Application potential of herbicidal ionic liquids

Tadeusz PRACZYK* – Institute of Plant Protection – National Research Institute, Poznań, Poland

Please cite as: CHEMIK 2016, **70**, 9, 485–490

Introduction

In the modern farming, the main method of crop protection against weed infestation is the use of chemical products. The 1940s discovery of the herbicidal action of (4-chloro-2-methylphenoxy) acetic acid (MCPA) and (2,4-dichlorophenoxy)acetic acid (2,4-D) was the beginning of a selective weed control. These products are very effective against many species of dicityledonous weeds without a negative impact on cereal plants. The achievements of the phytopharmaceutical industry in the field of new compound synthesis in the following years resulted in the introduction of many new herbicides into the market. Many new products, including glyphosate, pendimethalin, isoproturon, metamitron, clopyralid, metazachlor, as well as the first herbicide of the sulfonylurea family – chlorosulfuron, were introduced into the market in the 1970s. Currently, approx. 140 chemical compounds are used as the active ingredients in herbicides. Apart from theobvious advantages, such as: high effectiveness, low application costs, possibility of application on large areas in a short time, the wide-spread use of herbicides may cause the degradation of the natural environment, particularly the contamination of groundwater, as well as poses a risk of contaminating agricultural products with the residues of active ingredients and their metabolites.

Therefore, it is an urgent matter to undertake measures mitigating the negative effects of chemical plant protection. This matter is particularly stressed in the EU Member States. This is evidenced by legal regulations in force, especially by Council Directive 92/43/EEC of 21st May 1992 on the conservation of natural habitats and of wild fauna and flora, Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23rd February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin, Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21st October 2009 concerning the placing of plant protection products on the market and Directive 2009/128/EC of the European Parliament and of the Council of 21st October 2009 establishing a framework for the Community action to achieve the sustainable use of pesticides. The last two of these documents introduce the obligation for all professional users to apply the principles of integrated plant protection, which focus on producing healthy a product while minimising the disturbances of the agricultural ecosystem. According to the integrated plant protection, the EU Member States shall promote the introduction of plant protection products that have a reduced risk of the negative impact on human health and the environment.

Properties of herbicidal ionic liquids

The idea of a herbicidal ionic liquid, which was developed and published in 2011 as a result of a collaboration between scientists from Poznan University of Technology and the Institute of Plant Protection in Poznan, addresses these expectations [1]. Herbicidal ionic liquids are organic salts that contain a phytotoxic ion or ions, with a melting point below 100°C.

*Corresponding author:
Professor Tadeusz PRACZYK – Ph.D., D.Sc., e-mail: T.Praczyk@iorpib.poznan.pl

There are descriptions of synthesis methods, certain physicochemical properties as well as the effectiveness of many new herbicidal compounds belonging to the groups of ammonium, pyridinium, imidazolium and morpholinium ionic liquids. When designing ionic liquids for crop protection, it is possible to obtain dual function compounds, i.e. the ones acting as a herbicide and growth regulator at the same time [2÷4]. The dual function compounds contain a herbicidal anion (e.g. MCPA, 2,4-D), while a cation is a plant growth inhibitor, e.g. chlorocholine chloride (CCC) Another type of dual function ionic liquids is the combination of a fungicidal cation (e.g. tebuconazole) with a herbicidal anion [7].

Herbicidal ionic liquids have many advantages such as high thermal stability, low vapour pressure, high biological activity, and favourable ecotoxicological profile [8÷10].

Table 1 presents decomposition temperatures for 5% weight loss ($T_{onset\ 5\%}$) and for 50% weight loss ($T_{onset\ 50\%}$) of some ionic liquids containing a herbicidal ion.

Table 1

Physicochemical properties of herbicidal ionic liquids

Compound name	$T_{onset\ 5\%}$ °C	$T_{onset\ 50\%}$ °C	Solubility
[DDA][MCPA]	207	255	ethanol, chloroform, DMSO
[Arquad 2C-75][MCPA]	204	274	ethanol, chloroform, DMSO
[Arquad C-35][MCPA]	209	238	water, ethanol, chloroform, DMSO
[Ethoquad C/12][MCPA]	229	246	water, ethanol, chloroform, DMSO
[Arquad 2C75][2,4-D]	213	267	ethanol, chloroform, DMSO
[Arquad C-35][2,4-D]	213	235	water, ethanol, chloroform, DMSO
[Ethoquad C/12][2,4-D]	229	245	water, ethanol, chloroform, DMSO
[DDA][Glyphosate]	161	218	ethanol, chloroform, DMSO
[Arquad 2HT][Glyphosate]	196	353	water, ethanol, chloroform, DMSO
[Ethoquad C/12][Glyphosate]	208	342	water, ethanol, chloroform, DMSO
[Ethoquad O/12][Glyphosate]	155	290	water, ethanol, chloroform, DMSO

The data (Tab. 1) clearly show the high thermal stability of herbicidal ionic liquids, as the decomposition of these compounds occurs only at temperatures of 155°C – 229°C. Depending on the cation selected, one can obtain water soluble or insoluble compounds. The hydrophobicity of some herbicidal ionic liquids can prevent their fast penetration of ground waters. In the studies conducted in China, the penetration in the soil profile of herbicidal ionic liquids containing clopyralid was 25% to 60% lower than for a commercial product containing the same active ingredient [11].

The surface active properties of foliar PPP spray solutions play an important role in their effectiveness. Low surface tension (25–40 mN m^{-1}) and low wetting angle (angle of contact) of the drop results in good wetting of the leaf surface, which enable the penetration with a sufficient quantity of the active ingredient of plant tissues. Herbicidal ionic liquids have good surface active properties (Tab. 2).

Table 2

Contact angle and surface tension of herbicidal ionic liquids

Compound name	Contact angle degrees	Surface tension mN m^{-1}
[DDA][MCPA]	36.8	26.8
[Arquad 2C-75][MCPA]	43.9	28.0
[Arquad C-35][MCPA]	57.3	33.2
[Ethoquad C/12][MCPA]	66.5	32.5
[Arquad 2C75][2,4-D]	41.0	27.7
[Arquad C-35][2,4-D]	49.7	28.9
[Ethoquad C/12][2,4-D]	54.3	30.4
[DDA][Glyphosate]	51.2	28.5
[Arquad 2HT][Glyphosate]	45.9	31.9
[Ethoquad C/12][Glyphosate]	70.6	40.7
[Ethoquad O/12][Glyphosate]	53.8	32.3

The integrated plant protection aims at decreasing the amount of chemical substances entering the environment, while at the same time ensuring high effectiveness against harmful organisms. Herbicidal ionic liquids exhibit high biological activity, which makes it possible to use reduced doses of active ingredients (Tab. 3, 4). As it was found in the field trials, the application of the ionic liquid with the MCPA anion at a dose of 400 g/ha of a.i. provides a sufficient protection of wheat against dicotyledonous weeds, while the currently recommended dose for sodium-potassium MCPA salts (Chwastox Extrea 300 SL) is 900 g/ha. Similar observations were made for the 2,4-D – 450 g/ha of a.i., when the ionic liquid is used – is enough to provide a sufficient protection of cereals against annual dicotyledonous weeds that can be commonly found in such crops.

Table 3

Weed control effectiveness (%) in winter wheat after 4 weeks from the application (dose of active substance expressed as acid – 400 g/ha)

Compound name	Pennycress *(Thlaspi arvense)*	Shepherd's purse *(Capsella bursa pastoris)*	Volunteer rapeseed *(Brassica napus)*
[DDA][MCPA]	95	89	89
[Arquad 2C-75] [MCPA]	95	89	88
[Arquad C-35][MCPA]	91	87	89
[Ethoquad C/12] [MCPA]	90	84	86
MCPA – EHE*	94	95	92
MCPA – DMA**	87	82	84

*2-ethylhexyl ester; **dimethylammonium salt

– source: E. Jakubiak – doctoral thesis, 2016)

Table 4

Weed control effectiveness (%) in winter wheat after 6 weeks from the application (dose of active ingredient expressed as acid – 450 g/ha)

Compound name	Pennycress *(Thlaspi arvense)*	Shepherd's purse *(Capsella bursa pastoris)*	Volunteer rapeseed *(Brassica napus)*
[Arquad 2C75][2,4-D]	97	98	97
[Arquad C-35][2,4-D]	98	97	96
[Ethoquad C/12] [2,4-D]	92	99	98
2,4-D - EHE	99	98	98
2,4-D - DMA	21	23	20

– source: P. Kardasz – doctoral thesis, 2016)

The effectiveness of glyphosate in the form of an ionic liquid is comparable to the effect of Roundup 360 SL (Tab. 5). Due to the good surface active properties, there is no need to add any compounds acting as surfactants to the ionic liquid solution, whereas the commercial herbicide contains such additives.

Table 5

Effectiveness against couch grass under field conditions after 6 weeks from application (%) (Source: Pernak et al., ACS Sustainable Chem. Eng.)

Compound name	Couch grass *(Elymus repens)*
[DDA][Glyphosate]	100
[Arquad 2HT][Glyphosate]	100
[Ethoquad C/12][Glyphosate]	99
[Ethoquad O/12][Glyphosate]	100
Roundup 360 SL	100

In terms of the application, the fact that herbicidal ionic liquids are non-volatile plays a very important role. As shown by the measurements of dicamba volatility in the form of acid and herbicidal ionic liquids containing a dicamba anion, the weight loss of this a.i. in the form of acid after 12 hours at 75°C was 10.6%, while for a dicamba ionic liquid the loss varied in a range of 0.5% – 2.4% [9]. This means that ionic liquids virtually did not evaporate, which decreases the risk of exposure of humans to that substance, as well as eliminates the risk of damaging non-target plants due to herbicide evaporation.

It is worth noting that it is possible to control toxic and ecotoxic properties of herbicidal ionic liquids by a careful choice of a cation [12, 13]. In this case, natural compounds such as amino acids may serve as a source of cations [14, 15].

The development in herbicidal ionic liquid syntheses resulted in obtaining compounds that contain a few herbicidal anions [16, 18]. This is an important accomplishment in terms of their application. It is possible to design a formulation that would have different weed control mechanisms, which is important to reduce the development of weed resistance to herbicides.

Summary

Herbicidal ionic liquids have a very significant application aspect due to their beneficial physicochemical properties, high effectiveness against weeds and a reduced risk of the negative effect on the environment and human health. It is possible to design a herbicide dedicated to specific field conditions, while the possibility to obtain a compound with two or even more herbicidal anions makes them even more attractive.

The plant protection products used in farming tend to penetrate the soil considerably.

Modern formulations should not disturb soil microflora significantly, but rather undergo biodegradation. This challenge can be met to a large extent in the future if herbicidal ionic liquids leave the phase of laboratory research and field trials and gain an adequate interest of phytopharmaceutical industry.

Literature

1. Pernak J., Syguda A., Janiszewska D., Materna K., Praczyk T.: Tetrahedron 2011, **67**, 4838–4844.
2. Pernak J., Niemczak M., Materna K., Marcinkowska K., Praczyk T.: Tetrahedron 2013, **69** (23), 4665–4669.
3. Pernak J., Niemczak M., Zakrocka K., Praczyk T.: Tetrahedron 2013, **69** (38), 8132–8136.
4. Praczyk T., Zakrocka K., Wyrzykowska D., Niemczak M., Pernak J.: Central European Journal of Chemistry 2013, **11** (11), 1816–1821.
5. Praczyk T., Kardasz P., Jakubiak E., Syguda A., Materna K., Pernak J.: Weed Science 2012, **60**, 189–192.
6. Pernak J., Czerniak K., Niemczak M., Chrzanowski Ł., Ławniczak Ł., Fochtman P., Marcinkowska K., Praczyk T.: New J. Chem. 2015, **39**, 5715–5724.

7. Pernak J., Markiewicz B., Zgoła-Grześkowiak A., Chrzanowski Ł., Gwiazdowski R., Marcinkowska K., Praczyk T.: RSC Adv. 2014, **4**, 39751–39754.
8. Pernak J., Niemczak M., Giszter R., Shamshina J., Gurau G., Cojocaru O. A., Praczyk T., Marcinkowska K., Rogers R. D.: ACS Sustainable Chem. Eng. 2014, **2** (12), 2845–2851.
9. Cojocaru O. A., Shamshina J., Gurau G., Syguda A., Praczyk T., Pernak J., Rogers R.: Green Chemistry 2013, **15**, 2110–2120.
10. Kordala-Markiewicz R., Rodak H., Markiewicz B., Walkiewicz F., Sznajdrowska A., Materna K., Marcinkowska K., Praczyk T., Pernak J.: Tetrahedron 2014, **70** (32), 4784–4789.
11. Zhu J., Ding G., Liu Y., Wang B., Zhang W., Guo M., Geng Q., Cao Y. Chemical Engineering Journal 2015, 279, 472–477.
12. Ławniczak Ł., Syguda A., Borkowski A., Cyplik P., Marcinkowska K., Praczyk T., Chrzanowski Ł., Pernak J.: Science of The Total Environment 2016, 563–564, 247–255.
13. Ding G., Liu Y., Wang B., Punyapitak D., Guo M., Duan Y., Li J., Cao Y.: New J. Chem. 2014, 38, 5590–5596.
14. Pernak J., Czerniak K., Niemczak M., Chrzanowski Ł., Ławniczak Ł., Fochtman P., Marcinkowska K., Praczyk T.: New J. Chem. 2015, 39, 5715–5724.
15. Pernak J., Czerniak K., Biedziak A., Marcinkowska K., Praczyk T., Erfurt K., Chrobok A.: RSC Adv. 2016, doi: 10.1039/C6RA06703D.
16. Marcinkowska K., Czerniak K., Giszter R., Niemczak M.: Przem. Chem. 2013, **92**, 9, 1633.
17. Niemczak M., Giszter R., Czerniak K., Marcinkowska K., Walkiewicz F.: RSC Adv. 2015, 5, 15487–15493.
18. Pernak J., Niemczak M., Chrzanowski Ł., Ławniczak Ł., Fochtman P., Marcinkowska K., Praczyk T.: Chem. Eur. J., 2016, 22: 12012–12021

Professor Tadeusz PRACZYK – Ph.D., D.Sc., has graduated from Poznań University of Life Sciences. From 1986 until today he is employed at Institute of Plant Protection – National Research Institute in Poznań. The research area is connected with biology of weeds and their control.

e-mail: T.Praczyk@iorpib.poznan.pl

Aktualności z firm

News from the Companies

Dokończenie ze strony 487

Selena: 20 mln PLN zysku za I półrocze 2016

Grupa Selena – globalny producent i dystrybutor chemii budowlanej z centralą w Polsce – w pierwszym półroczu br. osiągnęła skonsolidowane przychody ze sprzedaży w wysokości 456 mln PLN. Jednocześnie Grupa Selena zanotowała w analizowanym okresie zysk netto w wysokości 20,1 mln PLN, co oznacza poprawę o 16,9 mln PLN w stosunku do analogicznego okresu roku 2015, natomiast zysk operacyjny wyniósł 17 mln PLN i wzrósł rok do roku o niemal 70%. Spółka zanotowała również wzrost marży z poziomu 30,5% do 33,4%. *(kk)*

(*http://www.selena.com/, 31.08.2016*)

Synthos zostanie europejskim liderem w produkcji EPS

26 sierpnia br. Komisja Europejska zatwierdziła zakup INEOS Styrenics na rzecz Synthos SA Transakcja zakupu jednostki biznesowej Ineos Styrenics European Holding BV została z powodzeniem sfinalizowana 31 sierpnia br. Tym samym oświęcimska firma chemiczna stanie się europejskim liderem rynku polistyrenu spienialnego (EPS). Wartość transakcji wyniosła 80 mln EUR, a jej realizacja jest kolejnym krokiem rozwoju firmy w obszarze EPS. *(kk)*

(*http://synthosgroup.com/, 1.09.2016*)

BADANIA I ROZWÓJ

Rozwijamy współpracę polsko-chińską

Intensyfikacja współpracy w dziedzinie szkolnictwa wyższego i nauki pomiędzy Polską a Chinami była głównym tematem spotkania sekretarza stanu w MNiSW, prof. Aleksandra Bobko, z Zhao Jianjun, wicegubernatorem chińskiej prowincji Henan. Obaj rozmówcy podkreślili znaczenie kontaktów dwustronnych pomiędzy uczelniami oraz instytutami badawczymi obu krajów i zadeklarowali wsparcie dla przyszłych działań w zakresie wymiany studentów i naukowców oraz prowadzenia badań naukowych. Henan to największa chińska prowincja (ponad 100 mln mieszkańców) o wysokiej dynamice rozwoju gospodarczego oraz ważny ośrodek edukacyjno-naukowy (liczba studentów oraz nauczycieli akademickich w regionie to 27 mln osób). Podczas spotkania obaj rozmówcy uzgodnili, iż zostaną podjęte kroki zmierzające do zainicjowania programów edukacyjnych oraz naukowych pomiędzy uczelniami z Henan a zainteresowanymi uczelniami polskimi (uniwersytety, uczelnie techniczne, rolnicze). Ważnym elementem wspierającym te działania będą cykliczne (co 2 lata) spotkania grup eksperckich. *(kk)*

(*http://www.nauka.gov.pl/, 25.08.2016*)

Polsko-kazachtańska współpraca na rzecz rozwoju leków ziołowych

Grupa Polpharma wraz ze spółką Herbapol Warszawa podpisały porozumienie o współpracy z Południowokazachstańską Państwową Akademią Farmaceutyczną, której celem jest wspólny rozwój projektów naukowych, edukacyjnych i badawczych w zakresie preparatów ziołowych oraz leków pochodzenia naturalnego. Uroczyste podpisanie porozumienia odbyło się 23 sierpnia br. w czasie Forum Ekonomicznego Polska-Kazachstan, które towarzyszyło oficjalnej wizycie w Polsce Prezydenta Republiki Kazachstanu, Nursułtana Nazarbajewa. Współpraca obejmie m.in. ocenę właściwości terapeutycznych ziół występujących w regionie Południowego Kazachstanu oraz potencjału do ich komercjalizacji w Kazachstanie i innych krajach regionu, a także analizę możliwości ekstrakcji i formulacji gotowego produktu leczniczego w zakładzie firmy Santo w Szymkencie. *(kk)*

(*http://www.polpharma.pl/, 24.08.2016*)

NAGRODY, WYRÓŻNIENIA

Nagroda Pattersona 2017 dla Zbigniewa Dautera

Nagrodę Amerykańskiego Stowarzyszenia Krystalograficznego (ACA) im. Arthura Lindo Pattersona otrzymał dr hab. inż. Zbigniew Dauter z Argonne National Laboratory (USA). Nagroda ta, ustanowiona w 1980 r., przyznawana jest raz na trzy lata w dowód „uznania i zachęty do wybitnych badań w zakresie struktury materii metodami dyfrakcyjnymi, wliczając w to znaczący wkład w metodologię określania struktury i/lub innowacyjne zastosowania metod dyfrakcyjnych i/lub objaśnianie zjawisk biologicznych, chemicznych, geologicznych lub fizycznych z wykorzystaniem nowych informacji strukturalnych". Laureat otrzyma 1500 USD, pamiątkowy dyplom oraz bezpłatny udział w dorocznym spotkaniu ACA. *(kk)*

(*http://pg.edu.pl/, 10.08.2016*)

Dokończenie na stronie 493