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Preparation and characterization of new ionic liquid forms of 2,4-DP herbicide

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ABSTRACT

In this study, a series of new 2-(2,4-dichlorophenoxy)propionate-based herbicidal ionic liquids (HILs), incorporating well-known, commercially available tetraalkylammonium cations, were synthesized in high yield ($\geq 89\%$) via a simple two-step procedure. Generally, at room temperature, the products comprising at least one long alkyl substituent in the cation were viscous liquids. All the synthesized salts maintained biological activity against the selected dicotyledonous weeds (common lambsquarters and cornflower). Among the tested salts, the HILs with dodecyltrimethylammonium, trimethyl(tetradecyl) ammonium and trimethyl(octadecyl)ammonium cations were characterized by the highest herbicidal efficacy against both plants. The spray solutions of the prepared HILs revealed their good surface-activation and wetting properties (contact angle = $43\text{--}63^\circ$ and surface tension = $27\text{--}29\text{ mN m}^{-1}$), justifying an enhancement of the biological activity caused by the facilitated penetration of the active substance into the interior of the plant. The values of the octanol–water partition coefficient of the new salts indicate their low potential for bioaccumulation in the soil.

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1. Introduction

Chlorophenoxy acids are widely applied as plant growth regulators for agricultural and non-agricultural purposes.¹ These systemic herbicides are known as selective pre- and post-emergence substances and are widely utilized for the control of broad-leaved aquatic weeds and annual and perennial weeds in cereals, pastures and forestry.² The most popular representative of this group is 2,4-dichlorophenoxyacetic acid (2,4-D), which has been used as the main ingredient in many weed-killing preparations for over 70 years.³ Another popular chlorophenoxy compound is 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP or dichlorprop), which has a chiral carbon atom in the aliphatic side chain. Despite the possibility of two stereoisomeric forms of 2,4-DP, only the *R*-enantiomer exhibits herbicidal activity and was designated as commercial 2,4-DP-P.⁴ Interestingly, synthetic auxins, such as 2,4-DP, could also be applied to increase fruit size. The enhancement in fruit growth of certain citrus species, peach, litchi, apricot, plum and loquat has been described.⁵ For instance, the application of 2,4-

DP at the beginning of pit hardening stimulates the cell's enlargement in the mesocarp of five Japanese plum cultivars, which, in turn, caused a significant improvement in fruit size and total yield.⁶

Chlorophenoxyalkanoates turned out to be degradable by microbes, as was found for a number of bacterial strains (e.g., *Sphingomonas herbicidovorans* MH, *Rhodoferrax* sp. P230 and *Delftia acidovorans* MC1) with respect to 2,4-D and both enantiomers of 2,4-DP (herbicidally active as well as inactive).⁷ The toxicity of the phenoxy acids changes depending on the type of the compound, and the lethal dose (LD₅₀) varies from 300 to 3000 mg per kg of body weight.⁸ Therefore, phenoxy acids were assigned to toxicity class II (moderately hazardous) or class III (slightly hazardous) by the World Health Organization. Although they are not considered highly toxic, chlorophenoxy herbicides were designated as “possibly” carcinogenic to humans.^{2,8} However, in 2014, the Health Canada Pest Management Regulatory Agency revealed that 2,4-DP-P in the form of a free acid and 2-ethylhexyl ester is not genotoxic, carcinogenic, neurotoxic or teratogenic according to the latest experimental data.⁹ Due to the results of examining extensive toxicity in environmental risk studies, the US Environmental Protection Agency enabled the re-registration of 2,4-DP-P in 2007.¹⁰ An acute oral toxicity of 2,4-DP is similar to 2,4-D. A propionic acid derivative is characterized by slightly lower values of LD₅₀ for rats and mice (344 mg kg⁻¹ and 309 mg kg⁻¹, respectively). However,

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for guinea pigs, LD₅₀ for 2,4-DP is greater (620 mg kg⁻¹) by approximately 150 mg kg⁻¹ compared to 2,4-D.^{11,12} After application, the herbicides can enter the water flow system, provoking side effects in humans and the environment. The high water solubility of some forms of phenoxy herbicides highlighted the need for the monitoring of their residues in the ground, as well as drinking water, by using fast and highly sensitive methods.^{13–15} In recent years, the presence of chlorophenoxy herbicide traces in natural environments has become a great concern. Hence, the development of novel technological approaches for their removal from water and soil is a challenging task.¹⁶ Currently, an increasing amount of studies on the removal of 2,4-DP have focused on applying two phase extraction methods,²⁰ ozonation catalysed by H₂O₂, UV light, Fe²⁺ and TiO₂,^{12,17} sorption on organoclays,¹⁸ biosorption on materials of biological origin,^{8,14} degradation in activated sludge plants,¹⁹ oxidation methods, such as anodic oxidation, electro-Fenton and photoelectro-Fenton,²⁰ or electro-dissolution processes.²¹

For the first time, in 2011, a very promising way of transforming phenoxyacids into ionic liquids was described.²² The combination of quaternary ammonium or phosphonium cations with herbicidally active anions led to the formation of a new group of ionic liquids (ILs) called herbicidal ionic liquids (HILs).^{22–24} So far, HILs have been synthesized from phenoxyacids (2,4-D, MCPA, mecoprop),^{22–25} benzoic acid derivatives (dicamba),²⁶ sulfonylureas (metsulfuron-methyl),²⁷ pyridine derivatives (clopyralid),²⁸ glyphosate,²⁹ fomesafen³⁰ and bentazone.³¹ The development of HILs yielded new substances exhibiting significantly increased biological activity and multifunctional properties.^{23,28,32} In comparison to the commercial herbicidal formulations, HILs possess various additional advantages, such as lower volatility,²⁶ toxicity^{22,33} and water mobility.³⁰ These properties may be further modified by cation selection to regulate HIL solubility in water, their environmental impact and the biodegradability of the compound.^{25,33–35} Accordingly, the reports presenting HILs derived from renewable sources, such as betaine and carnitine, proved that new herbicides may be more eco-friendly than their commercial analogues.^{36–38} As a result of intensive research, ILs with dual pesticidal functions (an anion as the herbicide and a cation as a plant growth regulator^{32,39} or a fungicide⁴⁰) have been described and characterized as a second generation of HILs that retained both biological activities. Recently, a new series of double salt herbicidal ionic liquids (DSHILs) have been described as the successful result of the incorporation of two different herbicides into a single compound.⁴¹

Here, we present a series of new 2,4-DP-based HILs, comprising popular and abundant tetraalkylammonium cations, which exhibit different physicochemical properties such as hydrophilicity or surface activity. The source of the anion was 2-(2,4-dichlorophenoxy)propionic acid, a systemic, selective herbicide, whose total annual usage in only US territory is estimated at nearly 2 thousand tonnes per year. Its unabated popularity may be explained by the fact that the risk of formation of biotypes resistant towards phenoxyacids is relatively low compared to other classes of herbicides (e.g., sulfonylureas). This study focuses on evaluating the influence of the length of the alkyl chains on the ammonium cation on the physicochemical properties of the tested HILs (i.e., thermal stability, solubility, viscosity or density), as well as their herbicidal efficiency as determined in greenhouse experiments.

2. Results and discussion

2.1. Synthesis

Ammonium salts (Table 1) were synthesized using a two-step

Table 1
Synthesized 2,4-DP-based tetraalkylammonium salts.

Salt	R ¹	R ²	R ³	R ⁴	Yield (%)	Purity (%)	State at 25 °C
1	–CH ₃	–CH ₃	alkyl ^a	benzyl	94	97	Liquid
2	–CH ₃	–CH ₂ CH ₂ OH	–CH ₂ CH ₂ OH	alkyl ^b	89	99	Liquid
3	–CH ₃	–CH ₃	–C ₁₀ H ₂₁	–C ₁₀ H ₂₁	90	98	Liquid
4	–CH ₃	–CH ₃	alkyl ^a	alkyl ^b	92	98	Liquid
5	–CH ₃	–CH ₃	–CH ₃	–C ₁₂ H ₂₅	95	98	Liquid
6	–CH ₃	–CH ₃	–CH ₃	–C ₁₄ H ₂₉	93	99	Liquid
7	–CH ₃	–CH ₃	–CH ₃	–C ₁₈ H ₃₇	91	99	Liquid
8	–CH ₃	–CH ₂ CH ₂ OH	–CH ₃	–CH ₃	95	–	Solid ^c
9	–C ₄ H ₉	–C ₄ H ₉	–C ₄ H ₉	–C ₄ H ₉	92	–	Wax

^a Hydrogenated tallow - mixture of saturated alkyl substituents C₁₂–1%, C₁₄–4%, C₁₆–31%, C₁₈–64%.

^b Oleyl - mixture of unsaturated alkyl substituents C₁₂–5%, C₁₄–1%, C₁₆–14%, C₁₈–80%.

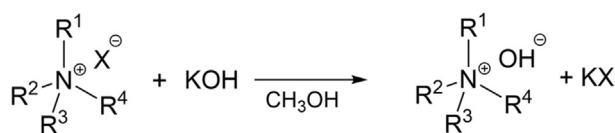
^c T_m = 114–116 °C.

approach as follows: an anion exchange reaction in methanol producing tetraalkylammonium hydroxides, and a subsequent neutralization of the obtained intermediates with 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP). The acid-base reaction, (Scheme 1), was carried out at 25 °C in an EasyMax™ semi-automatic reactor equipped with a glass electrode to control a decrease in the pH of the reaction mixture. The utilized approach minimized the difficulties (i.e., separation of the phases as well as foam formation) of the methodology based on a two-phase extraction from the aqueous environment.

All products were obtained with high yields in the range of 89–99% (Table 1). The purity of the salts comprising at least one long alkyl chain in the cation benzalkonium (**1**), bis(2-hydroxyethyl)methylolelammonium (**2**), didecyldimethylammonium (**3**), di(hydrogenated tallow)dimethylammonium (**4**), dodecyltrimethylammonium (**5**), trimethyl(tetradecyl)ammonium (**6**) and trimethyl(octadecyl)ammonium (**7**) was determined *via* the direct two-phase titration technique. The synthesized salts were determined to be of high purity, from 97% for **1**–99% for **2**, **6** and **7**. Their structures were also confirmed by IR, ¹H NMR, ¹³C NMR spectroscopy and mass spectrometry. All spectral descriptions are provided in the Electronic Supporting Information (Figs. S1–S27). Additionally, the elemental analysis results helped to validate the identity and purity of the synthesized salts **3** and **5**–**9**.

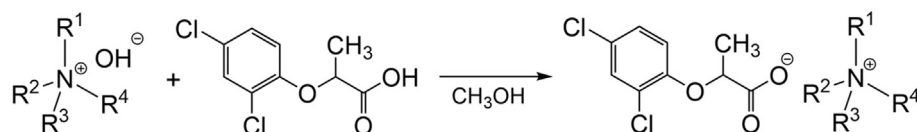
As presented in Table 1, the seven salts (**1**–**7**) were liquids at room temperature, whereas tetrabutylammonium 2-(2,4-dichlorophenoxy)propionate (**9**) was a wax. Only one compound containing a choline (2-hydroxyethyltrimethylammonium) cation (**8**), was at 25 °C, a highly hygroscopic solid melting above 100 °C (T_m = 114–116 °C). The presence of at least one hydrophobic long alkyl chain decreased water absorption from the air, hence the appropriate cation selection may influence the hygroscopicity of the obtained 2,4-DP based salts. The synthesized compounds, except choline 2-(2,4-dichlorophenoxy)propionate (**8**), are characterized by a melting point below 100 °C; therefore, they may be classified as ionic liquids (ILs). Furthermore, according to their appearance at 25 °C, **1**–**7** and **9** may be classified as room temperature ionic liquids (RTILs). The collected results prove that the transformation of the solid forms of herbicides (i.e., phenoxyacids of form of free acids or inorganic salts) into herbicidal ionic liquids may enable a liquefaction of the above-mentioned biologically active ingredients. This fact, reported first by Rogers et al.,⁴² can be particularly useful for the agrochemical industry which must face many problems associated with the solid form of the produced substances, including polymorphic conversion, low solubility or bioavailability and the tendency of the amorphous forms to crystallize spontaneously.

Step 1



X = Cl; Br

Step 2



Scheme 1. Synthesis of tetraalkylammonium 2-(2,4-dichlorophenoxy)propionates (1–9).

2.2. Physicochemical properties

2.2.1. Viscosity analysis

The temperature dependence of the viscosity of RILs 1–7 in the range from 20 to 80 °C is presented in Fig. 1 (specific values are provided in ESI in Table S1). At 20 °C, their viscosity values vary from approximately 2.0 Pa s (3) to 77.4 Pa s (6). In the case of ILs with dialkyldimethylammonium (3, 4) cations, the viscosity increased as the size of the non-polar part of the cation became larger, which is consistent with the other reports on ILs.⁴³ The exceptionally high values of viscosity among ILs with a trialkylmethylammonium cation (5–7) at 20 °C (77.4 Pa s) was determined for salt 6. It is worth mentioning that for other homologous series of HILs containing a 4-chloro-2-methylphenoxyacetate anion (MCPA), the highest value of viscosity was also possessed by the product with a tetradecyl substituent.⁴⁴ Such specific behaviour of the discussed HILs may be related with the altered coordinating ability of the phenoxycarboxylate anions compared with conventional, structurally simpler anions.

Similar to cases of other viscous ILs, the viscosity of all 2,4-DP-based ILs decreased nonlinearly with the increase of temperature, whereas the temperature change from 20 to 80 °C caused a rapid reduction of the analysed parameter, which finally reached approximately 0.051–0.217 Pa s. Generally, the bis(2-hydroxyethyl)

methylolammonium cation is recognized to cause the waxy form of the synthesized ILs.^{26,29,45} The lower viscosity of 2 may arise from a less effective assembly resulting in a weaker interaction of the chains of the neighbouring cations.⁴⁶ Since the presence of the aromatic substituent in the cation reduces the viscosity, mainly as a consequence of their higher fragilities,⁴⁷ ILs with alkyltrimethylammonium cation (5–7) were characterized by higher viscosities than the salt comprising benzyl cation (1).

2.2.2. Density analysis

The density of the tested ILs at 20 °C ranged from 0.98 g mL⁻¹ for 4 to 1.10 g mL⁻¹ for 7 (Fig. 2 and Table S2 in ESI). The density of all salts, except 4, was greater compared to the density of pure water. In the case of ILs with an alkyltrimethylammonium cation (5–7), the alkyl chain extension resulted in a slight decrease in the density at the analysed temperature range, which is consistent with the literature reports.^{48–50} Accordingly, for ILs containing a dialkyldimethylammonium cation (3, 4), the chain extension caused a decrease in the density as well. Due to the increase of the molar volume of the cation, the presence of two hydroxyethyl groups resulted in a reduction of the density of salt 2 compared to the ILs 5–7. The measured density values decreased linearly with an increase in the temperature, and the line describing this relationship was expressed by the equation $y = a \cdot x + b$, where a was equal to

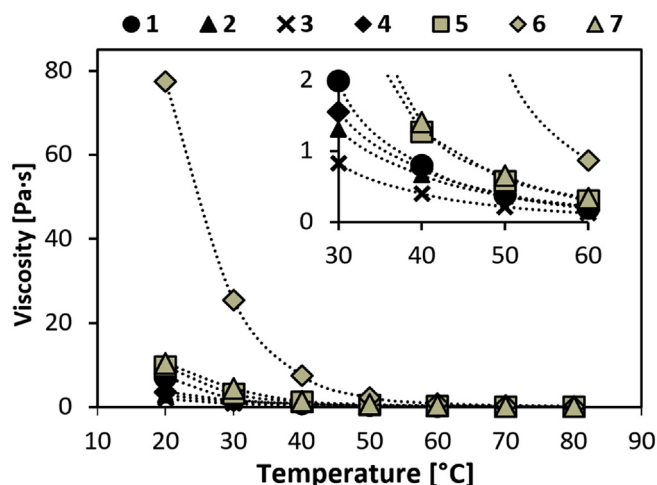


Fig. 1. Influence of temperature on the viscosity of 2,4-DP-based ILs (1–7).

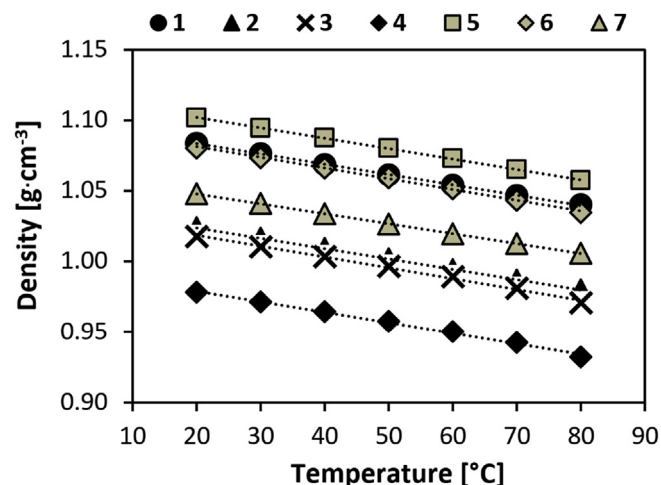


Fig. 2. Influence of temperature on the density of 2,4-DP-based ILs (1–7).

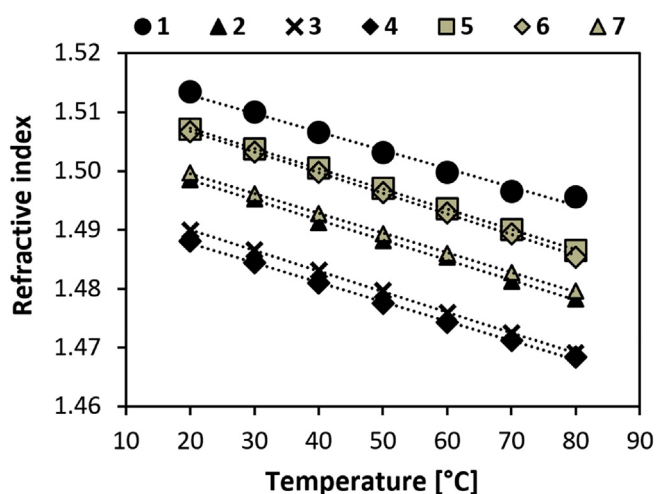


Fig. 3. Influence of temperature on the refractive index of 2,4-DP-based ILs (1–7).

approximately -0.00074 and b varied from 0.94 g mL^{-1} for **4** to 1.12 g mL^{-1} for **5** (the correlation coefficients (R^2) for all tested ILs amounted to at least 0.99 – see Table S3 in ESI).

Heating the samples to $80 \text{ }^\circ\text{C}$ resulted in a reduction in the density by approximately 0.04 g mL^{-1} for all tested salts. Generally, ILs **1–7** exhibit noticeably lower densities in comparison to other HILs comprising smaller cations, which were characterized by values varying from 1.15 to 1.26 g mL^{-1} at $20 \text{ }^\circ\text{C}$.^{33,36} This observation may be explained by the fact that ILs with a long alkyl chain present in the cation tend to occupy larger molar volumes, leading to the reduction of the values of their density.

2.2.3. Refractive index analysis

Generally, the refractive index (RI) values depend on the structure of both the cation and the anion comprising ILs.⁵¹ The RI of ILs **1–7** at $20 \text{ }^\circ\text{C}$ ranged from 1.488 for **4** to 1.513 for **1** (Fig. 3 and Table S4 in ESI). The results for the ILs with an alkyl-trimethylammonium cation (**5–7**) show that the extension of the alkyl chain results in a decrease of the refractive index values. Furthermore, for ILs with a dialkyldimethylammonium cation (**3, 4**) a similar relationship was found.

In general, the RI of a substance is higher when its molecules are more tightly packed, thus when the compound possesses a higher density.⁵² By taking this into account, we observed that the

refractive indices presented for ILs **3–7** are correlated with their density. The presence of hydroxyethyl groups attached to a nitrogen atom had a minor effect on the refractive indices. Analogously to the density measurements, the temperature increase caused a linear decrease of the RI (Fig. 3). Linear regression allowed a description of this relationship by the equation $y = a \cdot x + b$, where a was equal to approximately -0.00033 , and the b parameter ranged from 1.494 for **4** to 1.519 for **1** (R^2 for all tested ILs amounted to at least 0.99 – see Table S5 in ESI).

2.2.4. Thermal analysis

The thermal properties (phase transitions and thermal stability) of the 2,4-DP-based tetraalkylammonium salts are shown in Table 2. The melting point of one obtained compound (**8**) exceeded the threshold of $100 \text{ }^\circ\text{C}$, whereas salts **1–7** and **9** may be classified as ILs. For five of the synthesized salts, **1, 2, 5, 6** and **9**, neither melting nor crystallization events were observed in the analysed temperature range.

In the case of **8**, during the second cycle of heating, a glass transition ($T_g = 7.0 \text{ }^\circ\text{C}$) followed by cold crystallization ($T_c = 66.8 \text{ }^\circ\text{C}$) and a melting point above $100 \text{ }^\circ\text{C}$ ($T_m = 119.3 \text{ }^\circ\text{C}$) was observed (Fig. 4). The appearance of this unexpected cold crystallization event is an effect of its supercooling behaviour, where only a glass transition was observed on cooling in the first cycle. Regarding the literature, during heating in the second cycle, the supercooled liquid usually exhibits a T_g , and as a metastable system (with a substantially reduced viscosity), it adapts its conformation. Finally, this state results in a crystallization of the sample during the heating defined as ‘cold crystallization’.⁵³ Such behaviour has already been reported for HILs, e.g., comprising phenoxyacids such as 2,4-D²⁴ or MCPB⁴⁹ as the anions. In contrast, the structurally similar choline 2,4-dichlorophenoxyacetate was characterized by only a T_m at $127 \text{ }^\circ\text{C}$, and no cold crystallization was observed during the heating of this salt.⁵⁴ This difference may be explained by the high hygroscopicity of **8**, which, according to the literature,⁵⁵ may also result in observation of cold crystallization during the second cycle of heating for some ILs.

The analysis of structure vs. glass transition relationships confirmed a known trend - the longer the alkyl chain substituent attached to the nitrogen atom, the lower the T_g of the resulting HIL.⁴⁹ The lowest T_g was observed for **2** ($-38.0 \text{ }^\circ\text{C}$), which contains mainly the octadecyl substituent in the cation. Surprisingly, no glass transition was observed for both ILs with a dialkyldimethylammonium cation (**3** and **4**), even though the

Table 2
Thermal properties of the obtained 2,4-DP-based salts.

Salt	T_g^a ($^\circ\text{C}$)	T_m^b ($^\circ\text{C}$)	T_c^c ($^\circ\text{C}$)	Steps of degradation	$T_{\text{onset}5\%}^d$ ($^\circ\text{C}$)	T_{onset}^e ($^\circ\text{C}$)
1	-9.9	–	–	3	165	212
2	-38.0	–	–	3	211	258
3	–	0.4	-0.8	2	179	215
4	–	-0.2	2.9	2	190	298
5	-11.9	–	–	2	179	215
6	-24.8	–	–	2	189	221
7	–	-12.2	-4.7	2	185	220
8	7.0	119.3	66.8 ^f	2	201	235
9	-7.0	–	–	1	172	208
2,4-DP free acid	–	113.3	94.1	1	160	205

^a T_g – glass transition temperature.

^b T_m – melting point.

^c T_c – temperature of crystallization.

^d $T_{\text{onset}5\%}$ – decomposition temperature of 5% sample.

^e T_{onset} – decomposition temperature.

^f Cold crystallization.

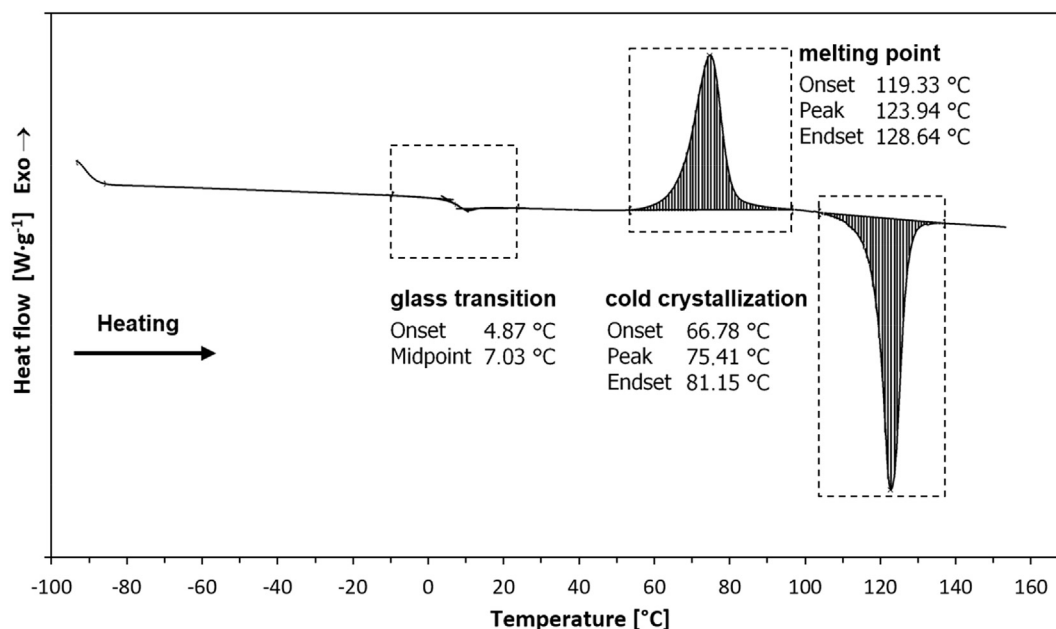


Fig. 4. DSC thermogram of the choline 2-(2,4-dichlorophenoxy)propionate (**8**) - the second cycle of heating.

Table 3

Solubility of prepared 2,4-DP-based salts at 25 °C.

Salt	Water	Methanol	DMSO	Acetonitrile	Acetone	Isopropanol	Ethyl acetate	Chloroform	Toluene	Hexane
	9.0 ^a	6.6	6.5	6.2	5.1	4.3	4.3	4.1	2.3	0.0
1	–	+	+	+	+	+	±	+	+	+
2	–	+	+	+	+	+	±	+	+	+
3	–	+	+	+	+	+	+	+	+	+
4	–	+	+	+	+	+	+	+	+	+
5	–	+	+	+	+	+	±	+	+	+
6	–	+	+	+	+	+	+	+	+	+
7	–	+	+	+	+	+	+	+	+	+
8	+	+	+	±	–	+	–	+	+	–
9	+	+	+	+	+	+	–	+	–	–
2,4-DP free acid	–	+	+	+	+	+	+	+	+	+

^a Snyder polarity index; +: good solubility; ±: limited solubility. –: poor solubility.

previously described HILs containing a didecyltrimethylammonium cation and phenoxyacetate (MCPA or 2,4-D) anions had a glass transition at approximately –50 °C.^{22,24}

The thermogravimetric analysis revealed that only an IL comprising a symmetrical tetrabutylammonium cation (**9**) exhibited the simple thermal decomposition behaviour with a single decomposition step (Fig. S28 in ESI). According to the data in Table 2, the transformation of 2,4-DP into ionic liquids results in the enhancement of the thermal stability manifested by an increase of thermal decomposition temperatures ($T_{\text{onset}5\%}$ and T_{onset}). The lowest decomposition temperature of 5% of the sample was observed for 2-(2,4-dichlorophenoxy)propionic acid in the form of a free acid ($T_{\text{onset}5\%} = 160$ °C). The presence of the ionic bond in all the obtained salts **1–9** caused an increase of $T_{\text{onset}5\%}$ parameter from approximately 5 °C to more than 50 °C. It can be presumed that the presence of the 2-hydroxyethyl group in the cation improves their resistance to thermal decomposition, which agrees with a high $T_{\text{onset}5\%}$ (equal to 201 °C), as observed for **8**, with an incorporated choline cation.

The temperature values of 50% decomposition of the sample (T_{onset}) ranged from 205 °C for 2,4-DP in acidic form to 298 °C for IL **4**. Generally, all the obtained ionic derivatives of 2,4-DP (**1–9**) were characterized by higher T_{onset} values, which underlines the

beneficial role of the utilized ammonium cations. High values of T_{onset} were recorded for ILs comprising at least one 2-hydroxyethyl group (**2** and **8**); for these salts, the analysed parameter increased by approximately 40 °C in comparison to 2-(2,4-dichlorophenoxy)propionic acid.

2.2.5. Solubility

The solubility of the prepared ILs were tested according to ten representative solvents, varying from high to low polarity (Table 3). All tested ILs were soluble in DMSO, acetonitrile and short chain alcohols, such as methanol or isopropanol. Their solubility in water turned out to be cation structure dependent; only two salts (**8**, **9**) were soluble in water due to the lack of long alkyl chains present in the cations. Therefore, the significantly lower solubility in water of ILs **1–7** was mainly caused by a high hydrophobicity of the utilized cations. On the other hand, hexane, as the least polar solvent, dissolved compounds containing long chain carbon substituents (**1–7**).

Almost all prepared ILs were soluble in toluene and acetone. Moreover, chloroform, dissolved all synthesized ILs even though it has a relatively low polarity. The solubility in ethyl acetate was related to the structure of the cation; only salts possessing hydrophobic cations (**1–7**) exhibited an affinity with this solvent.

Surprisingly, the compounds that dissolved in ethyl acetate were also characterized by good solubility in hexane. According to the results from Table 3, 2-(2,4-dichlorophenoxy)propionic acid was soluble in all of the tested organic solvents, and its transformation into ionic salts allowed for the alteration of the solubility mainly in water, ethyl acetate and hexane.

2.2.6. Surface activity

By the selection of specific cations, some ILs exhibiting herbicidal activity (HILs) could reduce both the surface tension as well as the contact angle and act as adjuvants.^{22–24,35,38,54} This approach eliminates the necessity of using the above-mentioned agricultural additives (often characterized by an unspecified toxicity and negative environmental impact) recommended for commercial crop protection agents. The main surface activity parameters (contact angle (CA) as well as surface tension (γ)) of the spray solutions of salts 1–9 utilized in the greenhouse experiments were determined (values are provided in Fig. 5 as well as in ESI – Table S6). Generally, the values of the surface tension and contact angle of the solutions of the commercial preparations are significantly higher ($\gamma \approx 65–72 \text{ mN m}^{-1}$; $\text{CA} \approx 104–108^\circ$).³⁸ Therefore, on the basis of the results in Fig. 5, all obtained HILs could be considered as the novel surface-active compounds. The measured γ values for salts 1–9 were similar and varied from 27.1 mN m^{-1} for 3– 29.2 mN m^{-1} for 9, which possesses only short butyl substituents attached to the nitrogen atom.

Theoretically, the lower values of CA should enhance the wetting of plants, spray retention, absorption, cuticle penetration and translocation of the active ingredient. As is shown in Fig. 5, the highest values of CA were observed for salts 2 (63.2°), 8 (63.4°) and 9 (61.0°). Therefore, the lowest results of the fresh weight reduction of the tested plants was observed for these salts (see Fig. 6). As expected, the elongation of the saturated alkyl chain from dodecyl (5) to tetradecyl (6) in HILs with an alkyltrimethylammonium cation caused an increase in the contact angle by approximately 5° , to 56.8° . However, further elongation from tetradecyl (6) to octadecyl (7) led to a decrease of CA to 52.2° . This specific tendency has also been recently observed for herbicidal ionic liquids synthesized from derivatives of D-glucose.³⁷ Surprisingly, ILs 3 and 4 were characterized by good wetting properties; however, their herbicidal activity was much lower than expected. The possible explanation of this phenomenon related to the size of the molecule that could impede the absorption, cuticle penetration and translocation of the

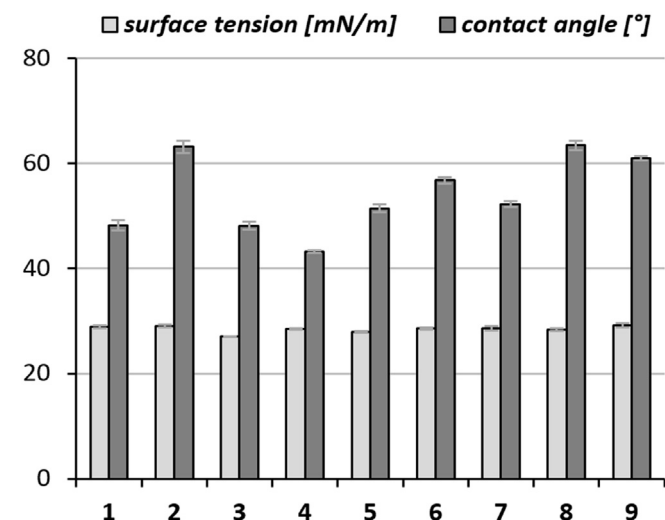


Fig. 5. Surface tension (γ) and contact angle (CA) of spray solutions of salts 1–9.

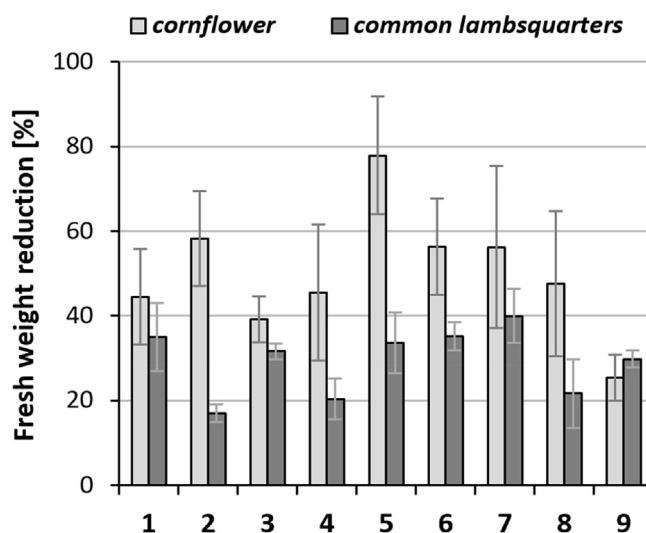


Fig. 6. Fresh weight reduction of cornflower and common lambsquarters (2 weeks after treatment).

active ingredient. These findings prove that further experiments should be conducted to determine the relationship between the size of the cations in HILs and their biological activity.

2.2.7. Octanol–water partition coefficient

The hydrophobicity of compounds is often characterized by the octanol–water partition coefficient ($\log K_{OW}$) value. The determination of this parameter is significantly important in the case of herbicides because it is strongly related with the assessment of their environmental risk (e.g., bioaccumulation, toxicity or sorption to soils).⁵⁶ Because the K_{OW} coefficient in the case of ionic liquids depends on the concentration,⁵⁷ all measurements have been made for a concentration equal to the dose applied in the herbicidal activity experiment (300 g of active ingredient per hectare with correspondence to the concentration equal to 12.8 mM of 2,4-DP). The obtained results are shown in Table 4. In the case of salts 1–7, the lowest $\log K_{OW}$ was characterized by the compound containing benzalkonium cation (1). This value relates to the presence of the benzyl group in the structure of this ionic liquid. Similar results were also noted for other HILs based on fomesafen.³⁰ It is worth mentioning that the highest lipophilicity was measured for the salt 7, containing the longest (octadecyl) alkyl substituent in the cation.

Generally, increasing the number of carbon atoms in the alkyl chains of dialkyldimethylammonium (3 and 4) as well as alkyltrimethylammonium (5–7) caused a slight growth of the $\log K_{OW}$ values.⁵⁸ This tendency is also visible for salts containing only short

Table 4
Values of logarithm of octanol–water partition coefficient of 1–9 and 2,4-DP at 25 °C.

Salt	Log K_{OW}
1	0.63 ± 0.14
2	0.85 ± 0.10
3	0.71 ± 0.07
4	0.82 ± 0.09
5	0.86 ± 0.14
6	0.73 ± 0.12
7	0.98 ± 0.06
8	-1.26 ± 0.01
9	0.35 ± 0.12
2,4-DP free acid	1.11 ± 0.14

alkyl chains as the substituents (**8** and **9**). A very low value observed for **8** is due to the presence of a hydroxyl group which additionally enhances the hydrophilicity of this salt.⁵⁹ It should also be emphasized that all the obtained compounds show lower values of the log K_{OW} compared to the 2,4-DP free acid. Therefore, we can conclude that new ionic forms of 2,4-DP will be characterized by a lower accumulation in the environment because smaller K_{OW} values have been correlated with reduction of bioaccumulation and toxicity in fish, as well as sorption to soils and sediments.⁵⁶ On the other hand, HILs with a low lipophilicity may exhibit a negative impact on the environment. According to present findings, some pesticides could be easily leached from the soil into watercourses, thus the negative values of the log K_{OW} (as in the case of salt **8**) may result in an increased risk of pollution of the hydrosphere.⁶⁰ Moreover, a low lipophilicity may also hinder the penetration of the active ingredient through the leaf membrane and facilitate the volatilization of herbicides (particularly in forms of esters and protic ammonium salts) from plants.^{61,62}

2.3. Herbicidal activity

The efficacy of synthesized salts **1–9** has been determined in greenhouse experiments towards cornflower and common lambsquarters. The enhancement of the herbicidal efficacy of HILs comprising at least one long alkyl chain attached to the nitrogen atom in the cation has been confirmed repeatedly.^{22–29,54} Therefore, the obtained salts were used at a dose of 300 g of active ingredient per hectare, which corresponds to 25% of the average recommended dose for commercial preparations comprising 2,4-DP (i.e., Optica DP 600SL, AH Marks and Company Ltd. and Duplosan DP 600SL, Nufarm GmbH & Co KG). Despite an extremely low amount of the active substance, the main symptoms of plant damage, such as deformation of shoots, leaves and disruption of plant growth caused by auxin-like herbicides, were observed during the experiment for all the examined salts.

The results of the greenhouse experiments (Fig. 6 and Table S7 in ESI) indicate that the herbicidal activity of the 2-(2,4-dichlorophenoxy)propionate anion was preserved, while all compounds (except **8**, which, due to its melting point above 100 °C, is not an IL) may be classified as new herbicidal ionic liquids (HILs). The level of weed control depended on both the weed species and the tested compound. HILs with a shorter alkyl chain (particularly salt with a tetrabutylammonium cation (**9**)) were characterized by a slightly lower herbicidal activity compared to some HILs with longer chains on the cation (**2**, **5–7**), especially against common lambsquarters. The most active compound in the performed experiment towards cornflower was HIL with a dodecyltrimethylammonium cation (**5**), which almost reached the efficacy of approx. 80%. Furthermore, good results exceeding 50% of fresh weight reduction of cornflower were also reported for **2**, **6** and **7**. It should be mentioned that the increase of alkyl chain length in dialkyldimethylammonium HILs (**3**, **4**) as well as in alkyltrimethylammonium HILs (**5–7**) had a low impact on the increase of efficacy towards common lambsquarters. Among all synthesized salts, HILs comprising an alkyltrimethylammonium cation (**5–7**) may be selected as the compounds characterized by the highest biological activity towards both plants. Nevertheless, the obtained new forms of 2,4-DP require additional tests associated with the determination of the influence of the applied dose of the active ingredient on the herbicidal efficiency.

3. Conclusion

The combination of cost effective and commercially available tetraalkylammonium cations with a common phenoxyacid

herbicide - 2-(2,4-dichlorophenoxy)propionate anion (2,4-DP) resulted in the synthesis of nine new salts, eight of which could be classified as ionic liquids. The products comprising at least one long alkyl substituent were liquids at room temperature. Thus, the utilization of specific cations may result in the liquefaction of new derivatives of 2,4-DP. Generally, the alkyl length elongation caused a decrease in their density, refractive index and solubility in water. Choline 2-(2,4-dichlorophenoxy)propionate exhibited a melting point at 119 °C and an unexpected cold crystallization at 67 °C, which may be explained by the extremely high hygroscopicity of this salt. The thermal stability results indicate that the novel forms of phenoxy acids, due to the presence of an ionic bonding, possess low volatility; therefore, the risk of drift during and after their application may be minimalized. The greenhouse experiments towards cornflower and common lambsquarters confirmed that the synthesized salts possess herbicidal activity. Due to the observed typical, auxin-like herbicide injury symptoms, such as shoot deformation and disruption of plant growth, eight of the obtained products may be classified as herbicidal ionic liquids (HILs). Despite the good surface properties of dialkyldimethylammonium based HILs, they demonstrated a moderate herbicidal efficiency. This phenomenon may be caused by the large molar volume of the applied cations which hindered the absorption of the active ingredient into the plant. The obtained values of the logarithm of the octanol–water partition coefficient for new ionic forms of 2,4-DP indicate their lower potential of bioaccumulation in comparison to 2-(2,4-dichlorophenoxy)propionic acid.

4. Experimental section

4.1. Materials

Tetrabutylammonium bromide (99%), trimethyl(tetradecyl) ammonium bromide (98%), 2-hydroxyethyltrimethylammonium chloride (choline chloride, 99%), (hydrogenated tallow)benzyltrimethylammonium chloride (benzalkonium chloride, 95%) and all solvents (methanol, DMSO, acetonitrile, acetone, isopropanol, ethyl acetate, chloroform, toluene, hexane) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Di(hydrogenated tallow)dimethylammonium chloride (76% solution in isopropanol) and bis(2-hydroxyethyl)methylolammonium chloride (80% solution in isopropanol) were purchased from AkzoNobel (Amsterdam, Netherlands), didcyltrimethylammonium chloride (40% solution in water), dodecyltrimethylammonium chloride (99%), trimethyl(octadecyl)ammonium chloride (95%) were purchased from KCI Limited (Seoul, South Korea). Potassium hydroxide (>85%) was purchased from Avantor Performance Materials Poland S.A (Gliwice, Poland). All quaternary ammonium chlorides were thoroughly dehydrated/dried and then stored over P_2O_5 before the synthesis. Other chemicals were used without further purification.

4.2. General

¹H NMR spectra were recorded on a Mercury Gemini 300 and Varian VNMR-S 400 MHz spectrometers operating at 300 MHz and 400 MHz with TMS as the internal standard. ¹³C NMR spectra were obtained with the same instruments at 75 and 100 MHz. The elemental analyses (CHN) were performed at the Adam Mickiewicz University, Poznan (Poland). The IR spectra were collected by using semi-automated system EasyMax 102 (Mettler Toledo) connected with ReactIR iC15 (Mettler Toledo) probe equipped with an MCT detector and a 9.5-mm AgX probe with a diamond tip. The data were sampled from 3000 to 650 cm^{-1} with 8- cm^{-1} resolution and processed by iCIR 4.3 software. High resolution mass spectra (HRMS) were performed in a Bruker Impact HD ESI-Q-TOF

(electrospray ionization - quadrupole - time of flight) mass spectrometer. The positive ionization mode was used to record cations, whereas the negative ionization mode was applied to record anion in obtained ILs. The melting point was assayed using the METTLER TOLEDO MP 90 melting point system. The samples were placed in capillary and transferred to the measuring cell. The heating rate was set to $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The water content for salts **1–7** and **9** was determined using an Aquastar volumetric Karl Fischer titration with Composite 5 solution as the titrant, and the anhydrous methanol was found to be less than 5000 ppm H_2O . The amount of water in the choline 2-(2,4-dichlorophenoxy)propionate (**8**) has not been analysed due to its very high hygroscopicity.

4.3. Density measurements

The density was determined using an Automatic Density Meter DDM2911 with a mechanical oscillator method. The density of the samples, approximately 2.0 mL, was measured with respect to temperature controlled conditions *via* Peltier, from 20 to $80\text{ }^{\circ}\text{C}$. The apparatus used was calibrated using deionized water as the reference substance. After each series of measurements, the densimeter was washed by two kinds of solvents (methanol and acetone) and dried.

4.4. Viscosity measurements

The viscosity was determined using a rheometer (Rheotec RC30-CPS) with a cone-shaped geometry (C50-2). The viscosity of the samples, approximately 1.5 mL was measured with respect to temperature, from 20 to $80\text{ }^{\circ}\text{C}$. The uncertainty of the viscosity measurement was estimated to be less than 10^{-4} Pa s.

4.5. Refractive index measurements

The refractive index was determined using an Automatic Refractometer J357 with an electronic temperature control. The samples, in a volume of approximately 1 mL, were measured in a range of temperatures from $20\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$. The uncertainty of measurement was estimated as value 10^{-5} .

4.6. Thermal analysis

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. The samples between 5 and 15 mg were placed in aluminium pans and were heated from 25 to $160\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\text{ min}^{-1}$ and cooled at a cooling rate of $10\text{ }^{\circ}\text{C}\text{ min}^{-1}$ to $-100\text{ }^{\circ}\text{C}$. The thermogravimetric analyses were performed on a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. The samples between 2 and 10 mg were placed in aluminium pans and were heated from 30 to $500\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C}\text{ min}^{-1}$.

4.7. Cationic active substance content

The cationic active substance content was assayed by a direct two-phase titration according to EN ISO 2871-1:2010. The method is based on the titration in the water-chloroform biphasic system (or water-methanol-chloroform in the case of compounds with limited solubility in water) of the solution of the ammonium salt by a standard solution of sodium dodecylsulfate(VI) in the presence of the mixed indicator (for determination of cationic active, dimidium bromide indicator (CAS: 518-67-2) is used; and for determination of anionic active, sulfan blue indicator (CAS: 129-17-9) is employed.

4.8. Solubilities

The solubilities of the prepared salts in the ten representative solvents were determined according to the protocols in Vogel's Textbook of Practical Organic Chemistry.⁶³ A 0.1 g sample of each salt was added to a certain volume of solvent, and the samples were thermostated in a Water Bath (MEMMERT Model WNB 7) at $25\text{ }^{\circ}\text{C}$. Based on the volume of the solvent used, 3 types of behaviours were recorded as follows: 'good solubility' applies to compounds which dissolved in 1 mL of solvent, 'limited solubility' applies to compounds that dissolved in 3 mL of solvent, and 'poor solubility' applies to the compounds which did not dissolve in 3 mL of solvent.

4.9. Surface activity

The surface tension and contact angle measurements were carried out using a DSA 100E analyser (Krüss, Germany, accuracy $\pm 0.01\text{ mN m}^{-1}$), at $25\text{ }^{\circ}\text{C}$. The surface tension was determined using the shape drop method. Basically, the principle of this method is to form an axisymmetric drop at the tip of a needle of a syringe. The image of the drop is taken with a CCD camera and digitized. The surface tension (γ in $\text{mN}\cdot\text{m}^{-1}$) was calculated by analysing the profile of the drop according to the Laplace equation. The temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy $\pm 0.1\text{ }^{\circ}\text{C}$). The determination of the contact angle was based on the sessile drop method, *i.e.*, drops of liquid are deposited on a solid surface (paraffin). During the measurement, a photo of the tested droplet was taken.

4.10. Octanol–water partition coefficients

The octanol–water partition coefficients (K_{OW}) of the herbicidal salts and 2,4-DP free acid were estimated by the shake-flask method according to OECD guidelines.⁶⁴ Measurements of K_{OW} values were conducted using mutually saturated water and *n*-octanol in a glass vial containing a magnetic stir bar. First, synthesized salts or 2,4-DP in form of free acid were saturated in 5 mL of octanol and then 5 mL of distilled water was added. All vials have been shaken at a constant temperature of $25\text{ }^{\circ}\text{C}$. After 24 h, all samples were centrifuged and the octanol phase was collected by a syringe. The concentrations compounds in the octanol were determined spectrophotometrically using a UV/Vis spectrophotometer (based on formerly made calibration curves with plots of absorbance (at $\lambda_{\text{max}} = 286\text{ nm}$) vs. concentration for each substance). Three repetitions of each measurement were performed.

4.11. Greenhouse experiments

The cornflower (*Centaurea cyanus* L.) and common lambsquarters (*Chenopodium album* L.) plants were grown in 0.5-L plastic pots containing commercial peat-based potting material. Within 10 days after emergence, the plants were thinned to five per pot and watered as needed. All ILs were dissolved in a mixture of water and ethanol (1:1 v/v) in an amount corresponding to the dose of 300 g of 2,4-DP-P per 1 ha (which corresponds to 600 g of the obtained products containing a racemic mixture of 2,4-DP per 1 ha). The treatments were applied at the 4 leaf stage using a moving sprayer occupied with Tee Jet 110/02 flat-fan nozzles delivering 200 L of spray solution per 1 ha at 0.2 MPa pressure. The plants were placed in a greenhouse at a temperature of $20\text{ }^{\circ}\text{C}$, a humidity of 60% and a photoperiod of 16/8 (day/night hours). The study was carried out in four replications in a completely randomized setup. After 2 weeks, the plants were cut to soil level and weighed (at 0.01 g accuracy). The reduction of plant fresh weight was determined in comparison to the water:ethanol treatment (control).

4.12. Preparation of HILs

First, 0.015 mol of dried tetraalkylammonium halide was dissolved in 25 mL of anhydrous methanol. Then, a stoichiometric amount of potassium hydroxide (0.84 g, 0.015 mol) dissolved in 25 mL of anhydrous methanol was added. The reaction was conducted for 30 min, and the precipitated inorganic by-product (potassium chloride or potassium bromide) was removed by filtration. Then, the filtrate containing tetraalkylammonium hydroxide was neutralized with 2-(2,4-dichlorophenoxy)propionic acid (3.53 g, 0.015 mol). All neutralization reactions were conducted in a Mettler Toledo semi-automated reactor system EasyMax™ equipped with a glass electrode at 25 °C. Next, the solvent was removed under reduced pressure and the residue was dissolved in 50 mL of acetonitrile. The insoluble impurities were filtered off, and after the evaporation of the acetonitrile under reduced pressure, the obtained products were dried under vacuum for 24 h at 60 °C.

4.12.1. (Hydrogenated tallow)benzyltrimethylammonium 2-(2,4-dichlorophenoxy)propionate (**1**)

Colourless liquid (9.16 g, 94% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm] = 0.86 (3H, t, *J* = 5.4 Hz, CH₂CH₃); 1.16–1.35 (26H, m, (CH₂)_nCH₃); 1.43 (3H, d, *J* = 5.7 Hz, CHCH₃); 1.69–1.82 (2H, m, ⁺NCH₂CH₂); 2.96 (6H, s, ⁺N(CH₃)₂); 3.22–3.30 (2H, m, ⁺NCH₂CH₂); 4.27–4.37 (1H, m, CHCH₃); 4.59 (2H, s, ⁺NCH₂C₆H₅); 6.88 (1H, d, *J* = 8.5 Hz, CCICH=CHC); 7.17–7.23 (1H, m, CCICH=CHC); 7.40 (1H, d, *J* = 3.8 Hz, CCICH=CCI); 7.48–7.57 (5H, m, ⁺NCH₂C₆H₅); ¹³C NMR (100 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 19.1, 21.9, 22.1, 25.9, 28.4, 28.8, 28.9, 29.1, 31.4, 48.9, 63.3, 66.0, 76.6, 115.3, 121.7, 122.8, 127.4, 128.3, 128.6, 128.8, 130.1, 133.0, 153.6, 172.3. IR ν_{max} [cm⁻¹] = 654, 679, 702, 736, 779, 807, 832, 864, 941, 1037, 1056, 1088, 1126, 1152, 1246, 1266, 1280, 1360, 1391, 1478, 1611, 2854, 2955. HRMS (ESI-Q-TOF), (ES⁺) for C₂₁H₃₈N⁺ [m/z] = 304.2999 (calculated), 304.3001 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9770 (found).

4.12.2. Bis(2-hydroxyethyl)methylololeylammonium 2-(2,4-dichlorophenoxy)propionate (**2**)

Colourless liquid (8.97 g, 89% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm] = 0.80 (3H, s, -CH₂CH₃); 1.08–1.32 (20H, m, (CH₂)_nCH₃); 1.38 (3H, d, *J* = 5.0 Hz, CHCH₃); 1.52–1.65 (2H, m, ⁺NCH₂CH₂); 1.85–2.00 (3H, m, CH₂CHCH₂); 3.03 (3H, s, ⁺NCH₃); 3.30 (2H, t, *J* = 9.0 Hz, ⁺NCH₂CH₂); 3.39 (4H, s, ⁺N(CH₂CH₂OH)₂); 3.76 (4H, t, *J* = 5.0 Hz, ⁺N(CH₂CH₂OH)₂); 4.20–4.28 (1H, m, CHCH₃); 5.21–5.33 (1H, m, CH₂CHCH₂); 6.16 (2H, s, ⁺N(CH₂CH₂OH)₂); 6.77 (1H, t, *J* = 9.0 Hz, CCICH=CHC); 7.17–7.22 (1H, m, CCICH=CHC); 7.37 (1H, t, *J* = 3.0 Hz, CCICH=CCI); ¹³C NMR (100 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 19.1, 21.6, 22.1, 25.5, 25.9, 26.6, 28.6, 29.1, 32.3, 32.0, 49.0, 54.7, 62.0, 62.4, 63.3, 76.5, 115.2, 121.8, 122.9, 127.5, 128.7, 129.6, 130.0, 153.6, 173.0. IR ν_{max} [cm⁻¹] = 655, 684, 740, 809, 833, 869, 955, 1041, 1059, 1092, 1130, 1159, 1248, 1268, 1283, 1365, 1394, 1479, 1609, 2856, 2927. HRMS (ESI-Q-TOF), (ES⁺) for C₂₃H₄₈NO₂⁺ [m/z] = 370.3680 (calculated), 370.3688 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9767 (found).

4.12.3. Didecyltrimethylammonium 2-(2,4-dichlorophenoxy)propionate (**3**)

Colourless liquid (8.41 g, 90% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm] = 0.86 (6H, t, *J* = 7.6 Hz, CH₂CH₃); 1.16–1.34 (28H, m, (CH₂)₇CH₃); 1.40 (3H, d, *J* = 6.8 Hz, CHCH₃); 1.54–1.67 (4H, m, ⁺N(CH₂CH₂)₂); 2.92–3.09 (6H, m, ⁺N(CH₃)₂); 3.16–3.32 (4H, m, ⁺N(CH₂CH₂)₂); 4.16–4.27 (1H, m, CHCH₃); 6.85 (1H, d, *J* = 8.9 Hz, CCICH=CHC); 7.19–7.24 (1H, m, CCICH=CHC); 7.41 (1H, d, *J* = 3.4 Hz, CCICH=CCI); ¹³C NMR (100 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 19.4, 21.7, 22.0, 22.1, 25.8, 28.4, 28.5, 28.7, 28.9, 28.9,

29.0, 31.2, 31.3, 49.9, 62.7, 76.9, 115.4, 121.6, 122.6, 127.4, 128.5, 153.7, 171.9. IR ν_{max} [cm⁻¹] = 653, 680, 741, 808, 831, 867, 902, 941, 956, 1035, 1060, 1091, 1104, 1127, 1158, 1248, 1268, 1279, 1291, 1360, 1389, 1479, 1614, 2856, 2926. Elemental analysis calculated for C₃₁H₅₅Cl₂NO₃ (M_{mol} = 560.61 g mol⁻¹) (%): C = 66.41, H = 9.89, N = 2.50; found: C = 66.15, H = 10.05, N = 2.69. HRMS (ESI-Q-TOF), (ES⁺) for C₂₂H₄₈N⁺ [m/z] = 326.3781 (calculated), 326.3785 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9773 (found).

4.12.4. Di(hydrogenated tallow)dimethylammonium 2-(2,4-dichlorophenoxy)propionate (**4**)

Colourless liquid (11.42 g, 92% yield). ¹H NMR (300 MHz, DMSO-*d*₆) δ [ppm] = 0.74–0.98 (6H, m, CH₂CH₃), 1.08–1.36 (56H, m, (CH₂)_nCH₃), 1.37 (3H, d, *J* = 6.7 Hz, CHCH₃), 1.61 (4H, s, ⁺N(CH₂CH₂)₂), 2.99 (6H, s, ⁺N(CH₃)₂), 3.13–3.26 (4H, m, ⁺N(CH₂CH₂)₂), 4.20 (1H, q, *J* = 7.0 Hz, CHCH₃), 6.81 (1H, d, *J* = 9.0 Hz, CCICH=CHC), 7.21 (1H, t, *J* = 5.8 Hz, CCICH=CHC), 7.42 (1H, d, *J* = 2.5 Hz, CCICH=CCI); ¹³C NMR (75 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 19.1, 21.6, 22.1, 25.7, 28.4, 28.7, 29.1, 32.3, 48.6, 76.9, 115.4, 121.6, 122.5, 127.4, 128.5, 153.7, 171.8. IR ν_{max} [cm⁻¹] = 654, 683, 722, 740, 778, 809, 831, 866, 939, 1037, 1059, 1091, 1128, 1151, 1249, 1267, 1279, 1290, 1360, 1388, 1481, 1614, 2856, 2927, 2984. HRMS (ESI-Q-TOF), (ES⁺) for C₃₈H₈₀N⁺ [m/z] = 550.6285 (calculated), 550.6273 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9773 (found).

4.12.5. Dodecyltrimethylammonium 2-(2,4-dichlorophenoxy)propionate (**5**)

Colourless liquid (6.94 g, 95% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm] = 0.86 (3H, t, *J* = 7.0 Hz, CH₂CH₃); 1.15–1.36 (18H, m, (CH₂)₉CH₃); 1.41 (3H, d, *J* = 7.0 Hz, CHCH₃); 1.58–1.68 (2H, m, ⁺NCH₂CH₂); 3.06 (9H, s, ⁺N(CH₃)₃); 3.25–3.32 (2H, m, ⁺NCH₂CH₂); 4.23 (1H, q, *J* = 7.0 Hz, CHCH₃); 6.86 (1H, d, *J* = 6.9 Hz, CCICH=CHC); 7.24 (1H, q, *J* = 4.9 Hz, CCICH=CHC); 7.41 (1H, d, *J* = 4.0 Hz, CCICH=CCI); ¹³C NMR (100 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 19.1, 22.1, 25.8, 28.6, 28.7, 28.8, 28.9, 29.0, 31.3, 51.9, 65.1, 76.9, 115.4, 121.6, 122.6, 127.4, 128.5, 153.7, 172.1. IR ν_{max} [cm⁻¹] = 655, 680, 740, 809, 831, 867, 911, 942, 969, 1036, 1058, 1091, 1105, 1125, 1247, 1267, 1280, 1360, 1391, 1478, 1609, 2856, 2927. Elemental analysis calculated for C₂₄H₄₁NCl₂NO₃ (M_{mol} = 462.50 g mol⁻¹) (%): C = 62.33, H = 8.94, N = 3.03; found: C = 62.58, H = 8.70, N = 2.80. HRMS (ESI-Q-TOF), (ES⁺) for C₁₅H₃₄N⁺ [m/z] = 228.2686 (calculated), 228.2685 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9765 (found).

4.12.6. Trimethyl(tetradecyl)ammonium 2-(2,4-dichlorophenoxy)propionate (**6**)

Colourless liquid (7.36 g, 93% yield). ¹H NMR (300 MHz, DMSO-*d*₆) δ [ppm] = 0.85 (3H, t, *J* = 5.2 Hz, CH₂CH₃); 1.13–1.37 (22H, m, (CH₂)₁₁CH₃); 1.43 (3H, d, *J* = 5.8 Hz, CHCH₃); 1.54–1.72 (2H, m, ⁺NCH₂CH₂); 3.05 (9H, s, ⁺N(CH₃)₃); 3.22–3.34 (2H, m, ⁺NCH₂CH₂); 4.36 (1H, q, *J* = 7.0 Hz, CHCH₃); 6.88 (1H, d, *J* = 9.4 Hz, CCICH=CHC); 7.19–7.27 (1H, m, CCICH=CHC); 7.43 (1H, d, *J* = 2.9 Hz, CCICH=CCI); ¹³C NMR (75 MHz, DMSO-*d*₆) δ [ppm] = 13.9, 18.9, 22.1, 28.6, 28.7, 28.9, 29.0, 29.01, 31.3, 52.0, 65.1, 76.1, 115.3, 121.8, 123.0, 127.4, 128.7, 153.4, 172.4. IR ν_{max} [cm⁻¹] = 655, 680, 740, 782, 809, 831, 866, 912, 941, 968, 1037, 1059, 1090, 1127, 1156, 1249, 1267, 1285, 1360, 1391, 1480, 1611, 2856, 2929, 2984. Elemental analysis calculated for C₂₆H₄₅Cl₂NO₃ (M_{mol} = 490.55 g mol⁻¹) (%): C = 63.66, H = 9.25, N = 2.86; found: C = 63.92, H = 9.43, N = 2.97. HRMS (ESI-Q-TOF), (ES⁺) for C₁₇H₃₈N⁺ [m/z] = 256.2999 (calculated), 256.2998 (found); (ES⁻) for C₉H₇C₁₂O₃⁻ [m/z] = 232.9778 (calculated), 232.9776 (found).

4.12.7. Trimethyl(octadecyl)ammonium 2-(2,4-dichlorophenoxy)propionate (**7**)

Colourless liquid (8.20 g, 91% yield). ^1H NMR (400 MHz, DMSO- d_6) δ [ppm] = 0.85 (3H, t, J = 7.0 Hz, CH_2CH_3); 1.16–1.34 (30H, m, $(\text{CH}_2)_{15}\text{CH}_3$); 1.41 (3H, d, J = 6.0 Hz, CHCH_3); 1.58–1.68 (2H, m, $^+\text{NCH}_2\text{CH}_2$); 3.06 (9H, s, $^+\text{N}(\text{CH}_3)_3$); 3.24–3.31 (2H, m, $^+\text{NCH}_2\text{CH}_2$); 4.28 (1H, q, J = 7.1 Hz, CHCH_3); 6.84 (1H, d, J = 7.9 Hz, $\text{CClCH}=\text{CHC}$); 7.20–7.25 (1H, m, $\text{CClCH}=\text{CHC}$); 7.41 (1H, d, J = 3.0 Hz, $\text{CClCH}=\text{CCl}$); ^{13}C NMR (100 MHz, DMSO- d_6) δ [ppm] = 13.9, 19.0, 22.1, 22.1, 25.8, 28.6, 28.8, 28.9, 29.0, 29.1, 31.3, 51.9, 65.1, 76.6, 115.3, 121.6, 122.7, 127.4, 128.6, 153.6, 172.0. IR ν_{max} [cm^{-1}] = 655, 680, 724, 740, 782, 809, 831, 869, 913, 942, 969, 1036, 1058, 1091, 1105, 1127, 1155, 1249, 1267, 1280, 1358, 1391, 1480, 1611, 2856, 2929, 2984. Elemental analysis calculated for $\text{C}_{30}\text{H}_{53}\text{NCl}_2\text{NO}_3$ (M_{mol} = 546.66 g mol $^{-1}$) (%): C = 65.92, H = 9.77, N = 2.56; found: C = 65.61, H = 9.94, N = 2.93. HRMS (ESI-Q-TOF), (ES+) for $\text{C}_{21}\text{H}_{46}\text{N}^+$ [m/z] = 312.3625 (calculated), 312.3625 (found); (ES-) for $\text{C}_9\text{H}_7\text{Cl}_2\text{O}_3^-$ [m/z] = 232.9778 (calculated), 232.9772 (found).

4.12.8. 2-Hydroxyethyltrimethylammonium 2-(2,4-dichlorophenoxy)propionate (**8**)

White crystalline solid (5.07 g, 95% yield). ^1H NMR (400 MHz, DMSO- d_6) δ [ppm] = 1.44 (3H, d, J = 6.7 Hz, CHCH_3); 3.13 (9H, s, $^+\text{N}(\text{CH}_3)_3$); 3.43 (2H, t, J = 5.1 Hz, $^+\text{NCH}_2\text{CH}_2\text{OH}$); 3.80–3.86 (2H, m, $^+\text{NCH}_2\text{CH}_2\text{OH}$); 4.30 (1H, q, J = 7.1 Hz, CHCH_3); 6.45 (1H, s, $^+\text{NCH}_2\text{CH}_2\text{OH}$); 6.85 (1H, d, J = 8.9 Hz, $\text{CClCH}=\text{CHC}$); 7.27 (1H, d, J = 5.8 Hz, $\text{CClCH}=\text{CHC}$); 7.46 (1H, d, J = 2.6 Hz, $\text{CClCH}=\text{CCl}$); ^{13}C NMR (100 MHz, DMSO- d_6) δ [ppm] = 19.1, 53.0, 55.0, 67.1, 76.5, 115.2, 121.7, 122.9, 127.5, 128.7, 153.5, 172.8. IR ν_{max} [cm^{-1}] = 654, 707, 740, 777, 820, 867, 955, 1005, 1041, 1059, 1088, 1130, 1248, 1270, 1283, 1358, 1395, 1479, 1605, 2159, 2917, 2950, 2998. Elemental analysis calculated for $\text{C}_{14}\text{H}_{21}\text{Cl}_2\text{NO}_4$ (M_{mol} = 338.23 g mol $^{-1}$) (%): C = 49.72, H = 6.26, N = 4.14; found: C = 49.64, H = 6.42, N = 4.04. HRMS (ESI-Q-TOF), (ES+) for $\text{C}_5\text{H}_{14}\text{NO}^+$ [m/z] = 104.1070 (calculated), 104.1071 (found); (ES-) for $\text{C}_9\text{H}_7\text{Cl}_2\text{O}_3^-$ [m/z] = 232.9778 (calculated), 232.9768 (found).

4.12.9. Tetrabutylammonium 2-(2,4-dichlorophenoxy)propionate (**9**)

White grease (7.15 g, 92% yield). ^1H NMR (300 MHz, DMSO- d_6) δ [ppm] = 0.84–1.05 (12H, m, CH_2CH_3); 1.21–1.36 (8H, m, CH_2CH_3); 1.41 (3H, d, J = 6.6 Hz, CHCH_3); 1.48–1.71 (8H, m, $^+\text{NCH}_2\text{CH}_2$); 3.03–3.32 (8H, m, $^+\text{NCH}_2\text{CH}_2$); 4.24 (1H, q, J = 7.1 Hz, CHCH_3); 6.86 (1H, d, J = 9.4 Hz, $\text{CClCH}=\text{CHC}$); 7.20–7.25 (1H, m, $\text{CClCH}=\text{CHC}$); 7.42 (1H, d, J = 2.2 Hz, $\text{CClCH}=\text{CCl}$); ^{13}C NMR (75 MHz, DMSO- d_6) δ [ppm] = 13.0, 18.6, 18.8, 22.6, 57.1, 76.4, 115.0, 121.2, 122.1, 126.9, 128.1, 153.25, 171.6. IR ν_{max} [cm^{-1}] = 654, 707, 740, 777, 820, 867, 955, 1005, 1041, 1059, 1088, 1130, 1248, 1270, 1283, 1358, 1395, 1479, 1605, 2159, 2917, 2950, 2998. Elemental analysis calculated for $\text{C}_{25}\text{H}_{43}\text{NCl}_2\text{NO}_3$ (M_{mol} = 476.52 g mol $^{-1}$) (%): C = 63.01, H = 9.10, N = 2.94; found: C = 63.35, H = 8.79, N = 2.64. HRMS (ESI-Q-TOF), (ES+) for $\text{C}_{16}\text{H}_{36}\text{N}^+$ [m/z] = 242.2842 (calculated), 242.2845 (found); (ES-) for $\text{C}_9\text{H}_7\text{Cl}_2\text{O}_3^-$ [m/z] = 232.9778 (calculated), 232.9764 (found).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.tet.2017.11.032>.

References

- Tong S, Shi R, Zhang H, Ma C. *J Environ Sci*. 2010;22:1623–1628.
- Brillas E, Cabot P-L, Rodriguez RM, Arias C, Garrido JA, Oliver R. *Appl Catal B-Environ*. 2004;51:117–127.
- Westendorf A, Benndorf D, Pribyl T, Harms H, Müller RH. *Eng Life Sci*. 2006;6:552–559.
- Romero E, Matallo MB, Peña A, Sánchez-Rasero F, Schmitt-Kopplin Ph Dios G. *Environ Pollut*. 2001;111:209–215.
- Yildirim B, Yeşiloğlu T, Incesu M, Kamiloğlu MU, Çimen B, Tamer Ş. *New Zeal J Crop and Hort*. 2012;40:55–64.
- Stern RA, Flaishman M, Ben-Arie R. *Sci Hortic*. 2007;112:304–309.
- Müller RH, Babel W. *Biosci Biotechnol Biochem*. 2004;68:622–630.
- Özdemir S, Bekler FM, Okumus V, Dündar A, Kilinc E. *Environ Prog Sustain Energy*. 2012;31:544–552.
- Registration Decision for Dichlorprop-P, RD2014–04. Canada: Pest Management Regulatory Agency; 2014.
- Reregistration Eligibility Decision for Dichlorprop-p (2,4-DP-p), EPA 738-R-07–008. United States of America: Environmental Protection Agency; 2007.
- TOXNET Databases: 2-(2,4-dichlorophenoxy)propionic acid, <https://chem.nlm.nih.gov/chemidplus/rn/120-36-5> (accessed 10th of July, 2017).
- TOXNET Databases: 2,4-dichlorophenoxyacetic acid, <https://chem.nlm.nih.gov/chemidplus/rn/94-75-7> (accessed 10th of July, 2017).
- Kavrovski ZS, Rafajlovska VG. *J Anal Chem*. 2015;70:995–1000.
- Okumus V, Çelik KS, Özdemir S, Dündar A, Kilinc E. *Water Treat*. 2015;56:1898–1907.
- Rosales-Conrado N, León-González ME, Pérez-Arribas LV, Polo-Díez LM. *J Chromatogr A*. 2005;1076:202–206.
- de Namor AFD, Zvietcovich-Guerra JA, Grachev V, Aparicio-Aragón WB, Zegarra-Fernandez K, Sueros-Velarde FJ. *New J Chem*. 2005;29:1072–1076.
- Tong S-P, Shi R, Zhang H, Ma C-A. *J Hazard Mater*. 2011;185:162–167.
- Liao C-J, Chen C-P, Wang M-K, Chiang P-N, Pai C-W. *Environ Toxicol*. 2006;21:71–79.
- González S, Müller J, Petrovic M, Barceló D, Knepper TP. *Environ Pollut*. 2006;144:926–932.
- Brillas E, Baños MA, Skoumal M, Cabot PL, Garrido JA, Rodriguez RM. *Chemosphere*. 2007;68:199–209.
- Kamaraj R, Davidson DJ, Sozhan G, Vasudevan S. *RSC Adv*. 2015;5:39799–39809.
- Pernak J, Syguda A, Janiszewska D, Materna K, Praczyk T. *Tetrahedron*. 2011;67:4838–4844.
- Praczyk T, Kardasz P, Jakubiak E, Syguda A, Materna K, Pernak J. *Weed Sci*. 2012;60:189–192.
- Pernak J, Syguda A, Materna K, Janus E, Kardasz P, Praczyk T. *Tetrahedron*. 2012;68:4267–4273.
- Niemczak M, Giszter R, Czerniak K, Marcinkowska K, Walkiewicz F. *RSC Adv*. 2015;5:15487–15493.
- Cojocar OA, Shamshina JL, Gurau G, et al. *Green Chem*. 2013;15:2110–2120.
- Pernak J, Niemczak M, Shamshina JL, et al. *J Agric Food Chem*. 2015;13:3357–3366.
- Zhu J, Ding G, Liu Y, et al. *Chem Eng J*. 2015;279:472–477.
- Pernak J, Niemczak M, Giszter R, et al. *ACS Sustain Chem Eng*. 2014;2:2845–2851.
- Ding G, Liu Y, Wang B, et al. *New J Chem*. 2014;38:5590–5596.
- Wang B, Ding G, Zhu J, et al. *Tetrahedron*. 2015;71:7860–7864.
- Pernak J, Niemczak M, Zakrocka K, Praczyk T. *Tetrahedron*. 2013;69:8132–8136.
- Pernak J, Czerniak K, Niemczak M, et al. *New J Chem*. 2015;39:5715–5724.
- Ławniczak Ł, Materna K, Framski G, Szulc A, Syguda A. *Biodegradation*. 2015;26:327–340.
- Pernak J, Giszter R, Biedziak A, et al. *J Agric Food Chem*. 2017;65:260–269.
- Pernak J, Niemczak M, Chrzanowski Ł, et al. *Chem Eur J*. 2016;22:12012–12021.
- Pernak J, Czerniak K, Biedziak A, et al. *RSC Adv*. 2016;6:52781–52789.
- Niemczak M, Chrzanowski Ł, Praczyk T, Pernak J. *New J Chem*. 2017;41:8066–8077.
- Pernak J, Niemczak M, Materna K, Marcinkowska K, Praczyk T. *Tetrahedron*. 2013;69:4665–4669.
- Pernak J, Markiewicz B, Zgola-Grzeskowiak A, et al. *RSC Adv*. 2014;4:39751–39754.
- Choudhary H, Pernak J, Shamshina JL, et al. *ACS Sustain Chem Eng*. 2017;5:6261–6273.
- Bica K, Rogers RD. *Chem Commun*. 2010;46:1215–1217.
- Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M. *J Phys Chem B*. 2005;109:6103–6110.
- Kordala-Markiewicz R, Rodak H, Markiewicz B, et al. *Tetrahedron*. 2014;70:4784–4789.
- Markiewicz B, Sznajdrowska A, Chrzanowski Ł, et al. *New J Chem*. 2014;38:3149–3153.
- Losetty V, Chennuri BK, Gardas RI. *J Chem Thermodyn*. 2016;92:175–181.
- Shirota H, Matsuzaki H, Ramati S, Wishart JF. *J Phys Chem B*. 2015;119:9173–9187.
- Jacquemin J, Husson P, Padua AA, Majer V. *Green Chem*. 2006;8:172–180.
- Pernak J, Niemczak M, Materna K, Zelechowski K, Marcinkowska K, Praczyk T. *RSC Adv*. 2016;6:7330–7338.

50. Kolbeck C, Lehmann J, Lovelock KRJ, et al. *J Phys Chem B*. 2010;114:17025–17036.
51. Seki S, Tsuzuki S, Hayamizu K, et al. *J Chem Eng*. 2012;57:2211–2216.
52. Almeida HFD, Lopes-da-Silva JA, Freire MG, Coutinho JAP. *J Chem Thermodyn*. 2013;57:372–379.
53. Gorska B, Timperman L, Anouti M, Pernak J, Béguin F. *RSC Adv*. 2016;6:55144–55158.
54. Marcinkowska K, Praczyk T, Gawlak M, Niemczak M, Pernak J. *Crop Prot*. 2017;98:85–93.
55. Lebga-Nebane JL, Rock SE, Franclemont J, Roy D, Krishnan S. *Ind Eng Chem Res*. 2012;51:14084–14098.
56. Ropel L, Belvêze LS, Aki SNVK, Stadtherr MA, Brennecke JF. *Green Chem*. 2005;7:83–90.
57. Jain P, Kumar A. *Phys Chem Chem Phys*. 2016;18:1105–1113.
58. Rybinska A, Sosnowska A, Grzonkowska M, Barycki M, Puzyn T. *J Hazard Mater*. 2016;303:137–144.
59. Tang S, Baker GA, Zhao H. *Chem Soc Rev*. 2012;41:4030–4066.
60. Carlile WR. *Pesticide Selectivity, Health and the Environment*. first ed. Cambridge University Press; 2006:192–193.
61. Tang G, Liu Y, Ding G, et al. *New J Chem*. 2017;41:8650–8655.
62. Lichiheb N, Personne E, Bedos C, Van den Berg F, Barriuso E. *Sci Total Environ*. 2016;550:1022–1031.
63. Vogel AI, Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR. In: Vogel's, ed. *Textbook of Practical Organic Chemistry*. fifth ed. New York: Wiley John & Sons Inc; 1989:1203–1204.
64. OECD, Product Properties Test Guidelines OPPTS 830.7550 Partition Coefficient (n-Octanol/Water), Shake Flask Method.