Herbicidal ionic liquids with bisammonium cations

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Introduction

Compound structure is one of the main properties used for classification of ionic liquids (ILs). There are liquids where a cation has a charge on nitrogen, phosphorus, oxygen or sulfur atoms. This group includes among others ammonium and phosphonium ionic liquids. The cation may have one or more quaternary atoms in its structure [1]. When there are two charges on nitrogen atoms, we have bisammonium liquids, whereas liquids with three charged atoms are known as trigeminal [2].

Bisammonium ionic liquids showing surface activity with a long alkyl chain form a new class of compounds, so-called *gemini* [3, 4]. Their characteristic property is the presence of two interconnected nitrogen atoms with positive charges and a symmetry axis in the molecule structure [5÷7]. The gemini structure causes the liquids to have low critical micelle concentration [3, 4]. They are also classified as amphiphilic ionic liquids due to their properties, with high surface activity and high thermal stability [7].

In 2007, W. L. Hough *et al.* proposed a classification of ILs into three generations [8]. The 3rd generation ILs have many applications, including pharmaceutical ones (analgesic, anti-inflammatory) thanks to the application of cations or anions from known pharmaceuticals [8, 9]. This group of ionic liquids also includes ILs with fungicidal or herbicidal activity [10, 11]. To obtain fungicidal activity, triazoles are used as a cation source, whereas herbicidal ionic liquids are obtained using anions: 2,4-dichlorophenoxsyacetate, 4-chloro-2-methylphenoxyacetate, 1-(3-chlorophenyl)-piperazine, 2-(phosphonomethyl-amine)acetate, or sulfonylurea (MS-M) [11÷18].

New ionic liquids were synthesized containing the bisammonium cation and herbicide anions, thus increasing their herbicidal activity. The new synthesis method of bisammonium dihalides and two methods of substitution of halides with herbicidal anions were developed. Moreover, the effect of a linker and anion on physicochemical properties and herbicidal activity was determined.

Experimental part

1,12–dibromododecane (**I**) or 1,4–dibromobutene (**II**) or bis(2-chloroethyl)amine (**III**) and 2,2'-[(9Z)-9-Octadecen-1-ylimino] diethanol were added in mole ratio 1:2. The whole mixture was stirred for 72 hours. Then the product was purified and dried.

Synthesised bisammonium dibromides and dichlorides were then subjected to a one-step substitution reaction. The reaction of dihalide with MCPA potassium salt (1:2) was conducted in methanol for 30 minutes at ambient temperature, after which the solvent was evaporated. The product obtained was dissolved in acetone and cooled in order to precipitate inorganic salt. The precipitate was then filtered off and then the filtrate evaporated. The products obtained (**Ia**), (**IIa**), (**IIIa**) were dried in a vacuum dryer at 70°C for 24 hours.

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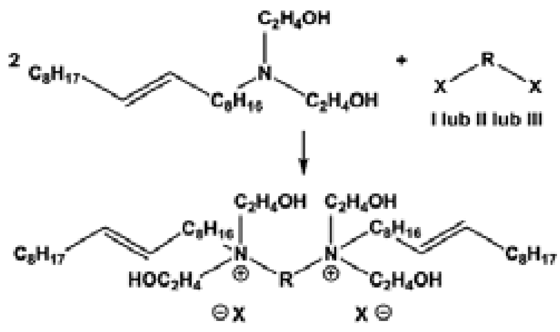
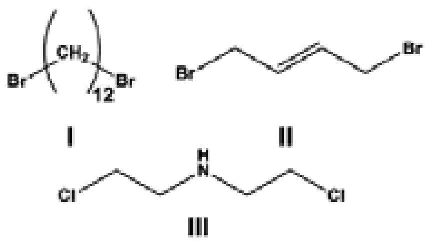
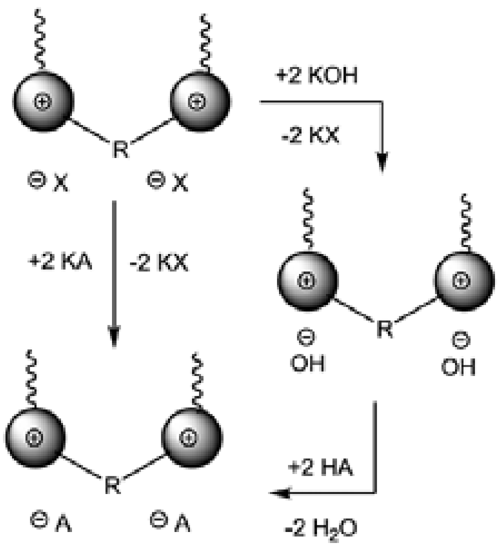




Bisammonium dihalide was subjected to a substitution reaction with potassium hydroxide in a mole ratio of 1:2. The reaction was conducted in methanol at ambient temperature for 30 minutes. The precipitated potassium bromide was filtered off and the filtrate was neutralised with an alcoholic solution of 2,4-D acid. After reaching neutral pH, the solvent was evaporated from the mixture. The residue was dissolved in acetone and then cooled. The precipitate was then filtered off and the solvent evaporated from the filtrate. The products obtained (**Ib**), (**IIb**), (**IIIb**) were dried in a vacuum drier at 50°C for 48 hours.



Ia-IIIb

The diagram of obtaining bisammonium ionic liquids, where X is a bromide or chloride anion, A – MCPA anion (Ia-IIIa) or 2,4-D(Ib-IIIb) anion.

Table 1

Bisammonium herbicidal ionic liquids

ILs	Symbol	R	Yield %	Surf. %
Ia	$[C_{12}C_{18}][MCPA]_2$	$–(CH_2)_{12}–$	92	99
IIa	$[CNC_{18}][MCPA]_2$	$–CH_2–CH_2–NH–CH_2–CH_2–$	89	97
IIIa	$[C_2C_2C_{18}][MCPA]_2$	$–CH_2–CH=CH–CH_2–$	90	95
Ib	$[C_{12}C_{18}][2,4\text{-}D]_2$	$–(CH_2)_{12}–$	93	90
IIb	$[CNC_{18}][2,4\text{-}D]_2$	$–CH_2–CH_2–NH–CH_2–CH_2–$	88	94
IIIb	$[C_2C_2C_{18}][2,4\text{-}D]_2$	$–CH_2–CH=CH–CH_2–$	91	91

The ion exchange reaction with MCPA potassium salt had greater yield than a two-stage reaction using ammonium hydroxide, whereas the synthesis of the liquid containing the 2,4-D anion using the two-stage method had approximately 10% higher yield than the one-stage method. All the liquids obtained at 25°C had high density and viscosity.

The compound structure was confirmed by means of a proton nuclear magnetic resonance analysis. The spectrum shows that the MCPA anion caused shift in the cation towards lower values than liquids with the 2,4-D anion. Shifts in CH_2 groups from carbons derived from the linker in bisammonium cation were also observed. The shift increases in the series **Ia>IIa>IIIa** for the liquids with the MCPA anion and **Ib>IIb>IIIb** for the liquids with the 2,4-D anion. ^{1}H NMR also showed peak at 5.34 ppm from a double bond in an oleic chain.

Table 3 presents the results of solubility tests for popular organic solvents and water. The test was performed following the A. Vogel's method and involved weighing out 0.1 g of substance and then the addition of 1 ml and 2 ml of the solvent. In the solubility test, "+" means a soluble compound (0.1g/1ml), "±" means poorly soluble (0.1g/3ml), whereas "–" means that 0.1 g does not dissolve in 3 ml of the solvent.

Table 2

Solubilities of the Bisammonium ionic liquids

Solvent \ ILs	Ia	IIa	IIIa	Ib	IIb	IIIb
Water	–	–	–	–	–	–
DMSO	+	–	–	–	–	±
Acetonitrile	–	–	±	–	–	±
Methanol	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
Isopropanol	+	+	±	–	–	+
Ethyl acetate	±	±	±	±	±	±
Chloroform	+	+	+	+	+	+
Toluene	+	±	+	±	±	+
Hexane	+	–	+	+	–	+

All the liquids obtained were soluble in methanol, acetone, ethyl acetate, chloroform and toluene. The synthesised ionic liquids were soluble in all the non-polar solvents, except **IIa** and **IIb**, which were not soluble in hexane. The liquid **IIIb** was soluble in all the polar solvents, except for water. **Ib** and **IIb** were not soluble in polar solvents such as DMSO, acetonitrile and isopropanol. The liquids **Ia–IIIa** were soluble in protic polar solvents, except for water.

The refractive index was measured using *ABBE Rudolph Research Analytical J357 Automatic Refractometer*.

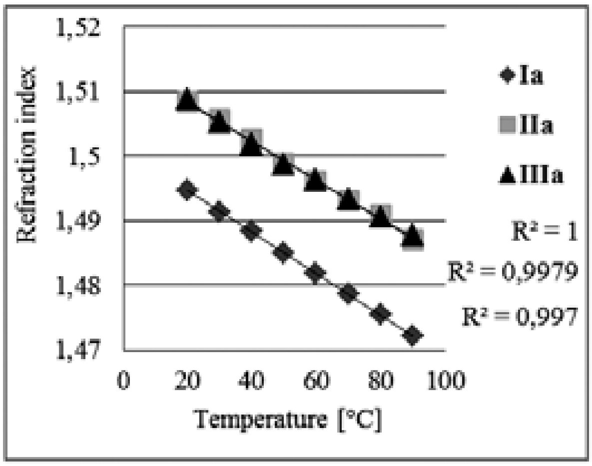


Fig. 1. Effect of temperature on the refractive index for ionic liquids Ia–IIIa with anion MCPA

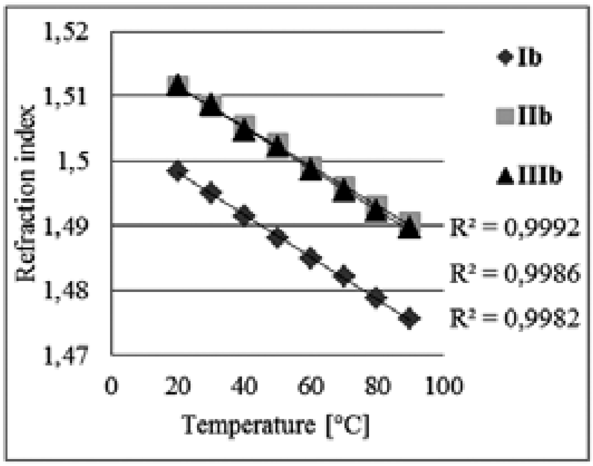


Fig. 2. Effect of temperature on the refractive index for ionic liquids Ib–IIIb with anion 2,4-D

The values of the refractive index for the liquid with the MCPA anion (Fig. 1) were in the range 1.472 to 1.509. It shall be noted that the ionic liquids with the bis(ethane)amine (**IIa)** and butene (**IIIa)** linker have similar values of the refractive index, whereas the liquid **Ia** with the dodecane linker has asignificantly lower refractive index. A Similar relation can be observed for the liquids **Ib–IIIb** (Fig. 2). The lowest value was observed for the liquid **Ib**– 1.476. The other liquids with the 2,4-D anion had a much higher refractive index; the highest value was reported for **IIIb**, equal to 1.512. Analysing the effect of the temperature, the linker and the MCPA (**Ia–IIIa**) and 2,4-D (**Ib–IIIb**) anions on the refractive index, it may be observed that the change in the refractive index in the temperature range of 20-90°C is linear. Correlation coefficients (R) were determined in order to confirm that. Their values close to unity, which prove the linear dependence.

The lowest value of the refractive index was found for the liquid **Ia.**

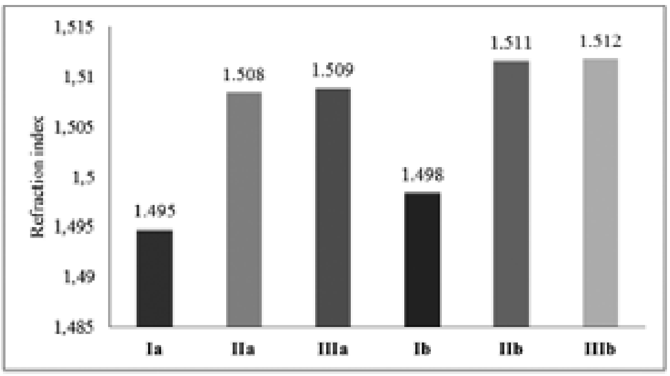


Fig. 3 Refractive index depend on cation and anion at 20°C

While comparing values of the refractive index (Fig. 3) for constant temperature of 20°C for synthesised new herbicidal ionic liquids containing various linkers and anions, one may observe a significant effect of introducing a double bond (**IIa, IIb**) or a nitrogen atom (**IIIa, IIIb**) to the linker on the change in the refractive index. The lowest value of the refractive index was reported for the ionic liquid **Ia**, while the highest – for **IIIb.**

Density and viscosity could not be measured due to high liquid viscosity preventing the tests.

Herbicidal activity of the ionic liquids obtained was conducted in a greenhouse experiment for three test plants: the winter oilseed rape (*Brassica napus* L.), lamb's quarter (*Chenopodium album* L.) and cornflower (*Centaurea cyanus* L.). The activity was tested according to the methodology described in the paper [11]. Agents commercial herbicides were used as a reference: Chwastox Extra 300 SL (300 g of a.i. in 1 l of the product) containing 2,4-D and Aminopielik Standard 600 SL (300 g of a.i. in 1 l of the product) containing MCPA.

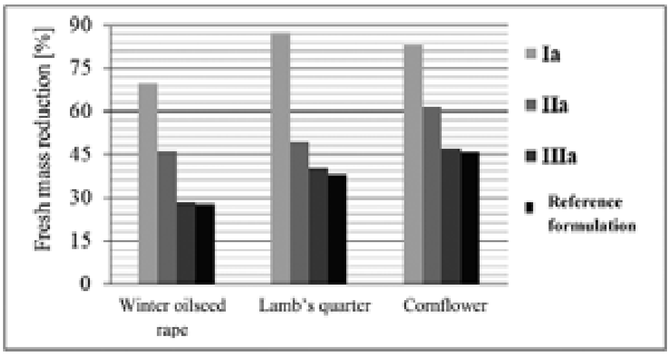


Fig. 4. The herbicidal activity of ionic liquids with anion MCPA

Biological activity of the ionic liquids obtained containing the MCPA anion and the commercial herbicide containing the MCPA anion in the form of dimethylammonium salt is presented in Figure 4. All the synthesised liquids (**Ia**–**IIIa**) showed higher herbicidal activity against the winter oilseed rape, lamb's quarter and cornflower. The best herbicidal properties in all the tests were shown by the liquid $[C_{12}C_{18}][MCPA]_2$ **Ia** with a dodecane linker. The bisammonium ionic liquids **IIa** and **IIIa** showed similar herbicidal activity.

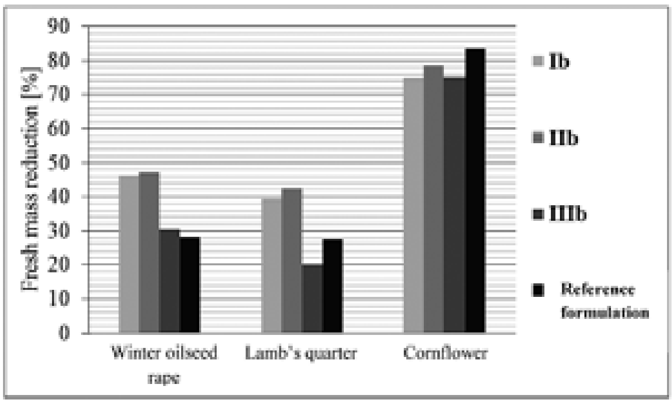


Fig. 5. The herbicidal activity of ionic liquids with anion 2,4-D

The ionic liquids with the 2,4–D anion (**Ib**–**IIIb**) (Fig. 5) also show higher herbicidal activity than their reference formulation against the winter oilseed rape and lamb's quarter, however, for the cornflower, the synthesised liquids showed slightly lower efficacy than the commercial herbicide. The liquid IIIb was the only one that showed lower herbicidal activity against the lamb's quarter.

Summary

The paper presents two methods for the synthesis of bisammonium ionic liquids with herbicidal ions. The used precursors were: dodecane-1,12-bis(bis(2-hydroxyethyl)octadecane-9-eneammonium), butene-1,4-bis(bis(2-hydroxyethyl)octadec-9-eneammonium) dibromides and bis(ethane)amine-2,2'-bis(bis(2-hydroxyethyl)octadec-9-eneammonium) dichlorides. All the ionic liquids obtained were soluble in polar solvents such as acetone and methanol and in non-polar solvents: ethyl acetate, toluene and chloroform, while none of them was soluble in water. The value of the refractive index depended strongly on the structure of the linker in a bisammonium cation, while the anion structure had a much less effect. The synthesised ionic liquids usually showed higher biological activity than the commercial herbicides. The highest efficacy against weeds was observed for dodecane-1, 12-bis(bis(2-hydroxyethyl)octadec-9-eneammonium) di(4-chloro-2-methylphenoxy)acetate.

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Weekend Rozwoju Regionu Dolnośląskiego z BASF Polska

Od 9 do 11 września br. BASF Polska, jako partner regionalnych i lokalnych działań realizowanych m.in. przez AHK Polska czy lokalne instytucje edukacyjno-kulturalne, zrealizowała cykl wydarzeń stanowiący strategiczny element działań BASF, w ramach których firma jako globalny partner wnosi wkład w społeczno – gospodarczy rozwój każdego z regionów, w których działa.

BASF w Polsce jest mocno związany z Regionem Dolnego Śląska od momentu otwarcia w 2014 r. na terenie Środy Śląskiej największego zakładu produkcji katalizatorów firmy w Europie, którego produkty zmniejszają emisję szkodliwych gazów o ok. 90%, dzięki czemu pojazdy wywierają mniejszy wpływ na środowisko.

BASF popularyzuje wśród Partnerów i społeczności lokalnej we wszystkich regionach, w których działa, innowacyjne rozwiązania wychodzące naprzeciw przyszłym wyzwaniom społeczeństwa. Za jedno z nich uznawany jest dynamicznie wzrastający poziom urbanizacji, który niesie za sobą jednoczesny rozwój zapotrzebowania na efektywne technologie dla budownictwa, gospodarowania ściekami komunalnymi czy wsparcia kształtowania zamkniętego systemu odpadów. Firma stara się upowszechniać wiedzę na temat konieczności poszukiwania odpowiedzi na przyszłe wyzwania globalne już w wymiarze regionalnym i lokalnym.

Okazją do przedstawienia najnowszych rozwiązań w tym zakresie wśród mieszkańców prężnie rozwijającego się Wrocławia był tradycyjny Oktoberfest, zorganizowany przez Polsko-Niemiecką Izbę Przemysłowo-Handlową, w ramach którego BASF zaprezentował jedną z najnowocześniejszych technologii pozwalających na znaczne usprawnienia w obszarze gospodarowania odpadami z gospodarstw domowych. Przedstawiono nowoczesne tworzywo sztuczne ecovio®, które spełnia międzynarodowe kryteria kompostowania. Proces produkcji oparty jest na innowacyjnej technologii, wykorzystującej właściwości kompostowalnego polimeru (Ecoflex®) i kwasu mlekowego (PLA) uzyskiwanego z kukurydzy. Dzięki temu ecovio® może ulec biologicznemu rozkładowi przez mikroorganizmy i ich enzymy. Ta technologia oferuje różne gatunki produktów spełniających międzynarodowe i krajowe wymogi dotyczące kompostowania przemysłowego. Dzięki innowacyjnym foliom, z których tworzone są torby na zakupy i worki, kompostowalnym naczyniom, a nawet kapsułkom kawy, które w pełni ulegają rozkładowi – BASF zaprezentował w jaki sposób współcześnie przemysł chemiczny może przyczynić się do zmniejszenia ilości odpadów komunalnych, a w efekcie także do ochrony środowiska naturalnego.

Chemia inspiruje do odkryć – nowa pracownia chemiczna w Środzie Śląskiej

BASF od lat stara się wspierać młodzież w odkrywaniu potencjału, jaki drzemie w nauce. 10 września br., w ramach Weekendu Rozwoju Regionu Dolnośląskiego, firma otworzyła pracownię chemiczną dla uczniów Liceum w Powiatowym Zespole Szkół Ponadgimnazjalnych nr 1 w Środzie Śląskiej. Partnerska współpraca z Liceum to owoc projektu zainicjowanego przez firmę w ramach obchodów 150-lecia BASF w 2015 roku.

Nowa pracownia to kolejne miejsce (po otwartym w maju laboratorium chemicznym w Humanitarium Wrocławskiego Centrum Badań EIT+), w którym młodzi ludzie będą mogli poznawać chemię od praktycznej strony. Z użyciem m.in. profesjonalnego stołu laboratoryjnego czy chemicznego dygestorium uczniowie będą mieli szansę przeprowadzać samodzielne eksperymenty. Już podczas otwarcia pracowni chemicznej pierwszą próbę swoich zaprezentowali licealiści z klasy o profilu biologiczno-chemicznym.

BASF wspiera także wymianę dobrych praktyk w ramach współpracy z Partnerami edukacyjnymi. Podczas otwarcia pracowni, wspólnie z licealistami wystąpili animatorzy z laboratorium chemicznego BASF w Humanitarium Wrocławskiego Centrum Badań EIT+. W wydarzeniu wzięli udział także studenci reprezentujący chemiczne koła naukowe, współpracujące z firmą BASF wraz z ambasadorkami profilu edukacyjnego chemiatomy na Facebooku – Adą Cytryniak (Uniwersytet Wrocławski) i Justyną Mielnik (Politechnika Wrocławska). Współpraca edukacyjna z uczelniami oraz prowadzenie laboratoriów i pracowni chemicznych dla dzieci i młodzieży to istotny element długofalowego zaangażowania społecznego firmy. Od 2010 r. BASF Polska współpracuje w Warszawie z Centrum Nauki Kopernik. Obecnie we wszystkich laboratoriach chemicznych BASF w Polsce tajniki chemii odkrywa rocznie blisko 40 tysięcy uczniów z całego Regionu. *(abc)*

(inf. BASF, 13 wrzesnia 2016 r.)

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