Pestycydy, 2007, (3-4), 61-46.
ISSN 0208-8703

Determination of ionic liquids by HPLC method. Involvement in biodegradation test

Sylwia GARBACZEWSKA and Jarosław HUPKO

Institute of Industrial Organic Chemistry,
6 Annopol St., 03-236 Warsaw, Poland
e-mail: sylwiagarbaczewska@wp.pl

Abstract: Some chromatographic methods (RP-HPLC) for analyses of different ionic liquids have been developed. The determination methods were suitable for the study of biodegradation of these substances.

Keywords: ionic liquid, HPLC, biodegradation test

INTRODUCTION

The room temperature ionic liquids are low melting salts, which represent a new class of non-molecular ionic solvents. Their most common representatives are typically composed of a small inorganic, weakly coordinating anion and an asymmetrically substituted bulky organic, nitrogen-containing heterocyclic cation, exhibiting no measurable vapor pressure [1]. Ionic liquid is also called a wide group of salts which contain ions, show ionic conductance and remain liquid below 100 °C (quaternary ammonium salts, imidazolium lactates).

The aim of this study was to develop methods for determination of ionic liquids and to present their involvement in biodegradation test for ionic liquids.

MATERIALS AND METHODS

Determination of ionic liquids

Ionic liquids used in these studies were as follows: 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-4-methylpyridine tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, from Fluka Chemica. (2-Hydroxyethyl)dimethyl-undecyloxymethylammonium trifluoroacetate, 1-methylimidazolium L-lactate, 1-butylimidazolium L-lactate, 1-decylimidazolium L-lactate, 1-butoxymethylimidazolium L-lactate were synthesized in the group of Prof. Pernak, from the Poznan Institute of Technology.

They were determined by HPLC method on a reverse phase column. The experiments were performed on a HPLC SpectraSeries P 200 equipped with: detector UV 100, autosampler A 100, pump P 200. The injection volume was 10 µl and the column temperature was ambient. Operating conditions, eluents and columns are listed in Table 1.

Table 1. Selected ionic liquids and chromatographic conditions of HPLC

Ionic liquid	Mobile phase	Column	Detection Wavelength (nm)	Flow rate (ml/min)
1-buthyl-3-methylimidazolium hexafluorophosphate , 1-buthyl-4-methylpirydine tetrafluoroborate, 1-buthyl-3-methylimidazolium tetrafluoroborate	acetonitrile/ water 1+4 (v/v), phosphate buffer pH 2.97	Nucleosil 5µ C_8 150 x4.6 mm Macherey-Nagel	210	0.8
quaternary ammonium salt: (2-hydroxyethyl)dimethyl-undecyloxymethylammonium trifluoroacetate	methanol/ water 1+1 (v/v), phosphoric acid, 4N sodium hydroxide, pH 3	OmniSpher $5C_{18}$ 150x4.6 mm Varian	200	0.4
lactates: 1-methylimidazolium L-lactate, 1-butylimidazolium L-lactate, 1-decylimidazolium L-lactate, 1-butoxymethylimidazolium L-lactate	acetonitrile/ water 7+3 (v/v), phosphoric acid 1ml / 1l phase	Spheri-S RP-18 100x4.6 mm 5µ Pierce	220	2.0

Biodegradation test of selected ionic liquids in surface water

Biodegradation test of ionic liquids in surface water was carried out according to the OECD 309 method [2].

Table 2. Relationship between time and content of selected ionic liquids in surface water obtained in biodegradation test

Name of ionic liquid	Time (day)	Concentration (%)
1-butyl-3-methylimidazolium hexafluorophosphate	1	0.00045
	14	0.00041
	33	0.00041
	48	0.00036
	62	0.00035
	98	0.00034
1-butyl-3-methylimidazolium tetrafluoroborate	1	0.00043
	14	0.00038
	33	0.00040
	48	0.00036
	62	0.00035
	98	0.00033
1-methylimidazolium L-lactate	1	0.00013
	13	0.00013
	32	0.00011
	43	0.00011
	55	0.00012
	77	0.00011
1-butylimidazolium L-lactate	1	0.00023
	13	0.00021
	32	0.00020
	43	0.00020
	55	0.00020
	77	0.00019
1-decylimidazolium L-lactate	1	0.00017
	13	0.00010
	32	0
	43	0
	55	0
	77	0
1-butoxymethylimidazolium L-lactate	1	0.00014
	13	0.00013
	32	0.00012
	43	0.00011
	55	0.00012
	77	0.00010

Ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-methylimidazolium

L-lactate, 1-butylimidazolium L-lactate, 1-decylimidazolium L-lactate and 1-butoxymethylimidazolium L-lactate were used for biodegradation test. The sample of the surface water was taken from a small river in the Warsaw – Białołęka quarter.

The test substance – selected ionic liquid with surface water (ca 1 mg/dm^3) – were placed in a flask and incubated in darkness at a constant temperature (20 °C) and agitated. Two samples of each test substance were tested in order to determine the degradation kinetics. Contents of ionic liquids were analyzed by HPLC at time intervals (see Table 2). The runs of the biodegradation were found to present the decreasing concentration of substances as time passed. The mean results of concentration of ionic liquids are listed in Table 2. Graphical forms of obtained results are presented in Figures 1-2.

RESULTS AND DISCUSSION

RP-HPLC methods were applied to assess biodegradability – the decreasing concentration (as a function of time) of: 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate and imidazolium lactates in surface water. The relationship between time and content of ionic liquids is presented in Figures 1-2. The shape of the curves of 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate (Figure 1) prove that the rate of degradation of investigated compounds does not depend on the anion ($[PF_6]^-$ and $[BF_4]^-$). The situation in Figure 2 show that the rate of biodegradability of tested alkyl – lactates increased with the alkyl chain length: for substance 1-methylimidazolium L-lactate (**1**)→ 1-butylimidazolium L-lactate (**2**) → 1-decylimidazolium L-lactate (**3**)**.** The 1-butoxymethylimidazolium L-lactate (**4**) proved to be of a better biodegradability than 1-butylimidazolium L-lactate (**2**)**.**

Generally it seems to be reasonable to state that the alkoxy lactates are expected to be of better biodegradability than the alkyl lactates of the same chain length. Research involved the use of the elaborated method in biodegradation test.

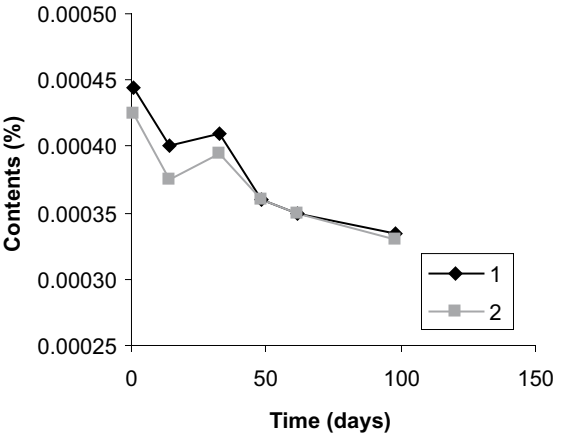

Figure 1. Biodegradation of 1-butyl-3-methylimidazolium hexafluorophosphate (**1**) and 1-butyl-3-methylimidazolium tetrafluoroborate (**2**) in surface water.

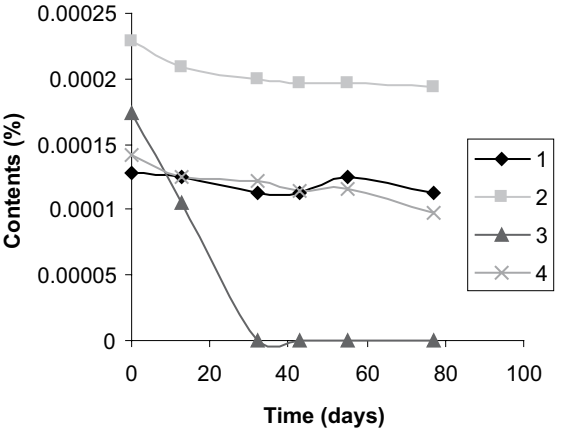

Figure 2. Biodegradation of lactates: 1-methylimidazolium L-lactate (**1**), 1-butylimidazolium L-lactate (**2**), 1-decylimidazolium L-lactate (**3**), 1-butoxymethylimidazolium L-lactate (**4**).

CONCLUSIONS

Using RP-HPLC with different columns, mobile phases, detection wavelengths and flow rates, chromatographic methods of determination of ionic liquids (imidazolium and pyridine rings, quaternary ammonium salts,

imidazolium lactates) were developed. The number of publications concerning the chromatographic methods determining room temperature of ionic liquids is limited, especially in environmental and biological studies. This paper is one of the few communications in this field. The reversed-phase high-performance liquid chromatography method developed permits to analyze different types of ionic liquids. This method was found to be useful for determination of investigated compounds in environmental samples.

REFERENCES

[1] Stepnowski P., Müller A., Behrendt P., Ranke J., Hoffmann J., Jastorff B., J. Chromatogr. A, 2003, 173, 993.
[2] OECD Guideline for the testing of chemicals. method 309: Aerobic mineralization in surface water – simulation biodegradation test, 2004.