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ECOTOXICITY OF IONIC LIQUIDS AS LUBRICANTS

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Abstract

In this article there is discussed the influence of ionic liquids on natural environment on the basis of detailed analysis of the literature information and the results of the Authors' researches carried out within the framework of the development and research project no. PBR/15-249/2007/WAT-OR00002904 financed by Ministry of Science and Higher Education during 2007-2011. The literature information about toxic features of ionic liquids is very skimpy, but the detailed analysis of it and the results of our own researches allow us to say that not all ionic liquids should be treated as fully environmentally friendly substances. Among these substances, there are non-toxic and moderately toxic but there are very toxic liquids, too. Therefore, uncritical rating all ionic liquids among Green Chemistry is inappropriate. The test results of ionic liquids ecotoxicity were compared with the results obtained for standard oils used at lubrication technologies, particularly at motorization. All reference oils, according to EU classification, were non-toxic. The tests were carried out in accordance with OECD 202 European normative document, which recommends carrying out the tests for Daphnia Magna crustaceans. There were carried out: acute immobilization tests to Daphnia Magna, calculation of the effective concentrations EC_{50-t} and evaluation of ionic and reference liquids toxicity with regard to used bioindicators.

Keywords: *ionic liquids, ecotoxicity tests, Daphnia Magna*

1. Introduction

Treating ionic liquids as representatives of so-called Green Chemistry is connected mostly with their extraordinary small (simply negligible) vapour pressure. Thanks to negligible volatility, one can say that they do not vaporize, and - in that sense and because of their incombustibility and inexplosivity – they are being treated as environmentally friendly substances. However, it does not mean that they are completely ecological. There is a very small data in the literature about toxic properties of ionic liquids. Advertising ionic liquids, by their manufacturers, as „Green Chemistry" is a kind of abuse. Although ILs do not evaporate, and thanks to this fact – they do not contaminate the air. This does not mean that they will not be harmful to natural environment, if they get into. Many ionic liquids, more or less, dissolve into water, and can get into the water environment or the soil through some accidental leakage or spilling. For example, the most common used ionic liquids $[BMIM]^-$ $[PF_6]^-$ and $[BMIM^+[BF_4]^-$ (i.e. 1-butyl-3-methylimidazole hexafluorophosphate and 1-butyl-3-methylimidazole tetrafluoroborate) can undergo partial degradation in the presence of water, what can result in formation of toxic and very corrosive acids: hydrofluoric and phosphoric [1, 2, 3, 4]. Therefore it is essential to form requirements in this respect, and demand information about ionic liquids toxicity and ecotoxicity providing them metabolism and susceptibility to degradation, in order to call them „green" solvents, or to investigate their negative influence on natural environment.

The ecotoxicity tests are being carried out in order to identify and determine the results of the influence of various liquids, including ionic liquids, on the enzymatic activity. Among other things, cells and microorganisms are being used in order to determine LC_{50} level (lethal concentration for 50% of population). Decreasing values of LC_{50} indicate higher toxicity of the liquid, according to Hodge and Sterner toxicity scale [4]. The scale shows that LC_{50} value (mg/l) equal to 10 or less defines extremely toxic substance, the value between 10 and 100 defines highly toxic substance, the value between 100 and 1000 states moderately toxic substance, and finally LC_{50} value between 1000 and 10 000 defines practically non-toxic substance.

Evaluation of the influence of ionic liquids on the water ecosystem is very important, because some ILs are water-soluble. Magin [5] determined LC_{50} levels for two ionic liquids with imidazole cation, i.e. $[BMIM]^+[PF_6]^-$ and $[BMIM]^+[BF]^-$, which are presented in table 1 beside other selected solvents.

Tab. 1. LC_{50} values for selected solvents [5]

Solvents	LC_{50} [mg/l]
$[BMIM]^+[PF_6]^-$	250-300
$[BMIM]^+[BF_4]^-$	225-275
Acetone	30642
Dichloromethane	310
Toluene	60-313
Benzene	203
Chlorobenzene	5-86
Phenol	5
Ammonia	0.53-4.94
Chlorine	0.028

Daphnia Magna - common freshwater crustaceans – were used for testing. In connection with a fact that Daphnia Magna are within the water trophic chain, so called "filter" eaters, knowledge of their reaction on ILs activity is important for understanding how ionic liquids can influence the ecosystem of natural environment. The influence of ionic liquids with 1-n-butyl-3-methylimidazole cation, with $[PF_6]^-$ and $[BF_4]^-$ anions was tested. The results of these tests are presented in table 1. These two ionic liquids are the same toxic for Daphnia Magna as benzene, dichloromethane or toluene, and even far more toxic than acetone, but much less toxic than chlorine, ammonia, phenol or chlorobenzene.

Wells and Combe [6] had also determined the ecotoxicity in fresh water of some known ionic liquids with cations: imidazole, ammonium, phosphate and pyridine. They had tested Daphnia Magna invertebrate and Pseudokirneriella Subcapitana green alga (also called Selenastrumcapricornutum). The test results were shown in the form of medium effective concentration of organisms' immobilisation (EC_{50}). EC_{50} value for the most toxic ionic liquid had been four orders of magnitude higher than the value for the least toxic ionic liquid. The connection between the toxicity degree and the length of the alkyl radical chain of cation had been found. Moderate toxicity the alkyl radical of C_4 type had been proved, while C_{12}, C_{16} and C_{18} types had been very toxic for both organisms used during the tests. The ionic liquids with pyridine, phosphate and ammonium with tested C_4 chain had been merely moderately toxic, while C_6 and longer side chains had demonstrated a high increase of toxicity. It had been proven that ecotoxicity of the least toxic ionic liquids had been comparable to hydrocarbons such as toluene and ethylene. It had also been proven that the most toxic ionic liquids had been many orders of magnitude more toxic than organic solvents such as methanol, tetra-butyl methyl ether, acetonitrile and dichloromethane. Furthermore, the authors [6] had emphasised that simply ecotocixity measurements had been insufficient for full characterization of solvent influence on natural environment, but they had been only a part of this evaluation.

The investigations on the ionic liquids toxicity were also being carried out with animal usage, such as nematode model of Caenorhabits Elegans organism [7], Physa Acuta freshwater pulmonary snails [8], Fischer 344 rats [9] and Danio Rerio zebra fish [10]. Recently even manufacturers of ionic liquids have begun to publish more information about the toxicity of their products. For example, in [2] BASF company information [11] about toxicity of some ionic liquids being manufactured by the company are given (Table 2).

Tab. 2. Toxic influence of selected ionic liquids on natural environment [2]

Influence Type	BMIMMCL a)	EMIMEtOSO$_3$ b)	MTEOAMeOSO$_3$ c)
Acute oral toxicity	Toxic	Harmless	Harmless
Skin irritation	Irritating	Non-irritating	Non-irritating
Eye irritation	Irritating	Non-irritating	Non-irritating
Allergy	Non-allergic	Non-allergic	Non-allergic
Mutagenicity	Non-mutagenic	Non-mutagenic	Non-mutagenic
Biodegradability	Not easily degraded	Not easily degraded	Not easily degraded
Toxicity for freshwater crustaceans	Acute toxic EC_{50} (48h) > 6.3 mg · l^{-1}	Not acute toxic EC_{50} (48h) > 100 mg · l^{-1}	Not acute toxic
Toxicity for fish	Not acute toxic LC_{50} (96h) > 100 mg · l^{-1}	-	Not acute toxic

a) BMIMCl = 1-butyl-3-methylimidazole chloride
b) EMIMEtOSO$_3$ = 1-ethyl-3- methylimidazole ethyl-sulphate
c) MTEOAMeOSO$_3$ = Tris-(2 hydroxyethyl)-methylammonium ethyl-sulphate.

2. Ecotoxicological Tests of Selected Ionic Liquids

2.1. Tested Ionic and Reference Liquids

As a part of the development project PBR/15-249/2007/WAT-OR00002904 founded by the Ministry of Science and Higher Education during 2007-2011, the were carried out the research works in order to, among other things, check the possibilities of using selected ionic liquids in the lubrication technologies. They were first of all, patented in 2009; new Polish ionic liquids [12] were based on 1-alkyl-3-alkoxymethylimidazole (CJ001 – CJ004). Such liquids have never been examined in detail, especially in terms of their using as lubricating substances for tribological nodes. One of the basic tests for such substance is evaluation of its influence on natural environment. Some other ionic liquids, with various cations or anions [12 – 14], perfluoropolyether oil [15] and some environmentally friendly hydrocarbon oils were selected for comparative tests:

- CJ001 – tetrafluoroborate 1-methyl-3-octyloxymethylimidazole ($C_{13}H_{25}BF_4N_2O$),
- CJ002 – bis-(trifluoromethylsulfonyl)-imide 1-methyl-3-octyloxymethylimidazole ($C_{15}H_{25}F_6N_3O_5S_2$),
- CJ003 – bis-(trifluoromethylsulfonyl)-imide 1-butylxymethyl-3-methylimidazole ($C_{11}H_{17}F_6N_3O_5S_2$),
- CJ004 – bis-(trifluoromethylsulfonyl)-imide 1-butylxymethyl-3-buthylimidazole ($C_{14}H_{23}F_6N_3O_5S_2$),

- CJ005 – tetrafluoroborate 1-benzyl-3-methylimidazole ($C_{11}H_{13}BF_4N_2$),
- CJ006 – bis-(trifluoromethylsulfonyl)-imide 3-methyl-1-propylpyridyne ($C_{11}H_{14}F_6N_2O_4S_2$),
- CJ007 – bis-(trifluoromethylsulfonyl)-imide 1.2-dimethyl-3-propylimidazole ($C_{10}H_{15}F_6N_3O_4S_2$),
- CJ008 – bis-(trifluoromethylsulfonyl)-amide trihexyltetradecylphosphonium ($C_{34}H_{68}F_6NO_4S_2P$),
- Fomblin Y04 – perfluoropolyether synthetic oil with branched molecular structure,
- PAO-6 – polyalphaolephine base oil, i.e. hydrogenated oligomers of olefins, achieved by catalytic polymerization of linear (aliphatic) alphaolefins,
- SN-650 – oil mineral base originated from the vacuum distillation of the residue of atmospheric distillation of petroleum, containing maximum 1.0% of secondary sulphur,
- Additin RC2515 – lubricity addition, composed of sulphur vegetable oils and olefins containing about 15% of sulphur,
- Platinum SL/CF 15W/40 – mineral engine oil, composed based on hydrotreated base oil with the addition of 0.8 – 1.6% of secondary zinc dithiophosphate,
- Mobilube 1SHC 75W/90 – synthetic gear oil, compound based on synthetic base oil, supplemented with improvers, among other things olefin sulphide (1 – 5% wt.), amine salts and phosphorous acid esters (< 2.5% wt).

Most essential physical-chemical parameters of tested ionic liquids and reference oils are presented in table 3.

Tab. 3. Physical-chemical parameters of tested ionic liquids and reference oils

Ionic liquids and reference oils	Melting point / Pour point T_m/T_p [°C]	Density at 25°C ρ_{25} [g/cm^3]	Absolute viscosity at 25°C η_{25} [mPa · s]	Viscosity index VI [-]
Ionic liquid CJ001	+10.80	1.116	552.42	110
Ionic liquid CJ002	-34.00	1.308	102.02	104
Ionic liquid CJ003	-40.70	1.354	76.01	156
Ionic liquid CJ004	-45.90	1.334	72.53	170
Ionic liquid CJ005	+77.00	at 100°C 1.242	at 100°C 18.37	-
Ionic liquid CJ006	0	1.447	51.53	138
Ionic liquid CJ007	+15.00	1.449	86.61	134
Ionic liquid CJ008	-50.00	1.061	327.24	128
Fomblin PEPE Y 04	-54.00	1.868	60.04	56
PAO-6	-39.00	0.816	47.36	144
SN-650	-9.00	0.881	345.47	86
Additin RC2515 EP	-12.00	0.881	1407.76	220
Platinum SL/CF 15W/40	-30.00	0.872	199.56	146
Mobilube 1SHC 75W/90	-48.00	0.856	188.83	160

2.2. Methodology of the Ecotoxicological Tests

The tests were carried out in accordance with OECD 202 [16] European normative document, which recommends carrying out the tests for Daphnia Magna crustaceans. Both ISO at this standard recommend to carry out 48-hour acute tests for Daphnia Magna in order to determine EC_{50} (Effective Concentration), not LC_{50} (Lethal Concentration). EC_{50}-t is a concentration causing some effect after a given period of contact with toxic substance. LC_{50}-t is a concentration causing death of

50% of specimen after a given period of contact with toxic substance. In accordance with applicable EC_{50} standards, the effect is immobilization of the organisms (which is, in essence, their permanent damage and, consequently, death). That is why (because of aesthetic reasons) EC_{50} index is being nowadays used more often than LC_{50}. The second one is being still used with respect to fish.

So, during the tests, there were carried out:

- acute immobilization tests to Daphnia Magna,
- calculation of the effective concentrations EC_{50}-t,
- evaluation of ionic and reference liquids toxicity with regard to used bioindicators.

The tested organism was Daphnia Magna Straus that is freshwater cladoceran, occurring in slightly polluted water. It feeds on suspension filtered from water, and is valuable food for fish. It reproduces via parthenogenesis during spring and summer seasons. In autumn, after fertilization, females lay winter eggs within a chitin ephippium (type of spore), from which, in spring, the young hatch out. These crustaceans are commonly used for ecotoxicological tests because of short life cycle, easy culture, small size and sensibility to a wide spectrum of poisons [17]. The obtained results allow us to make the comparative analysis with results occasionally mentioned in the literature with regard to some ionic liquids other than the ones tested [2, 4, 8, 9, 10].

Daphnia Magna organisms not older than 24 hours, or so-called neonats, were used during the tests. Basic solutions of ionic and reference liquids, of 1000 mg/dm^3 concentration, had been prepared in the conditioned water after biofiltering. In order to receive homogeneous samples, they were subjected to the sonication process. A series of dilutions was made of such prepared stock solutions for the preliminary and right tests. The preliminary test was carried out in order to determine the concentration range for the right test, with common ratio for dilutions q = 1.3. 10 test organisms were entered to each solution with the given concentration. The tests were being carried out at the temperature of 20°C, for 48 hours. For each concentration, the percentage of immobilized animals after 24 and 48 hours was determined. During the test, the animals were not fed. The right test was carried in three iterations, and the average value was calculated from the obtained results.

EC_{50}-t effective concentration, i.e. concentration causing immobilization of 50% of organisms after 24 and 48 hours of contact with the tested substances, was calculated with the use of the probit method [18, 19], in accordance with the following formula:

$$EC(LC)_{50} - t = 10^{\frac{5-\bar{y}+a\cdot\bar{x}}{a}}, \tag{1}$$

where: $\bar{x}$ – average value of logarithms of individual concentrations,

a – regression coefficient,

5 – probit constant value equal to 50% of immobilization,

$\bar{y}$ – average value of probits equal to the percentage of immobilization for individual concentrations.

Toxicity evaluation was carried out because of criteria concerning acute toxicity [16], proposed by United States Environmental Protection Agency (USEPA) [20]. These criteria coincide with classification [21] commonly used in the European Union – Table 4.

Tab. 4. The criteria used for rating acute toxicity of the tested ionic liquids and reference oils

EC_{50}-t [mg/dm^3]	Evaluation of toxicity
≤ 0.1	Very highly toxic
> 0.1 - ≤ 1	Highly toxic
> 1 - ≤ 10	Moderately toxic
> 10 - ≤ 100	Slightly toxic
> 100	Non-toxic

2.3. The Tests Results and Analysis

The results of the tests of ionic liquids and reference oils ecotoxicity relative to Daphnia Magna freshwater crustaceans are presented in table 5.

Tab. 5. The results of the ecotoxicity tests of ionic liquids and reference oils

Tested liquid	EC_{50} – 24h [mg/dm^3]	EC_{50} – 48h [mg/dm^3]	Evaluation of toxicity
CJ001 ionic liquid	0.25	0.11	Highly toxic
CJ002 ionic liquid	4.86	2.81	Moderately toxic
CJ003 ionic liquid	12.54	9.11	Moderately toxic
CJ004 ionic liquid	4.80	1.97	Moderately toxic
CJ005 ionic liquid	23.93	11.40	Slightly toxic
CJ006 ionic liquid	76.71	70.54	Slightly toxic
CJ007 ionic liquid	114.12	96.51	Slightly toxic
CJ008 ionic liquid	77.15	3.89	Moderately toxic
PFPE Fomblin Y04	401.32	247.09	Non-toxic
PAO-6	> 1000	805.27	Non-toxic
SN-650	> 1000	821.31	Non-toxic
Additin RC2515	> 1000	718.04	Non-toxic
Platinum 14W/40	> 1000	> 1000	Non-toxic
Mobilube 75W/90	485.63	375.68	Non-toxic

On the basis of the results presented in table 5 it can be found that only CJ001 ionic liquid showed acute toxicity in EC_{50} – 48h acute test. As a matter of fact, it could be determined as highly toxic after 24 hours yet. CJ002 and CJ004 ionic liquids were ranked within the range of the moderate toxicity, but they were close to the limit of 1 mg/dm^3, under which they would be placed among highly toxic substances. Whereas CJ003 ionic liquid, moderately toxic, was close to the limit of 10 mg/dm^3, above which it could be determined as slightly toxic substance. CJ008 was also moderately toxic (after 24 hours it was better than all other ionic liquids, except CJ007, but after 48 hours, it was slightly worse than CJ003). CJ007 liquid turned out to be the most environmentally friendly from among the tested liquids. CJ005 and CJ006 could be also classified, aside from CJ007 liquid, as slightly toxic (CJ005 can be less "effective" because it is solid body under test conditions – insoluble powder). The evaluation results presented in table 5 EC_{50} confirmed earlier literature reports [2, 4, 8, 9, 10] showing that ionic liquids can be very highly toxic, slightly toxic, and even non-toxic. CJ007 ionic liquid was very close to the limit determining non-toxic substances, i.e. 100 mg/dm^3 in the 48-hour test, and if it passed that border, it would be worthy of this title. This liquid, in the 24-hour test, achieved the value higher than 100 mg/dm^3 and not much lower in the 48-hour test. So called test response rate increment over time was small (114.12 mg/dm^3 → 96.51 mg/dm^3). CJ006 liquid was slightly worse.

The length of ionic liquids alkyl chains, first of all, significantly influences their ecotoxicity, in accordance with the results from the literature reports mentioned above. The most toxic were CJ001 and CJ002 ionic liquids with the same cations and the longest R_3 alkoxymethylimidazole chain. CJ002 ionic liquid has more hydrophobic anion ($[N(CF_3SO_2)_2]^-$, than CJ001 ionic liquid ($[BF_4]^-$. Reduction of R_3 cation substituent of CJ002 ionic liquid by C_3H_6 component, with the same anion $[(CF_3SO_2)_2N)]^-$, caused considerable decrease of CJ003 ionic liquid ecotoxicity, while concurrent addition of this element (C_3H_6) to R_1 substituent caused worsening of CJ004 liquid toxicity again. Repeated reduction of R_1 substituent to the initial state (CH_3) and – most of all – as it is supposed, displacement of the part of R_3 substituent containing oxygen (CH_2-O-CH_2), influenced distinct improvement of ecotoxic properties of CJ007 ionic liquid. The presence of another R_2 short substituent in this liquid (CH_3) was probably of minor significance in this process. Other ionic liquids not containing alkoxymethylimidazole chain, especially with ($[N(CF_3SO_2)_2]^-$ anion, turned out to be slightly toxic.

All reference oils, including PFPE oils, deserved being called non-toxic. EC_{50} values, after both 24 and 48 hours, exceeded several times the limit value 100 mg/dm^3. Being guided by the literature reports [15] and knowledge of PFPE oils structure, the Authors decided to carry out the check tests only for PFPE Y04, assuming that other PFPE oils would be non-toxic too, and obtained results would be similar to the ones for Y04.

However, hydrocarbon oils turned out to be the most environmentally friendly during Daphnia Magna tests (Table 5). Their EC_{50} values after 24 and 48 hours exceeded several times the value of 100 mg/dm^3. Only Mobilube oil got relatively lower EC_{50} values (485.63 mg/dm^3 after 24 hours and 375.68 mg/dm^3 after 48 hours), closer to the ones reached by perfluoropolyether oils. The reason was probably the presence of the specific set of improvers in Mobilube oil, including some quantity of olefin sulphide and phosphorous acid esters.

3. Summary

Interest with ionic liquids is more and more for their unique properties, which are usually expected for high quality oils, particularly at motorization. These oils contain many various improver additives, even 30% vol. (anti-foaming agent, pour – point depressant, lubricity additive and others). Many ionic liquids have the necessary properties without any additives, so they will can probably replace the oils used up to now. However, must be obtained a minor harmfulness of ionic liquids influence on natural environment.

Of course, the results of the ecotoxicity tests, presented in table 5, are not enough for complete characterization of the influence of the tested substances on natural environment. Such results are only an introduction to some extensive researches, necessary to carrying out; in case of planned launching a new lubricate substance in order to make it commonly available. Considerably wider range of toxicity tests is presented in table 2, which contains information about ionic liquids manufactured by BASF.

This information, confirmed by the results of the Authors' research works, prove that ionic liquids can be even very highly toxic, but also could be harmless and biodegradable. However, ionic liquids harmlessness does not mean that they have the best functional properties for the given applications, e.g. as lubricating substances for various tribological nodes [22, 23]. In every case, it is necessary to make the balanced decision and selection of the most advantageous variant in order to achieve the intended goal.

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