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SORPTION OF IONIC LIQUIDS

Ionic liquids (ILs) attract growing attention and the range of their potential application is constantly expanding. To meet not only the technological but also environmental requirements for their implementation to wide-scale use, we undertook an extensive literature study into ILs interaction and sorption onto soils. The available data were compared and subjected to critical review. We also performed sorption batch test of 1-methyl-3-octylimidazolium chloride in a broad concentration range onto low pH and forest soil poor in organic matter. The sorption isotherm closely matched the isotherm described previously in the literature as corresponding to double layer sorption. From the sorption isotherm we calculated the partition coefficients (K_d).

1. INTRODUCTION

1.1. ROLE AND IMPACT OF IONIC LIQUIDS

Ionic liquids (ILs) are a new class of chemicals with a broad range of potential industrial applications, with the some important applications being the BASIL (Biphasic Acid Scavenging using Ionic Liquids) process for alkoxyphenylphosphines production, lithium-ion battery electrolyte, the replacement of phosgene in arenes chlorination, electroplating of aluminium, polymerization reactions, metal extraction, analytical separation techniques (liquid-liquid extraction, liquid phase microextraction, solid phase microextraction), biocatalysis (transesterification, oxidation, synthesis), dissolution and recovery of cellulose, and separation of products in biphasic systems. ILs have been proven to have several advantages over conventional volatile organic sol-

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vents, namely, higher efficiencies in some reactions, better solvent properties, miscibility with water, and most importantly from an environmental point of view – almost no measurable vapour pressure (Kragl, Eckstein et al. 2002, Kubisa 2004, Jain, Kumar et al. 2005, Liu, Jonsson et al. 2005, Plechkova, Seddon 2008). Due to their low vapour pressures, ILs are unlikely to act as air contaminants. Nevertheless, they possess a potential to contaminate soil and water. A broad range of international programs already exist which aim to protect human health and the surrounding environment by introducing regulations concerning safe usage and management of chemical substances. The European Commission *REACH* system (2007) and United Nations Agenda 21 (2004), are two of the more significant ones that attempt to gather information about the environmental impact, mobility, toxicity and contamination potential of chemicals used in industrial processes and agriculture prior to their implementation. This knowledge is needed to provide a defined set of data on the properties of chemical substances used and potential risk management strategies.

This paper will attempt to summarize the literature to date on the sorption process of ILs onto soils. The data from this literature summary was collated, and the sorption mechanism was described.

1.2. SORPTION PHENOMENON

Sorption onto solid particles of minerals or/and organic matter in terrestrial or aquatic environments has a marked influence on the mobility of chemical substances. Investigation of the bonding strength and the mechanism of this process is one of the crucial parameters required in predicting or modelling the distribution of chemicals. Sorption can temporarily immobilize contaminants allowing for biodegradation to occur and in this way influence their removal from the environment. The rate at which microbial cells can degrade contaminants depends on the rate of metabolism and the rate of transfer to the cell. Increased microbial conversion capacities do not lead to higher biotransformation rates when mass transfer is a limiting factor (Boopathy 2000). Chemicals strongly bound to solid particles can not be utilized by microorganisms; hence, they become biologically unavailable. Strong bonding to soil particles or organic matter can also prevent leaching to groundwater and drinking water contamination or decrease toxicity to flora and fauna since bound chemicals are not available for uptake. Similarly partitioning between sediments and water in water bodies will decrease toxicity towards aquatic living organisms (Matzke, Stolte et al. 2008).

1.3. CRITICAL REVIEW OF LITERATURE DATA

Sorption of ionic liquids to soils and sediments has been investigated by several research groups. Gorman-Lewis and Fein (Gorman-Lewis, Fein 2004) was one of

the first groups that performed sorption tests in simplified systems using butyl-methyl-imidazolium chloride and minerals: quartz, gibbsite, montmorillonite – without organic matter and *Bacillus subtilis* cells. No sorption onto quartz, gibbsite and bacterial cells was observed. Since gibbsite's point of zero charge is 9.8, within the pH range of the experiment (6–10), it was mainly positively charged. Due to this fact electrostatic repulsion between gibbsite particles and IL cations should have been expected, which limits the sorption by charge-charge interaction. Nevertheless quartz, having point of zero charge approximately 2–3 is negatively charged in the pH range of the experiment, but did not showed any adsorption of [BMIM] [Cl]. The explanation of this phenomenon can be the low surface area of quartz, more than one order of magnitude lower than gibbsite's. Although potential active sites for electrostatic attraction exist, they are not easily accessible for large IL's cations, and thus not allowing for sorption. The authors claimed, on the basis of literature data, that the amount of binding sites was at least one order of magnitude higher than the concentration of test substance and; therefore, attributed the lack of sorption to the chemical properties of IL.

Bacillus subtilis is a gram positive, common soil micro-organism possessing carboxyl-, phosphoryl- and hydroxyl-groups on the surface. Those functional groups deprotonate within pH range of the presented experiment; thereby, creating a negatively charged surface capable of attracting IL molecules. Bacterial cell walls also present a possibility of hydrophobic interactions with organic compounds. Despite these factors no sorption of IL was detected. In their opinion the lack of sorption onto bacterial cells can be explained by rather low hydrophobicity of [BMIM] [Cl].

In contrast, the authors detected significant sorption onto montmorillonite. Montmorillonite differs in a composition from the other tested minerals by possessing a layered 2:1 lattice structure. This class of clay minerals are well known to be far more able to sorb cations by electrostatic attraction than minerals of gibbsite and quartz type. The authors (GORMAN-LEWIS, FEIN 2004) concluded that dialkylimidazolium ILs are unlikely to be sorbed in most geological systems unless significant amounts of clays are present. Consequently, ILs possess a potential to enter ground water systems and to act as contaminants.

Beaulieu et al. (BEAULIEU, TANK et al. 2008) conducted an experimental study aiming to describe dependence of the sorption strength on sediments/sand organic matter content and IL's side chain length. Four methylimidazolium ILs substituted with methyl, butyl, hexyl, and octyl chains were subjected to the test as they were expected to have different sorption behaviours due to an increasing hydrophobicity. No measurable sorption to sand was observed, whereas sorption to sediments was very strong and positively correlated with organic carbon (OC) content but interestingly not with alkyl chain length. This suggested that interaction with the organic matter is the primary sorption mechanism, although hydrophobic interaction can not be the exclusive justification of this phenomenon. No correlation of partitioning with

cation exchange capacity (CEC) of solids was proven, suggesting that electrostatic interaction is not a major sorption mechanism. It was interesting to note that no correlation with alkyl chain length was observed. In our opinion this may be due to the low OC content of the samples, and thus the coulombic interaction was dominating the sorption process.

STĘPNOWSKI (2005) determined the behaviour of several alkyylimidazolium IIs with a side chain length of C₃ to C₆ in soil and sediments in order to assess their potential to spread into the environment and predict possible contaminant compartmentalization. His research showed that those IIs were strongly bound to the soil, with the sorption increasing with the lengths of alkyl side chain which would suggest mostly hydrophobic interaction based retention of ionic liquids in the soil. In contrast, binding to the peaty soils (with the highest organic matter content) was relatively weak indicating that other mechanisms like electrostatic interactions might be involved (STĘPNOWSKI 2005).

Another experiment conducted by Stępnowski et al. (STĘPNOWSKI, MROZIK et al. 2007) utilizing alkyylimidazolium- and – pyridinium IIs has proven strong correlation of sorption with fine clay particles content of a soil and the alkyl side chain length of IIs. However, the side chain length correlations were observed for concentrations up to 1 mM. This research group was the first to suggest multilayer sorption of IIs since the amount of IL sorbed onto the soil particles significantly exceeded the CEC of the soil.

Studzińska et al. (STUDZIŃSKA, SPRYNSKY et al. 2008) conducted sorption kinetics experiment of alkyylimidazolium (C₂, C₄, C₆) IIs onto soils differing in organic carbon content. They found hydrophobic interaction of IIs with soil organic matter to be the main sorption mechanism. Less polar IIs with long alkyl chains were strongly retained in soils with high organic matter content whereas more polar IIs with short side chains were sorbed stronger to soils with lower organic matter content. The experimental procedure applied in this study differs significantly from the other tests mentioned. First, of all authors used different methods for soil characterization, including determination of CEC by ammonium acetate buffered method which is not recommended in the literature. There are two main sources of charge in minerals: pH independent being a result of crystal lattice defects and pH dependant coming mainly from surface hydroxyl groups or edge sites. Because pH dependent charge is present not only on the surface of minerals but also on organic matter, pH change during measurement can influence the result significantly (CIESIELSKI, STERCKEMAN 1997; ROBERTSON, SOLLINS et al. 1999). After performing a simple analysis of the correlations: K_d – OC, K_d – CEC, we have come to substantially different conclusions than authors of the tests. Correlation between K_d and CEC was comparable with correlation between K_d and OC for [BMIM] [Cl] and [HMIM] [Cl]. In the case of [EMIM] [Cl], both were quite poor; however, the first one was significantly better, which would be expected since short-chained [EMIM] [Cl] does not possess the ability to sorb strongly through hydrophobic interaction.

Matzke et al. (MATZKE, STOLTE et al. 2008) conducted IIs sorption experiments utilizing soil with kaolinite and smectite in order to establish their toxicities. The authors proved that the 2:1 structured mineral – smectite possessed the potential for IIs adsorption due to interlayer cation exchange whereas kaolinite, a 1:1 lattice, mineral is not capable of retaining IIs due to lack of interlayer adsorption sites. It was also stated that more hydrophilic IIs (with shorter alkyl side chain) would be more mobile in the environment than hydrophobic ones due to a reduced amount of possible interactions with soil/organic matter system since organic substances present in soil were proven to be responsible for IIs retention. However, it was not possible to unequivocally attribute sorption to one of mentioned above mechanisms.

Most of sorption experiments conducted so far were focusing on IL cation sorption. Although anion sorption has been examined previously, only chloride has been taken into account so far. Thus, further research, involving lipophilic organic anions, is required (STUDZIŃSKA, SPRYNSKY et al. 2008).

1.4. COMPARISON AND EVALUATION OF LITERATURE RESULTS

To obtain a better overview of the sorption mechanism we prepared a comparison of the literature results that describe IL's sorption (Table 1).

Table 1

Summary of literature data concerning sorption of IIs. Cations investigated were EMIM (1-ethyl-3-methylimidazolium), PMIM (1-methyl-3-propylimidazolium), BMIM (1-butyl-3-methylimidazolium), AMIM (1-allyl-3-methylimidazolium), HMIM (1-hexyl-3-methylimidazolium), OMIM (1-methyl-3-octylimidazolium), BMMIM (1-butyl-2,3-dimethylimidazolium) and MBPy (methyl-butylpyridinium). The anion for each IL is chloride

Name of and type of sorbent	Clay content [%]	CEC [$\mu\text{eq/g}$]	OC content [%]	Type of IL	K_D [L/kg]
1	2	3	4	5	6
Clayley agricultural soil (Stępnowski, Mrozik et al. 2007)	4.4	3.67	3.67	HMIM Cl	11.9
				BMIM Cl	3.8
				BMPy Cl	4.4
Fluvial meadow soil (Stępnowski, Mrozik et al. 2007)	28.82	3.04	4.88	HMIM Cl	1.7
				BMIM Cl	1.7
				BMPy Cl	1.7
Forest soil (Stępnowski, Mrozik et al. 2007)	35.86	1.43	3.90	HMIM Cl	2.2
				BMIM Cl	1.3
				BMPy Cl	0.7
Fluvial agricultural soil (Stępnowski, Mrozik et al. 2007)	60.50	7.69	5.49	HMIM Cl	77.1
				BMIM Cl	14.5
				BMPy Cl	6.5
Quartz (Gorman-Lewis, Fein 2004)	0	0.93	0.00035	BMIM Cl	0



1	2	3	4	5	6
Gibbsite (Gorman-Lewis, Fein 2004)	0	7.14	0.002	BMIM Cl	0
Montmorillonite (Gorman-Lewis, Fein 2004)	100	2060	0	BMIM Cl	3.2
Bacillus subtilis (Gorman-Lewis, Fein 2004)	0	11.8	N/A	BMIM Cl	0
Pond sediment – (size fraction 8000–500 µm) (Beaulieu, Tank et al. 2008)	~0% (estimated)	14	72	BMIM Cl	95
				BMMIM Cl	110
				HMIM Cl	110
				OMIM Cl	30
Pond sediment – (size fraction 500–63 µm.) (Beaulieu, Tank et al. 2008)	~45% (estimated)	193	32	BMIM Cl	35
				BMMIM Cl	80
				HMIM Cl	70
				OMIM Cl	15
Lake sediment – profundal zone fraction (Beaulieu, Tank et al. 2008)		95	16	BMIM Cl	27
				BMMIM Cl	20
				HMIM Cl	30
				OMIM Cl	25
Sand (Beaulieu, Tank et al. 2008)		N/A	0.01	BMIM Cl	0
				BMMIM Cl	0
				HMIM Cl	0
				OMIM Cl	0
Agricultural soil (Stępnowski 2005)			7.7	PMIM Cl	20
				BMIM Cl	25
				AMIM Cl	60
				HMIM Cl	225
Clayey soil (Stępnowski 2005)			2.9	PMIM Cl	8
				BMIM Cl	20
				AMIM Cl	31
				HMIM Cl	81
Peaty soil (Stępnowski 2005)			38.9	PMIM Cl	3
				BMIM Cl	6
				AMIM Cl	21
				HMIM Cl	24
Marine sediments (Stępnowski 2005)			10.5	PMIM Cl	50
				BMIM Cl	400
				AMIM Cl	1650
				HMIM Cl	2450
Soil – SI (Studzińska, Sprynskyy et al. 2008)		61	<0.1	EMIM Cl	3
				BMIM Cl	2
				HMIM Cl	2
Soil – SII (Studzińska, Sprynskyy et al. 2008)		75	0.5	EMIM Cl	3
				BMIM Cl	3
				HMIM Cl	3

1	2	3	4	5	6
Soil – SIII (Studzińska, Sprynskyy et al. 2008)		107	4.1	EMIM Cl	4
				BMIM Cl	6
				HMIM Cl	7
Soil – SIV (Studzińska, Sprynskyy et al. 2008)		2286	9.9	EMIM Cl	35
				BMIM Cl	18
				HMIM Cl	30
Soil – SV (Studzińska, Sprynskyy et al. 2008)		6405	44.8	EMIM Cl	12
				BMIM Cl	92
				HMIM Cl	404
Kaolinite (Mrozik, Jungnickel et al. 2008)	100	32	0	EMIM Cl	4.4

It was already established that two main types of interactions play a role in ILs sorption: interactions with soil organic matter (hydrophobic or coulombic) and interactions with mineral surfaces. It is common in the literature to describe soil/sediments sorption potential on the basis of three parameters: clay content, CEC and OC content. Soil clay content can be used to estimate CEC; however, it was proven to be very inaccurate in some cases since cation exchange is possible with both minerals and organic matter. Thus, clay content is a fairly good means of estimation of CEC in soils low in organic matter but in soils rich in organic substance, it can lead to serious underestimation.

There is a substantial lack of consistent data considering ILs sorption. Only a small number of ILs have been taken into account as summarized in a table above. It should also be noted that the soil types and sources are variable, making a direct comparison complicated. Additionally, in some cases, measurements of basic soil properties (e.g. CEC or clay content) have been neglected; thus, creating difficulties in making a conclusion about sorption mechanisms. Therefore, the comparison of measured values is not straight forward since authors have been using different methods and different conditions, for example both CEC and OC content of the soils are paramount to determine and estimate interaction potentials.

The Walkley–Black method was considered a reference method for determination of OC content in soil. However this method involves the use of hot potassium dichromate and concentrated sulphuric acid; thus, is not recommended due to health and safety concerns, especially when other, accurate methods for OC measurements exist (ROSS 1995; SCHUMACHER 2002). The loss-on-ignition approach is a simplification of dry combustion in the oxygen atmosphere with the application of oxidizers (V_2O_5 , Co_3O_4 , MnO_2) often applied since it is significantly less expensive and was proven to show strong correlation with values obtained by a reference method. However, there are some drawbacks of loss-on-ignition method since it is possible that at temperatures above 420 °C, decomposition of inorganic forms of carbon may occur. Additionally, values obtained as a mass loss by thermal oxidation is considered as organic matter content. To obtain organic carbon content of the sample, the von Bemmelen conversion factor of 1.724 was

widely used assuming that organic carbon accounts for 58% of organic matter in soils. Although widely accepted, this conversion factor was proven to be too low in some cases (SUTHERLAND 1998; SANTISTEBAN, MEDIAVILLA et al. 2004). Most of OC content measurements displayed in Table 1 were conducted using a loss-on-ignition method; however, very often the temperatures of combustion varied or were not presented. Factors for conversion of organic matter content measured by loss-on-ignition method to organic carbon content were not mentioned at all making results ambiguous.

The CEC measurement method can also influence the results. There are two types of methods existing: using buffered solution (ammonium acetate, sodium acetate) or unbuffered solutions (barium chloride, ammonium chloride). As the iron and aluminium oxides, kaolinitic clays, and organic matter have variable, pH dependent charge, the result can be highly sensitive to method applied (HENDERSHOT, LALANDE et al. 1993, CIESIELSKI, STERCKEMAN 1997, ROBERTSON, SOLLINS et al. 1999). As identified for OC, not all of the researchers have stated a method for CEC measurements making a critical evaluation of their results impossible.

Apart from the different methods used in evaluation of basic properties of soils, one has to always bear in mind the enormous complexity and variability of the soil composition making this matrix extremely difficult to describe by simple factors. It is for this reason that all of the parameters mentioned above can only be treated as estimators of the soil sorption capacity.

The variety of experiments conducted by other researchers on various soils, has led this group to conduct their own experiments to further investigate the sorption mechanism.

2. METHODS

2.1. MATERIALS

The IL subjected to the test was methyl-octylimidazolium chloride [OMIM] [Cl] kindly supplied by UFT Bremen (Germany). For preparation of IL's solutions $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (POCh – Gliwice, Poland) was used. IL was prepared as 2 M stock solution in 0.01 M CaCl_2 . Extraction of exchangeable cations was performed with NH_4Cl (POCh – Gliwice, Poland). For preparation of HPLC mobile phase HPLC – grade acetonitrile from Lab – Scan (Dublin, Ireland) and spectrophotometric – grade trifluoroacetic acid (Sigma-Aldrich, Germany).

2.2. SOIL CHARACTERISATION

The soil used in a test was a forest soil with a pH of 3.5 measured in 0.01 M CaCl_2 . OC content was measured by loss-on-ignition method – thermal oxidation in

the muffle furnace at a temperature of 500 °C for 5 hours. For conversion of organic matter to organic carbon content the von Bemmelen factor of 1.724 was applied resulting in 1.23% of organic carbon. CEC was measured by extraction with 1 M NH_4Cl unbuffered solution and the concentration of exchangeable cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) was determined by AAS method using flame photometer (BWB-1 Technologies Ltd. UK) and AAS spectroscope (SenseAA, GBC Scientific Equipment). The sum of exchangeable cations was $1.92 \mu\text{eq}\cdot\text{g}^{-1}$.

2.3. SORPTION BATCH TEST

Sorption testing was performed according to OECD (*Organisation for Economic Co-operation and Development*) batch test method (OECD 2000). 1g of forest soil was equilibrated by shaking overnight with 7 mL of 0.01 M CaCl_2 solution. The IL was added yielding a concentration from 0.1 to 150 mM and a final solution volume of 8 mL. The mixture was shaken for another 24 hours at room temperature, then centrifuged at 17000 rpm for 4 minutes. The supernatant was recovered for HPLC/UV analysis. All experiments were performed in duplicate accompanied by blank and control samples to exclude sorption on the test vessel or degradation as potential factors influencing the final results.

2.4. HPLC ANALYSIS

Analysis of the IL concentrations in the supernatant was performed using HPLC. For the IL separation, a Gemini (Phenomenex) 150×4.6 mm column was used in conjunction with detection by UV adsorption at a wavelength of 218 nm. As a mobile phase acetonitrile/water + 0.01% (v/v) trifluoroacetic acid at the flow rate of 0.8 mLmin^{-1} was applied.

2.5. RESULTS AND DISCUSSION

We obtained sorption isotherm being a plot of amount of μmoles of IL sorbed onto 1 g of soil versus amount of μmoles of IL per 1 mL of solution (figure 1). From the sorption curve we estimated two K_d values. K_{d1} of the value of 3.05 Lkg^{-1} and K_{d2} of the value of 0.67 Lkg^{-1} . The first K_d corresponds to partitioning of [OMIM] [Cl] between soil and solution, whereas the second one describes the sorption of the second layer of [OMIM] [Cl] onto soil modified by the adsorption of the previous layer. The second K_d is noticeably smaller than the first. The justification for this is that the first K_d allowed for both coulombic and lipophilic interactions, and the second K_d only accounted for the lipophilic interaction potential between IL and soil. During the

sorption of the first layer, only the IL molecules which sorb by coulombic interaction, sorb headgroup first. The molecules which interact by lipophilic interaction – are attached by their alkyl chains. Thereby it might be concluded that in the second layer sorption, the ILs will interact with those molecules which sorbed headgroup first – that is by coulombic interaction.

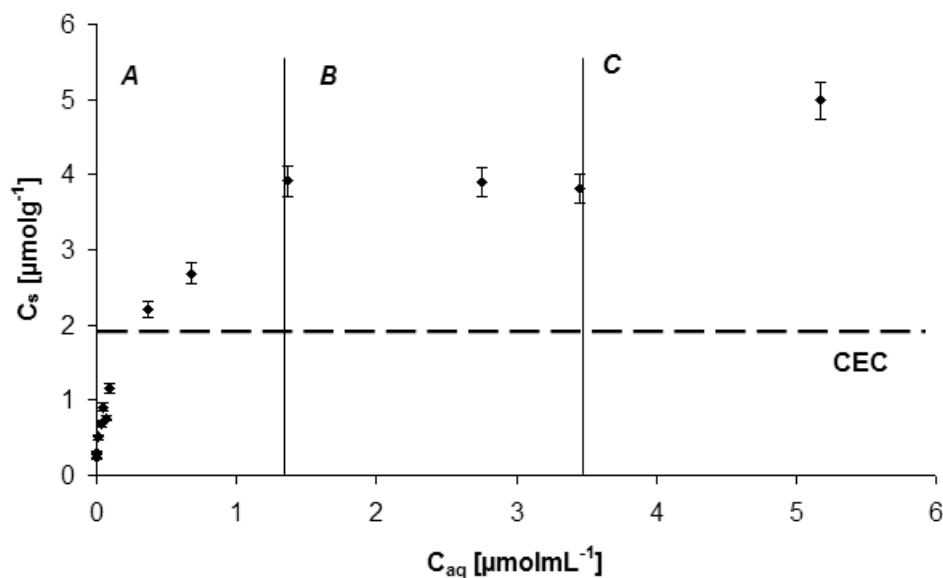


Fig. 1. [OMIM] [Cl] sorption isotherm with forest soil. The measured CEC is marked with the dotted line. The regions A, B and C indicate the proposed regions of sorption. Region A represents the sorption of the IL onto the soil by coulombic and lipophilic interaction. Region B is the plateau region in which the concentration on the soil surface is constant Region C shows the second sorption layer of the IL sorbed onto the previously sorbed IL.

3. CONCLUSIONS

Both partition coefficients measured were lower than those reported previously for [OMIM] [Cl] in the literature. One possibility for this result is due to the low organic matter content of the soil used in a test. Since hydrophobic interaction with organic matter would be expected to be a main sorption mechanism for non-polar OMIM cation, the soil simply did not possess the ability to interact in this way to a significant extent. Another phenomenon that could prevent partitioning of IL to the solid phase was its low pH. It is commonly known that sorption potential of soils can be highly affected by the change in the pH. In acidic forest soils, silica oxides (e.g., quartz) and aluminium hydroxides (e.g., gibbsite) in the mineral fraction are protonated and, thus

negatively charged adsorption sites are not available. Consequently, a sorption due to electrostatic interaction was not expected especially for large and non-polar cation.

From the comparison of literature, it is clearly identified that more experimental data is needed to understand the sorption phenomenon of ILs. The conclusions made by several other authors concerning sorption mechanism of ILs are not consistent. Therefore, more sorption tests on well defined sorbents should be conducted resulting in more reliable data. This data will allow for predicting sorption on the basis of IL's structure and soil characteristics.

ACKNOWLEDGEMENTS

The authors gratefully thank dr Piotr Stepnowski for performing the HPLC analysis and the UFT Bremen for supplying chemicals. Financial support of this work was provided by the Polish Ministry of Education and Research under grant No. 205 041 32/2340.

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