at room temperature for 0.5 h affording a heterogeneous mixture. Chloroform (50 mL) was added and the organic phase was washed with distilled water until bromide ions were no longer detected using $AgNO_3$. The volatile materials were removed under reduced pressure. The liquid product was prepared in 95% yield (11.8 g, 28.6 mmol), and dried at 80 °C in vacuum. Mp = 27.5 °C. ^{1}H NMR (360 MHz, DMSO-d_6) δ 3.22 (m, 4H), 2.98 (s, 6H), 1.63 (m, 4H), 1.26 (m, 28H), 0.86 (t, J = 7 Hz, 6H); ^{13}C NMR 62.7, 49.9, 31.2, 28.8, 28.7, 28.6, 28.4, 25.7, 22.0, 21.5, 13.8. Elemental analysis: Found: C 64.15, H 12.07, N 3.13. Calc. for $C_{22}H_{48}BF_4N$ (413.4): C 63.91, H 11.70, N 3.39%.

Preparation of benzalkonium bis(trifluoromethylsulfonyl) imide ([BA][TF_2N]). $(CF_3SO_2)NH$ as a 55.5% solution in water was added to a stoichiometric amount (0.03 mol) of a saturated, warm aqueous solution of [BA][Cl]. The reaction mixture was stirred at room temperature for 1 h and 50 mL of chloroform was added. The organic phase was separated and extracted with distilled water. The volatile materials were removed under reduced pressure and the liquid obtained was dried at 80 °C in vacuum to give the product in 95% yield (16.6 g, 28.5 mmol). ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.52 (m, 5H), 4.51 (s, 2H), 3.24 (m, 2H), 2.95 (s, 6H), 1.79 (m, 2H), 1.25 (m, 20H), 0.86 (t, J = 7 Hz, 3H); ^{13}C NMR cation: 132.7, 130.0, 128.7, 127.9, 66.1, 63.4, 48.9, 31.1, 28.91, 28.86, 28.78, 28.63, 28.57, 28.4, 25.7, 21.9, 21.6, 13.7, anion: 121.1–117.6 (d, J = 318 Hz).

Preparation of didecyldimethylammonium bis(trifluoromethylsulfonyl)imide ([DDA][Tf_2N]). $(CF_3SO_2)NH$ as a 55% solution in water was added to a stoichiometric amount (0.03 mol) of [DDA][Br] (tech., 75% gel in water). The solution was stirred at room temperature for 1 h and 50 mL of chloroform was added. The organic phase was separated and extracted with distilled water. The volatile materials were removed under reduced pressure and the liquid was dried at 80 °C in vacuum to give the product in 99% yield (18.0 g, 29.7 mmol). ^{1}H NMR (360 MHz, DMSO-d_6) δ 3.22 (m, 4H), 2.98 (s, 6H), 1.63 (m, 4H), 1.26 (m, 28H), 0.86 (t, J = 7 Hz, 6H); ^{13}C NMR 62.8, 49.9, 31.2, 28.8, 28.7, 28.6, 28.4, 25.6, 22.0, 21.6, 13.8, anion 121.2–117.6 (d, J = 321 Hz). Elemental analysis: Found: C 47.48, H 7.73, N 4.83. Calc. for $C_{24}H_{48}N_2F_6O_4S_2$ (606.8): C 47.51, H 7.97, N 4.62%.

Thermal analyses

Melting points were determined using both a hot stage apparatus and a differential scanning calorimeter (DSC), TA Instruments model 2920 Modulated DSC (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter was calibrated for temperature and cell constants using indium (melting point 156.61 °C, ΔH 28.71 J g^{-1}). Data were collected at constant atmospheric pressure, using samples between 10–40 mg in aluminum sample pans. Experiments were performed heating at the rate of 5 °C min^{-1}. The DSC was adjusted so that zero heat flow was between 0 and −0.5 mW, and the baseline drift was less than 0.1 mW over the temperature range 0–180 °C. An empty sample pan was used as reference.

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA (TA Instruments 2950) under air atmosphere. Samples between 2–10 mg were heated from 40–500 °C under constant heating at 5 °C min^{-1}. Decomposition temperatures ($T_{5\%dec}$) were determined from onset to 5 wt% mass loss, under air; which provides a more realistic representation of thermal stability at elevated temperatures.

X-Ray crystallography

Data was collected on a Bruker CCD area detector-equipped diffractometer with graphite monochromated MoKα (λ = 0.71073 Å) radiation and the structure solved using the SHELXTL software package.[22] Absorption corrections were made with SADABS.[23] All non-hydrogen atoms were readily located and refined anisotropically and all hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom unless otherwise noted. The structure was refined by full-matrix least-squares on F^2.

Initial structure solution refined to R1 = 0.1748, wR2 = 0.4824 [I > 2σ(I)] and R1 = 0.2130, wR2 = 0.4980 (for all data). Analysis of the Fo/Fc data using the program TwinRotLat in PLATON[24] indicated the possibility for a non-merohedrally twinned structure. The twin law was determined to be [−1 0 0 0 −1 0 1.075 0.355 1]. After inclusion of the BASF parameter and HKLF5 data file, the

twinned structure refined to [R1 = 0.1127, wR2 = 0.3204 and R1 = 0.1507, wR2 = 0.3400] with BASF = 0.27.

Bioactivity tests

Test microorganisms. The microorganisms used included *Staphylococcus aureus* NCTC 6538, *Enterococcus faecium* ATCC 49474, *Escherichia coli* ATCC 25922, and *Candida albicans* ATCC 10231. Standard strains were supplied by the American Type Culture Collection (ATCC).

Anti-microbial activity test procedure. Anti-microbial activity was determined by the tube dilution method. Bacteria strains were cultured on a Müller-Hinton broth for 24 h, and fungi on Sabouraud agar for 48 h. A suspension of the microorganisms at a concentration of 10^6 cfu mL^{-1} was prepared from each culture. This suspension was then used to inoculate each dilution of the broth medium at a 1 : 1 ratio. Growth of the microorganisms (or lack thereof) was determined visually after incubation for 24 h at 35 °C (bacteria) or 48 h at 22 °C (fungi). The lowest concentration at which there was no visible growth (turbidity) was taken as the MIC (minimal inhibitory concentration). Then, an aliquot taken from each tube in a sample loop was cultured in an agar medium with inactivates (0.3% lecithin, 3% polysorbate 80, and 0.1% cysteine L) and incubated for 48 h at 35 °C (bacteria) or for 5 d at 22 °C (fungi). The lowest concentration of the studied salt supporting no colony formation was defined as the MBC (minimum bactericidal or fungicidal concentration).

The determinations of anti-fungal efficacy. The fungal growth rates were measured in 90 mm Petri dishes using the agar dilution test. Ten concentrations of the compounds were studied in a geometric progression from 10 to 5000 μg mL^{-1}. Stock solutions of each concentration of the studied chemicals were produced in sterile malt agar (1.5% agar and 4% malt-extract), 20 mL of which was added to each Petri dish. Three replicate plates of each concentration of each compound were centrally inoculated with a 5 mm diameter disc taken from the submargin of 10-day-old cultures of the desired test fungus grown on malt agar. The plates were incubated at 22 ± 1 °C in darkness. The duration of the test was either determined by waiting for complete plate coverage by growing mycelium or 12 days for *Sclerophoma pityophila* and *Coniophora puteana* fungi and 6 days for *Trametes versicolor* fungus (for which growth rates were higher than for the two earlier mentioned fungi). If growth on the preservative-containing agar had not begun after 12 days or 6 days, respectively, the inoculum was removed and transferred to a fresh malt agar plate for determination of the fungal viability.

The results were used to calculate ED_{50} (preservative concentrations retarding the fungal growth rate by 50 percent in comparison with plates where the toxic agent was omitted), the effective dose ED_{100} (preservative concentrations retarding the fungal growth rate by 100 percent in comparison with plates where the toxic agent was omitted), and LD (concentrations causing death of fungus inoculum) of the examined salts. The strains used for the tests, *Sclerophoma pityophila* (Corda) v.Höhn, strain S 231, *Coniophora puteana* (Schum.:Fr.) Karst. strain BAM 15, and *Trametes versicolor* (L.:Fr.) Pilát strain CTB, were obtained from the collection of the Institute of Wood Technology, Poznań, Poland.

Acute oral toxicity study

Wistar rats (outbred, symbol lmp: WIST) used in these studies originated from a culture in the Instytut Medycyny Pracy w Łodzi/Poland (Medical Institute of Work in Lodz/Poland) and were kept in cages of the conventional type. Before the study, the animals were quarantined for a minimum 5 days and observed daily during this period. The animals were marked individually. During quarantine and the experiments, the animals were kept in a conditioned room of the following parameters: temperature 20–23 °C, relative air humidity 30–40%, and artificial illumination 12 h light/12 h darkness. Rats were kept in cages with plastic bottom and wired superstructure, with the dimensions of 58 × 37 × 21 cm (length × width × height). The animals were kept in cages individually (in the observation study – the dose of 2000 or 500 mg kg^{-1} b.w.) or 4 rats per cage (in the main study – the dose of 500 and 50 mg kg^{-1} b.w.). UV-sterilized wooden shavings were used as litter. Each cage was equipped with a label containing information on name of test material, study code, used dose, start date and planned ending date of the experiment, sex, and animal numbers. The rats were given standard granulated GLM fodder and tap water *ad libitum*.

The day before the start of the experiment, about 18–19 h before administration of the test material, the animals were left with no food, but water was still available. The food was given again 3 h following administration of the material.

In the preliminary experiment, one female was given the tested material in the form of a solution in dimethylsulfoxide (DMSO), at the dose of 2000 mg kg^{-1} b.w. The material was administered as a single dose using a metal intragastric catheter. One mL of the administered solution contained 800 mg of the tested material. The total of 0.25 mL solution was given per 100 g rat body mass.

Subsequently, the tested material was administered to a following female rat, at the dose of 500 mg kg^{-1} b.w. The preparation for administration, administration procedure, and the administered volume corresponded to those described above. This time, 1 mL of the administered solution contained 200 mg of the tested material.

In the main experiment following the preliminary study, the materials were administered to five female rats (including the one from the preliminary experiment) at the dose of 500 mg kg^{-1} b.w. and, then, to another five female rats at the dose of 50 mg kg^{-1} b.w. The preparation for administration, administration procedure, and the administered volume corresponded to those used in the preliminary experiment. One mL of the administered solution contained 20 mg of the tested material. Since the tested material was administered in the form of a solution in DMSO, the five control female rats were administered a single dose of DMSO at 0.25 mL per 100 g b.w.

Wood penetration testing

Samples of Scots pine wood (*Pinus sylvestris* L.) were used. The density of the wood ranged between 480 and 540 kg m^{-3},

with the number of growth rings at 5–8 per 1 cm. Each block measured 50 × 50 × 20 mm (one of the longer edges had to be parallel to the fibers and the annual growth increment rings visible in cross section had to be positioned against the edge at an angle of 45 ± 10°) and was conditioned to a moisture content of 12 ± 1%. The investigated samples were cut out from the middle part of the trunk, the side surface and tight surface of which was smoothly planed.

On the 50 × 50 mm wood surface, 0.5 g of the investigated salts were applied. The samples were then conditioned in the dishes over a saturated solution of ammonium nitrate at 20 ± 2 °C for 7 days. Subsequently, the samples were cut perpendicularly into fibers by means of a cross cut saw, and were sprayed carefully on the cross-section surface with bromphenol blue indicator (giving a typical blue color on contact with the IL). The ranges of blue sections were marked with a sharp pencil, which permitted determination of the penetration depth of each IL. In each of the tests, penetration was recorded in 10 wood samples (2 samples from each of 5 fillets of Scots pine wood).

Wood leach testing

Defect-free sapwood boards of Scots pine (*Pinus sylvestris* L.) were used in this study. Cubes measuring 19 mm were prepared from the boards and stored in a climatic chamber maintained at 65% relative humidity (RH) and 20 °C until they reached an equilibrium moisture content (EMC) of 12 ± 1%. The conditioned cubes were then pressure-treated with the solutions of IL and mixtures of IL with polypropylene glycol (PPG), both disolved in 2-propanol. The concentrations of the solutions (ILs in 2-propanol) were 1.0 and 1.6% by weight. The treating procedure included an initial −88 kPa vacuum for 30 min and atmospheric pressure for 60 min. The treated samples were a subject to seasoning in the drying vessel at room temperature for 3 weeks before further testing. 2-Propanol was evaporated during the seasoning process.

After the conditioning of the treated cubes, the leach tests were carried out to determine the amount of ILs leaching from treated wood. Three treated wood cubes weighing about 10 g, were placed in Erlenmeyer flasks and immersed in 100 mL of distilled water. The flasks were positioned on a horizontal-shaking tray with continuous mild shaking at 150 rpm for 8 days. After this time the leached cubes were analyzed by a two-phase titration, according to standards for determination of quaternary ammonium compounds in wood by two-phase titration set by the American Wood-Presever's Association.[25]

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