FOLIA FORESTALIA POLONICA

© *PAN* *Series B, Issue 40, 89-100, 2009*

PHYSICOCHEMICAL RESEARCH ON ADSORPTION AND BONDING OF FUNGICIDES APPLIED IN WOOD PRESERVATION WITH LIGNOCELLULOSIC MATERIALS

Jadwiga Zabielska-Matejuk*, Anna Stangierska*,
Piotr Przybylski**

*Wood Technology Institute, Poznań
**Faculty of Chemistry, Adam Mickiewicz University

SYNOPSIS. In this paper methods for adsorption study of quaternary ammonium based ionic liquids and cationic surfactants on Scots pine (*Pinus sylvestris* L.), model lignin and cellulose are presented. Kinetic and equilibrium of compounds were evaluated. The equilibrium data fitted very well to the Langmuir and Freundlich adsorption models. The highest correlation coefficients determined from the pseudo-second order kinetic model confirm the key role of chemisorptions in the process of thickening of ionic liquids on the wood surface. The bonding identification of ammonium cations and long alkyl substituents (of investigated salts) into the Scots pine wood was carried out using IR spectroscopy.

KEY WORDS: ionic liquids, equilibrium and kinetic adsorption, pine wood, lignin, cellulose, FT-IR

INTRODUCTION

Wood is a renewable and environmentally friendly raw material; unfortunately it is not resistant to climate factors, fungi, insects, and fire. Enhancement of durability of wood and other lignocellulosic materials requires introduction of highly effective biocidal protective agents into these materials. At the same time these agents should bond with structural components of wood. Current research on acceleration of and increase in fixation of new copper fungicides into impregnated wood aim to reduce metal ion emission to the environment (Cao et al. 2004, Ung and Cooper 2004, Cihat et al. 2008, Ratajczak et al. 2008). Search for new solutions to lignocellulosic material protection against biotic and abiotic factors requires to conduct of specific physical and chemical tests which would evaluate the effectiveness of bonding with wood. Such tests, apart from standardized procedures for assessment of fungistatic action, will allow researchers to fully determine suitability of new bioactive substances for wood protection. Analysis of surface processes occurring at the border of phases: water solution of a fungicide – lignocellulosic material, and identification of sorption equilibria and kinetics may describe the mechanism of fungicide fixation into wood. Another step of research is usually IR spectroscopic analysis which identifies creation of bonds between active components of preparations and wood.

Quaternary ionic liquids, aliphatic and aromatic amines derivatives, which tend to be non-volatile substances in room temperature, on top of their biocidal effect demonstrate very good penetrating qualities on a wide spectrum of organisms (Pernak et al. 2004, 2006, Zabielska-Matejuk and Skrzypczak 2006, Kartal et al. 2005, 2006). The synthetic abilities of multiple amphiphilic compounds containing two or more quaternary atom of nitrogen, enjoying great aggregative ability in water environment, make it possible to launch a new group of structurally extended biocides of the desired qualities of monomeric ammonium salts (Pernak et al. 2007, Sokołowski et al. 2002). The presence of at least two long alkyl chains in the structure of geminal ionic liquids may contribute to easier dissolution of these compounds; while the twin cation obtained from N,N-dimethylalkylamines provides for more sustainable fixation of these salts in wood. Structure modification of ionic liquids by replacement with more hydrophobic anions, such as tetrafluoroborate or hexafluorophosphate, can decrease leaching of those salts from wood. The adsorption of cationic surfactans (fungicides for wood) with different hydrophobic chain lengths onto cellulose fiber in an aqueous media is interpreted as an aggregation and self-assembly of the molecules at the solid-liquids interface. The nature of a solid surface, that is hydrophobicity or hydrophilicity, and of electrostatic interactions plays an important role in kinetics of surfactants adsorption (Paria et al. 2005). This article presents the results of a study on the adsorption processes of ionic liquids on Scots pine wood, model lignin and cellulose. The determination and monitor of alteration in wood treated with these fungicides were performed using FT-IR spectroscopy.

In order to investigate the mechanism of ionic liquids adsorption two different kinetic models were used.

The first-order rate expression of Lagergren (1898) is:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ad}}{2.303} \cdot t \tag{1}$$

The second order (chemisorption) kinetic model (Ho and McKay 1999) is expressed as:

$$\frac{t}{q} = \frac{1}{k_{2,ad} \cdot q_e^2} + \frac{t}{q_e} \tag{2}$$

where: q_e and q (mg·g^{-1}) are the amounts of adsorbed salts on the biosorbent at the equilibrium and at any time t (min), respectively, and $k_{1,ad}$ (min^{-1}) and $k_{2,ad}$ (g·mg^{-1}·min^{-1}) are the rate constants of Lagergren and pseudo-seconds order models, respectively.

The Langmuir and Freundlich equations were used for modelling of the equilibrium adsorption data from solutions on lignocellulosic materials.

The Freundlich isotherm equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

The Langmuir isotherm (chemisorption) equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot b} + \frac{C_e}{K_L} \tag{4}$$

where: q_e (mM·g^{-1}) are the amounts of adsorbed salts on the soil at the equilibrium, c_e (mM) are the concentrations of adsorbate at equilibrium, K_F, n, Freundlich constants; b, K_L Langmuir constants, respectively.

MATERIALS AND METHODS

Chemicals

In the presented paper a new class of ionic liquids: mono-and bis quaternary ammonium based 1-alkylimidazolium and N.N-dimethylalkylammonium derivatives: nitrates, propionates and chlorides, was studied. The structures of mono- and geminal dicationic ionic liquids are presented in Figure 1. The prepared compounds were characterised by their ^{1}H NMR and ^{13}C NMR spectra (Varian 300 VT type spectroscope).

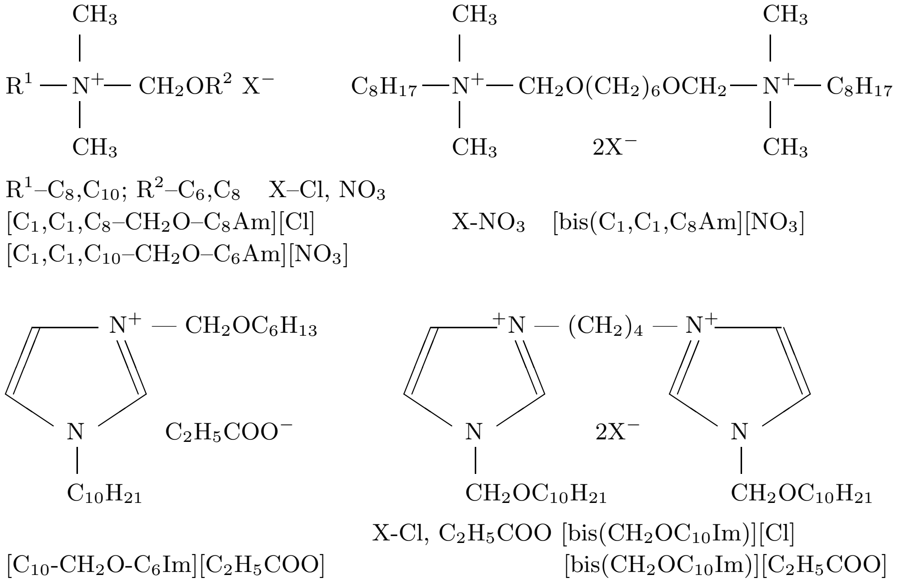
N,N-[1,10-(2,9-Dioxadecane)]bis(dimethyloctylammonium nitrate)
[bis(C_1,C_1,C_8Am)][NO_3] ^{1}H NMR ($CDCl_3$): 0.85-0.90 (t, 6H); 1.26-1.39(m, 24H); 1.55-1.70(m, 8H); 3.014(s, 12H); 3,32-3,37(m, 4H); 3.81-3.88(t, 4H); 4.80-4.84(s, 4H). ^{13}C NMR ($CDCl_3$): 14.0; 22.2; 22.5; 24.8; 25.1; 26.3; 28.9; 29.1; 31.5; 32.3; 47.0; 61.4; 73.1; 90.3.

Lignocellulosic materials

For the experiments Scots pine sawdust (*Pinus sylvestris* L.) was ground to pass a 1.0 mm mesh, mixed well to give a homogeneous sample and dried at 65°C for 24 hours. The fraction composition of wood sawdust was as follows: particle size 1.0-0.5 mm (2.45%), 0.5-0.25 mm (41.75%), $<$ 0.25 mm (55.76). Organosolv lignin of softwood purchased from Aldrich and cellulose from Sigma-Aldrich were investigated.

Kinetic studies

The experiments were performed adding 5.0 g of dried Scots pine sawdust ($\varphi <$ 1.0 mm), lignin or cellulose to 100 ml of ionic liquids solution (15 mM) in 250 ml Erlenmeyer flasks, which were placed on horizontal shaker at 150 rpm for 1,



R^1–C_8,C_{10}; R^2–C_6,C_8 X–Cl, NO_3

[C_1,C_1,C_8–CH_2O–C_8Am][Cl]

[C_1,C_1,C_{10}–CH_2O–C_6Am][NO_3]

X-NO_3 [bis(C_1,C_1,C_8Am)][NO_3]

[C_{10}-CH_2O-C_6Im][C_2H_5COO]

X-Cl, C_2H_5COO [bis(CH_2OC_{10}Im)][Cl]

[bis(CH_2OC_{10}Im)][C_2H_5COO]

Fig. 1. Structure and abbreviations for ammonium and imidazolium salts evaluated in the study

3, 5, 15, 60, 120, 180, 360 min to ensure that equilibrium was reached. The study was performed at 20°C. Materials were then filtered through a glass filter under vacuum without washing, and the filtrate was analysed.

Equilibrium studies

The experiments were conducted in Erlenmeyer flasks containing 100 ml of ionic liquids solution of 3, 5, 8, 12, 15, 30 and 45 mM concentration and 5.0000 g of dried Scots pine sawdust ($\varphi < 1.0$ mm), lignin or cellulose. The flasks were agitated at 150 rpm on horizontal shaker for 24 hours to ensure that equilibrium was reached. The study was performed at 20°C. Before the analysis samples were filtered under vacuum without washing and the filtrate was analysed by a two-phase titration of 0.0005 M sodium dodecyl sulphate as titrant, according to AWPA Standard... (1993). Wood sawdust, cellulose and lignin adsorption of studied salts was determined by the difference between the initial solutions concentration and that at each sampling time. All the experiments were carried out in duplicate analyses in three replicates.

FT-IR analysis

For the FT-IR analysis treated wood samples after agitation were filtrated and washed continuously with double-distilled water until no fungicides were present in the eluent water. The aim of continuous washing with water was to minimize physical absorption of ionic liquids in treated wood. The treated and water-washed samples were air-dried for two weeks and analysed by FT-IR analysis on a spectrometer IFS 66 V/S Bruker. Spectra were acquired in a 400 to 4000 cm^{-1} wave number range with a resolution of 2 cm^{-1}.

RESULTS

The adsorption kinetics of examined compounds depends on the cation structure of ionic liquids. The effect of agitation time of $[C_1,C_1,C_{10}\text{-}CH_2O\text{-}C_6Am][NO_3]$ and geminal dicationic ionic liquids $[bis(C_1,C_1,C_8Am)][NO_3]$ from aqueous solutions at initial concentration of 15 mM on adsorption on wood is presented in Figure 2. The greatest adsorption dynamics was achieved in the case of mono ammonium nitrate (51 $mg \cdot g^{-1}$). After 1 min of shaking it reached 65.9% of the equilibrium state. The equilibrium adsorption of this salt is 1.4 times greater than that of the dicationic ammonium nitrate which was only 37 $mg \cdot g^{-1}$. It can be noticed that after the equilibrium time of 360 min no more ionic liquids were adsorbed. It suggests that available site on the wood surface is an adsorption limiting factor. Figure 3 shows plots of the linearized form of the pseudo-second order model (Eq. 2) for studied compounds at the initial concentration of 15 mM and for the contact times of 360 min. The linear plots of t/q vs. t show good agreement between experimental and calculated values. The determination coefficients for the

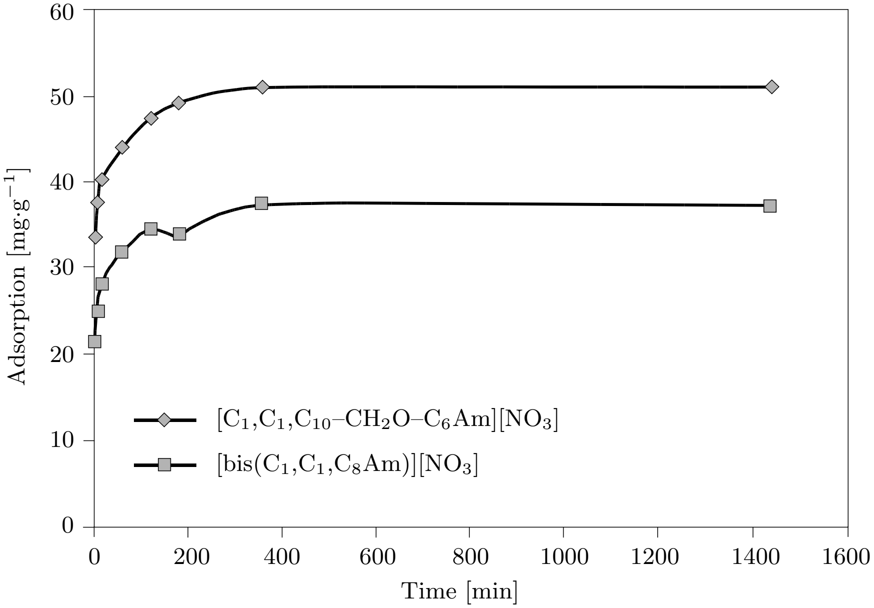


Fig. 2. Effect of the agitation time on adsorption of studied ionic liquids on wood sawdust at initial concentration $c_o = 15$ mM

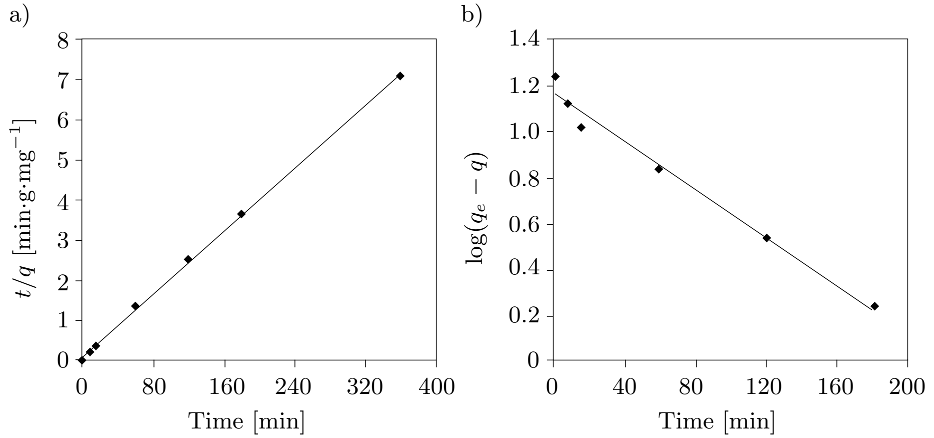


Fig. 3. Comparison of the [C_1,C_1,C_{10}-CH_2O-C_6Am][NO_3] adsorption plots for: a – pseudo second-order kinetic model, b – Lagergren first-order kinetic model; (c_o = 15 mM)

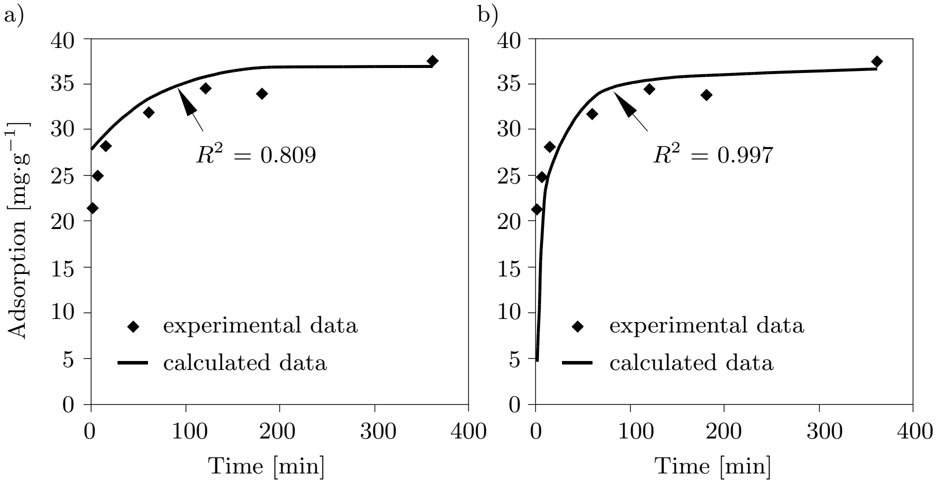


Fig. 4. Dependence between the experimental and calculated q_e values of [bis(C_1, C_1,C_8Am)][NO_3] for: a – Lagergren first-order kinetic model, b – pseudo second-order kinetic model; (c_o = 15 mM)

pseudo-second order kinetic model are greater than 0.997 but in the case of the Lagergren first-order kinetic model (the linear plot of log ($q_e - q$) vs. t – Eq. 1) they were lower than 0.985 (Fig. 3). The dependence between the experimental and calculated qe values of di cationic ionic liquids [bis(C_1,C_1,C_8Am)][NO_3] for the two kinetics models used is presented in Figure 4. The results indicated that adsorption of these salts on wood is not a pseudo-first model reaction ($R^2 = 0.809$). In the case of the second-order kinetics the calculated qe value also agreed very well with experimental values. It suggests that independently of chemical struc-

Table 1. Comparison of adsorption rate constants, qe estimated and coefficient of determination associated to the Lagergren pseudo first--order and pseudo second-rate kinetic models

Ionic liquids	Initial concentration (mM)	Pseudo second-order model				Lagergren pseudo first-order model		
		$q_{e,exp.}$ [mg·g^{-1}]	$k_{2,ad}$ [g·mg^{-1}·min^{-1}]	$q_{e,cal}$ [mg·g^{-1}]	R^2	$k_{1,ad}$ [min^{-1}]	$q_{e,cal}$ [mg·g^{-1}]	R^2
[C_1,C_1,C_{10}-CH_2O-C_6Am][NO_3]	15	51.05	0.0038	51.28	0.999	0.01197	51.35	0.985
[bis(C_1,C_1,C_8Am)][NO_3]	15	37.57	0.0042	36.70	0.997	0.01393	36.76	0.809

ture of ionic liquids chemisorption is involved in the process of their adsorption on wood. The rates of values of constants $k_{1,ad}$ and $k_{2,ad}$ for ammonium nitrate and diammonium nitrate were very similar (Table 1).

The comparison of Langmuir and Freundlich adsorption isotherms for bis-imidazolium propionate with the chloride anion confirms predominance of physical sorption of these salts on pine wood (Fig. 5). The appropriate coefficients for the Langmuir equation are $R^2 = 0.906$ [bis(CH_2OC_{10} Im][C_2H_5COO] and $R^2 = 0.849$ [bis(CH_2OC_{10} Im][Cl]; whereas for the Freundlich equation they are $R^2 = 0.987$ and $R^2 = 0.975$, respectively, see Table 2. Different determination coefficient indicates that the experimental data for those salts fulfills the Freundlich equation better. At the initial concentration of 45 mM the equilibrium adsorption of these salts was higher and reached 0.398 mM·g^{-1} and 0.368 mM·g^{-1} of wood sawdust. In the case of mono-imidazolium salt [C_{10}-CH_2O-C_6 Im][C_2H_5COO] high determination coefficient of the Langmuir isotherm equation indicates the predominance of the process of the chemical sorption of these salts (Table 2). The equilibrium adsorption at the initial concentration (c_o) of 45 mM was reached only at the level of 0.194 mM·g^{-1}. Table 3 shows difference in ionic liquids adsorption obtained for wood sawdust, model lignin and cellulose. The results of the experiment suggest that studied salts more easily bond with lignin but they do not adsorb on the cellulose surface. The equilibrium adsorption on cellulose ranged only from 1.37% to 5.21%. Leaching of ionic liquids from the treated cellulose was higher than leaching from the treated wood sawdust. However, compared to ionic liquids containing two geminal ammonium cations the single ammonium salts were fixed in lignocellulosic materials to the greatest degree (Table 3).

Table 2. Freundlich and Langmuir adsorption constants obtained from adsorption isotherms of ionic liquids on Scots pine sawdust

Ionic liquids	Freundlich constants			Langmuir constants		
	K_F	$1/n$	R^2	K_L [mM·g^{-1}]	b [dm^3·mM^{-1}]	R^2
[bis(CH_2OC_{10} Im][C_2H_5COO]	0.096	0.39	0.987	0.428	0.200	0.906
[bis(CH_2OC_{10} Im][Cl]	0.073	0.45	0.975	0.433	0.128	0.849
[C_{10}-CH_2O-C_6 Im][C_2H_5COO]	0.090	0.22	0.946	0.201	0.372	0.993

Table 3. Comparison of the equilibrium adsorption and leaching of ionic liquids from Scots pine sawdust, lignin and cellulose

Ionic liquids	Initial concentration [mM]	Adsorption on:		
		Wood sawdust $\varphi < 0.25$ mm	Lignin organosolv	cellulose
		%		
[C_1,C_1,C_{10}-CH_2O-C_6Am][NO_3]	15	55.24	76.99	5.21
[bis(C_1,C_1,C_8Am)][NO_3]		18.70	32.47	1.37
Leaching [%]				
[C_1,C_1,C_{10}-CH_2O-C_6Am][NO_3]		0.9	10.76	7.60
[bis(C_1,C_1,C_8Am)][NO_3]		2.73	11.95	10.2

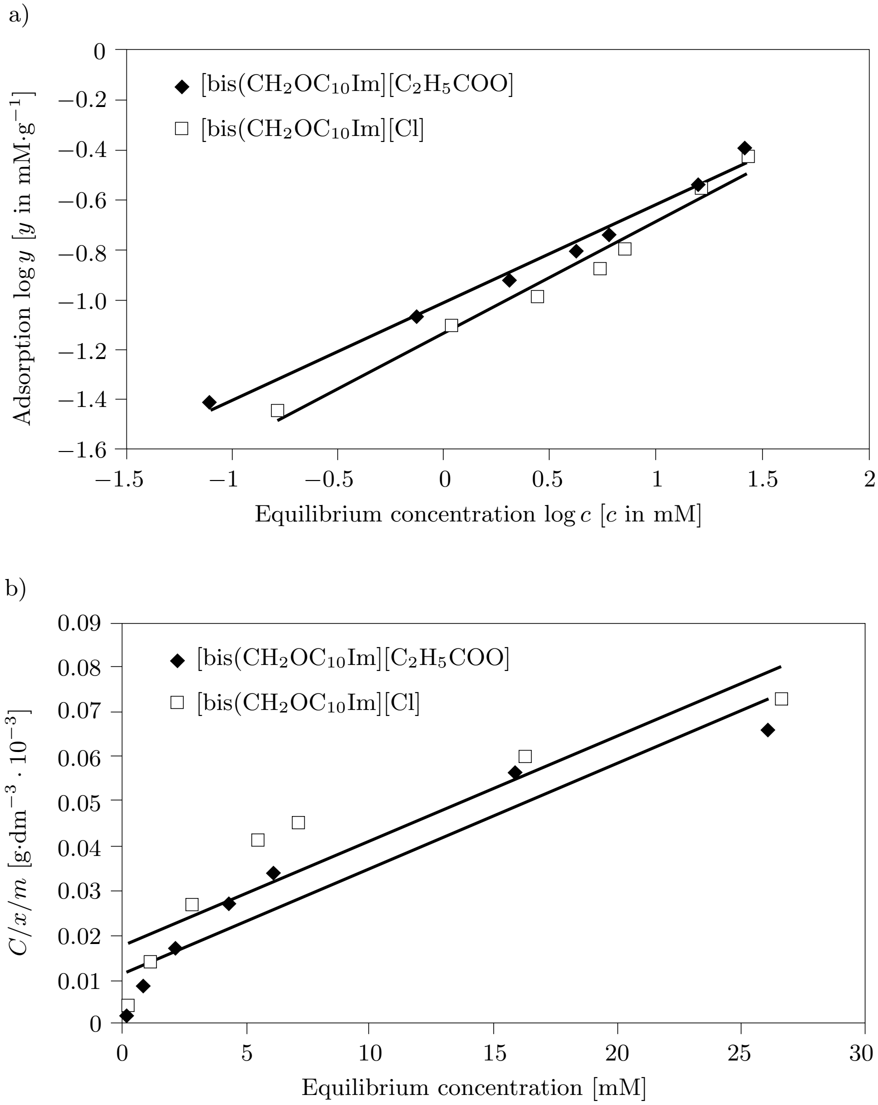


Fig. 5. Comparison of the bis-imidazolium chloride and propionate adsorption isotherms: a – Freundlich isoterms model, b – Langmuir isotherms model

FT-IR spectra

The spectra of Scots pine wood samples treated with single ammonium salts [C_1,C_1,C_{10}-CH_2O-C_6Am][Cl] differ from the spectra of control wood in the range of vibrations ν (C=O) and ν (O-H). Slight differences were also observed in the range of alkane valency vibrations ν (C-H) (Fig. 6). The band at 1735 cm^{-1}, assigned to carboxyl stretching vibration in carboxylic acid, diminished after treatment with

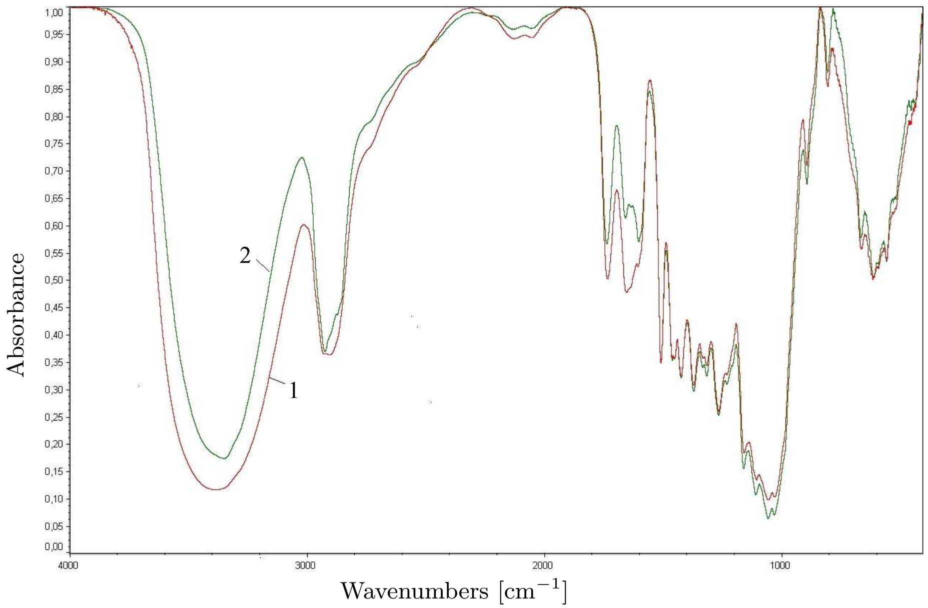


Fig. 6. FT-IR spectra of Scots pine wood: 1 – control wood, 2 – wood samples treated with ammonium chloride [C_1,C_1,C_8-CH_2O-C_8Am][Cl]

ammonium salts. The reduction of band at 1735 cm^{-1} is attributed to dissociation of carboxylic acid into carboxylate anion. At the same time Figure 6 shows appearance and increase of the relative intensity ν $(C{=}O)_{COO-}/\nu$ $(C{=}O)_{COOH}$ attributed to carbonyl stretching vibration band at 1606 and 1593 cm^{-1} in carboxylate salt. Development of R_4N^+–$^-$OOC– carboxylates in the presence of quaternary ammonium salts confirms that single ammonium salts build into the Scots pine wood structures most easily. The band ν $(C{=}O)_{COOH}$ in FT-IR spectra of treated wood in relation to control sample was shifting from 1735 to 1738 cm^{-1}. Reduction of intensity of hydroxyl group band of acid also confirmed development of ammonium carboxylate. The presence of the ν_s(–CH_2–) band in the methylene groups of ammonium salts alkyl chains at 2855 cm^{-1} in the FT-IR spectrum of the saturated wood is an additional confirmation of bonding.

CONCLUSION

1. Equilibrium adsorption data of investigated ionic liquids corresponded to both Langmuir and Freundlich isotherms. The Freundlich equation described better the geminal dicationic salts adsorption process onto Scots pine wood, wood sawdust. Adsorption of the single salts was governed to the greatest degree by chemical processes-Langmuir sorption model.

2. Kinetic investigation indicates that adsorption processes of ionic liquids on Scots pine wood follow the pseudo-second order kinetic model. It confirms the key role of chemisorptions in the process of thickening of ionic liquids on the wood surface.
3. The bond of the single quaternary ammonium based ionic liquids with wood and lignin is the strongest; while with cellulose the loosest. The FT-IR spectrum analysis of Scots pine wood confirmed development of $R_4N^+{-}^-OOC{-}$ carboxylates in the presence of single ammonium salts building into the pine wood structures and also in the presence of the ν_s ($-CH_2-$) band in the methylene groups of ammonium salts alkyl chain at 2855 cm^{-1} in the spectrum of the saturated wood.
4. It can be assumed that physicochemical research of these thickening processes of fungicides on the lignocellulosic materials surface is useful for assessment of the effectiveness of their bond with wood.

Acknowledgements

This investigation received financial support from the Polish Ministry of Science and Higher Education, Grant 3 TO8E 08929. We would like to thank Dr. Andrzej Skrzypczak from Poznań University of Technology for preparation of chemical compounds.

REFERENCES

AWPA Standard A 18-93 (1993): Standard for determination of quaternary ammonium compounds in wood by 2-phase titration. Am. Wood-Preserv. Assoc. Subcom. T-7.

Cihat T., Cooper P., Ung T. (2008): Effects of fixation temperature and environment on copper speciation in ACQ treated red pine. Holzforschung 62: 289-293.

Cao J., Kamdem P., Pasek E. (2004): Microdistribution of copper in copper-ethanoloamine (CuEA) treated southern yellow pine (*Pinus* spp.) related to density distribution. Doc. No. IRG/WP04-40270. International Research Group on Wood Preservation, IRG Secretariat, Stockholm.

Ho Y.S., McKay G. (1999): Pseudo-second order model for sorption processes. Proc. Biochem. 34: 451-465.

Kartal S.N., Hwang W.-J., Shinoda K., Imamura Y. (2006): Laboratory evaluation of boron-containing quaternary ammonia compound, didecyldimethylammonium tetrafluoroborate (DBF) for control of decay and termite attack and fungal staining of wood. Holz Roh-u. Werkst. 64: 62-67.

Kartal S.N., Shinoda K., Imamura Y. (2005): Laboratory evaluation of boron-containing quaternary ammonia compound, didecyldimethylammonium tetrafluoroborate (DBF) for inhibition of mold and stain fungi. Holz Roh-u. Werkst. 63: 73-77.

Lagergren S. (1898): Zur theorie der sogenannten adsorption gelöster stroffe. Kungliga Svenska Vetenskapsakademiens. Handlinger 24 (4): 1-39.

Paria S., Manohar C., Khiler K.C. (2005): Kinetics of adsorption of anionic, cationic and nonionic surfactants. Ind. Eng. Chem. Res. 49: 3091-3098.

Pernak J., Skrzypczak A., Lota G., Frąckowiak E. (2007): Synthesis and properties of trigeminal tricationic ionic liquids. Chemistry – Eur. J. 13 (11): 3106-3112.

Pernak J., Śmiglak M., Griffin S.T., Hough W. L., Wilson T. B., Pernak A., Zabielska-Matejuk J., Fojutowski A., Kita K., Rogers R.D. (2006): Long chain quaternary ammonium-based ionic liquids and potential applications. Green Chem. 8: 1-10.

Pernak J., Zabielska-Matejuk J., Kropacz A., Foksowicz-Flaczyk J. (2004): Ionic liquids in wood preservation. Holzforschung 58 (3): 286-291.

Ratajczak I., Hoffmann S.K., Goslar J., Mazela B. (2008): Fixation of coppert(II)-protesin formulation in wood: Part 1. Influence of tannic acid on fixation of copper in wood. Holzforschung 62: 294-299.

Sokołowski A., Wilk A., Komorek U., Rutkowski R., Syper L. (2002): Aggregation properties of cationic gemini surfactants in aqueous solution. Fizykochem. Probl. Mineral. 36: 51-64.

Ung Y.T., Cooper P.A. (2004): Effect od species, retention and conditioning temperature on copper stabilization and leaching for ACQ-D. Doc. No. IRG/WP04-302342. International Research Group on Wood Preservation, IRG Secretariat, Stockholm.

Zabielska-Matejuk J., Skrzypczak A. (2006): Ionic liquids with organic and inorganic anions as highly active wood preservatives. Doc. IRG/WP 06-30411. Int. Res. Group on Wood Preservation, IRG Secretariat, Stockholm.

Received in January 2009

Authors' addresses:
Dr. Jadwiga Zabielska-Matejuk
Anna Stangierska
Wood Technology Institute
60-654 Poznań
ul. Winiarska 1
Poland

Dr. Piotr Przybylski
Faculty of Chemistry
Adam Mickiewicz University
60-780 Poznań
ul. Grunwaldzka 6
Poland