## 8

## **Research Article**

Marcin Praczyk, Katarzyna Wielgusz, Witold Stachowiak, Michał Niemczak, Juliusz Pernak\*

# Synthesis and efficacy of herbicidal ionic liquids with chlorsulfuron as the anion

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Abstract: In the framework of this research, four new herbicidal ionic liquids (HILs) comprising chlorsulfuron as the anion were synthesized and characterized. The new salts with chlorsulfuron contained the following cations: tetramethylammonium, didecyldimethylammonium, benzyltrimethylammonium and cholinium. All products were obtained with high yields exceeding 90% via acid-base reaction or ion exchange reaction. by the use of environment-friendly solvents. The structures of all synthesized HILs were confirmed by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses. Their efficacy against weeds has been studied under field conditions in fiber flax. All HILs showed herbicidal activity but efficiency was highly dependent on the type of cation and weed species. There were no statistically significant differences in the effectiveness of HILs toward common lambsquarters compared to the reference herbicide, except for salt with cholinium cation that showed significantly lower efficiency. As regards barnyard grass control, all HILs exhibited significantly lower efficacy than that of the reference herbicide, except for didecyldimethylammonium salt that showed similar activity. The synthesized products did not cause damage to flax plants. The obtained results confirmed that the herbicidal effectiveness of the active ingredient (chlorsulfuron) in the form of an ionic liquid can be adjusted by the selection of an appropriate cation in the synthesis.

**Keywords:** herbicidal ionic liquids, sulfonylurea, spectral analysis, plant protection, herbicides

## 1 Introduction

Chlorsulfuron is a selective herbicide belonging to the group of sulfonylureas that was commercialized in the 1980s. It is mainly utilized in cereal crops for controlling broad-leaf weeds and some grasses. This herbicide is also characterized by high selectivity for flax plants (Linum usitatissimum L.) and is known to be a potential agent for the protection of this crop. Flax is one of the oldest cultivated crops used for fiber and seed [1,2]. The advantages of chlorsulfuron, such as low effective dose (approx. 10-40 g per hectare), relatively low toxicity (LD<sub>50</sub>, rat, orally =  $5.545 \,\mathrm{g/kg}$ ) and high popularity worldwide, make it a promising source of anion in the synthesis of new forms of this compound [3]. Currently, on the basis of the risk analysis related to the use of chlorsulfuron, the European Commission has decided to withdraw this substance from the market. The process of reviewing the pesticidally active substances lasts in the European Union for almost 30 years. The main basis for this action was a Directive 91/414/EEC, released in 1991. However, the policy regarding the use of chemicals has changed radically after the adoption of the REACH regulation in 2006. Subsequent legal acts such as Regulation No. 1107/2009 and Directive 128/2009/EC resulted in the implementation of even more drastic restrictions in the use of plant protection products. As a result, a large number of active substances in plant protection products have been withdrawn from the market and further restrictions are being planned in the near future. This action is also strongly related to the adopted strategy of the European Green Deal. The deterioration in the availability of the chemical plant protection products makes the farmers in the European Union extremely difficult to ensure plant health and high-quality of plant production. Nevertheless, due to the fact that other methods focused on the protection of agricultural plants against weeds are less effective and more expensive, the use of chemical herbicides is nowadays the basic approach and the most probably this situation will not change in the near future. It is indisputable that the use of herbicides, in addition to the

<sup>\*</sup> Corresponding author: Juliusz Pernak, Poznan University of Technology, Faculty of Chemical Technology, Berdychowo 4, 60-965 Poznan, Poland, e-mail: juliusz.pernak@put.poznan.pl Marcin Praczyk, Katarzyna Wielgusz: Institute of Natural Fibres and Medicinal Plants, Wojska Polskiego 71 B, Poznan, Poland Witold Stachowiak, Michał Niemczak: Poznan University of Technology, Faculty of Chemical Technology, Berdychowo 4, 60-965 Poznan, Poland

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obvious benefits, may have a negative impact on the environment and therefore we should focus our effort to minimize this phenomenon. In a current situation, when registration of new herbicidally active substances is much more difficult, the research on the improvement of existing substances, even if they have been removed from the market, is justified. This strategy indicates a new direction in the preparation of herbicidal formulations, which complies with the principles of "green chemistry." This is the reason why it is important to develop its novel herbicidal formulations that are characterized with even lower environmental impact and greater efficacy. One of the possibilities to reduce the negative environmental impact of herbicides is their transformation into ionic liquids (ILs) exhibiting herbicidal activity commonly known as herbicidal ionic liquids (HILs).

HILs belong to ILs which beside a melting temperature below 100°C contain at least one ion exhibiting herbicidal activity [4]. Their discovery in 2011 led to the formation of new chemical compounds from thirdgeneration ILs [5], characterized by increased herbicidal activity and multifunctional properties. This strategy demonstrates the possibility to develop more effective formulations starting from the commercially available herbicides, such as the derivatives of phenoxyacetic acid (2,4-Dichlorophenoxyacetic acid [2,4-D], 4-chloro-2-methylphenoxyacetic acid [MCPA], 2-(4-Chloro-2-methylphenoxy) propanoic acid [MCPP], 2-(2,4-dichlorophenoxy)propanoic acid [2,4-DP] and 4-(4-chloro-2-methylphenoxy)butanoic acid [MCPB]) [4,6–10], benzoic acid (dicamba) [11], clopyralid [12], fomesafen [13], glyphosate [14,15], metsulfuron methyl [16], bentazone [17], nicosulfuron [18], nonanoic acid [19] and picloram [20]. One of the most crucial advantages of HILs compared to the currently applied herbicidal formulations refers to their limited volatility [11]. This eliminates one of the most significant problems of pesticides, which leads to the contamination of neighboring areas through air emissions. Furthermore, utilization of HILs allows for a minimization of the herbicide dose per hectare, decrease of toxicity (toxic herbicides from the group of phenoxy acids were found to be nontoxic as HILs [4]) and introduction of specific physicochemical properties (such as surface activity, thermal stability and solubility in water). Additionally, the environmental impact including compounds' toxicity and biodegradability may be directly regulated by proper modification of the structure of the cation of HILs [21,22]. Previous publications demonstrate synthesis and characterization of HILs comprising the following anions: metsulfuron-methyl [16], iodosulfuron-methyl [23] and nicosulfuron [18]. However, HILs comprising chlorsulfuron as the anion have not been published so far.

Furthermore, tetraalkylammonium cations selected as the counterions for chlorsulfuron are commonly known, cost-effective and commercially available. It should also be emphasized that one of them are substance of natural origin. Choline (2-hydroxyethyltrimethylammonium) cation is an essential component of animal cells' membrane lipids and lipoproteins. However, due to insufficient production of choline in organism, this naturally occurring nutrient has to be provided by diet [24,25]. Additionally, choline derivatives were successfully utilized as blood preservatives [26], insect feeding deterrents [26], herbicides [27], antimicrobials [28] or as substrates for chemical synthesis [29]. It could be stressed that living organisms utilize choline to produce betaine and acetylcholine neurotransmitter, which mobilize muscles to motion thereby regulate breathing, heart rate and control skeletal muscles [24]. Interestingly, the cholinergic system is also found in plants [23] and non-neural tissues such as erythrocytes and placental cells [30]. Its stimulating effect on enzymes, which can affect metabolism [23,30,31], makes it an interesting source of cation for biologically active HILs.

# 2 Materials and methods

### 2.1 Materials

All materials were used as supplied unless otherwise noted. Chlorsulfuron (98%) was purchased from Pestinova. A 40% methanolic solution of tetramethylammonium hydroxide, 40% aqueous solution of benzyltrimethylammonium hydroxide, choline (2-hydroxyethyltrimethylammonium) chloride (98%) and all solvents (methanol (98%), dimethyl sulfoxide (DMSO; 98%), acetonitrile (99%), acetone (99%), 2-propanol (98%), ethyl acetate (99%), chloroform (98%), toluene (99.5%) and hexane (98%), were purchased from Sigma-Aldrich. A 50% isopropanol/water (2:3) solution of didecyldimethylammonium chloride was purchased from Merck. Water deionized (conductivity  $< 0.1 \,\mu\text{S cm}^{-1}$ ) with demineralizer HLP Smart 1000 (Hydrolab) was used.

#### 2.2 General

The IR spectra were recorded with a ReactIR iC15 (Mettler Toledo) spectrometer equipped with an MCT detector and a 9.5 mm AgX probe with a diamond tip in a range from 3,000 to 650 cm<sup>-1</sup> at 8 cm<sup>-1</sup> resolution. The iCIR 4.3 software was used to process the collected spectra. NMR spectra were recorded using tetramethylsilane (TMS) as the internal standard with the use of Mercury Gemini 300 spectrometer operating at 300 and 400 MHz (in the case of <sup>1</sup>H NMR spectra) or at 75 and 100 MHz (in the case of <sup>13</sup>C NMR spectra). The Karl Fisher TitroLine KF Trace coulometric titrator (SI Analytics) was utilized to analyze the water content in the obtained products.

## 2.3 Synthesis

#### 2.3.1 Method A

In a 50 cm<sup>3</sup> round-bottom flask equipped with a magnetic stirring bar, 0.01 mol of the solution of the corresponding tetraalkylammonium hydroxide (tetramethylammonium hydroxide, benzyltrimethylammonium hydroxide and choline hydroxide) was mixed with 5 cm<sup>3</sup> of methanol. Subsequently, an equimolar amount of chlorsulfuron herbicide (2-chloro-*N*-((4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoyl)benzenesulfonamide) was added to the flask. The mixture was then stirred for 10 min at room temperature and the progress of neutralization was monitored with Mettler Toledo SevenExcellence pH meter S400. Next, after evaporation of the solvent in a rotary evaporator, products (1, 3 and 4) were dried under vacuum (10 mbar) at 50°C for 48 h and stored over P<sub>4</sub>O<sub>10</sub>.

#### 2.3.2 Method B

First, the potassium salt of chlorsulfuron herbicide (2-chloro-*N*-((4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoyl) benzenesulfonamide) was obtained. After addition of equimolar amounts of chlorsulfuron to 20% methanolic solution of potassium hydroxide (0.04 mol), the progress of neutralization reaction was monitored with Mettler Toledo SevenExcellence pH meter S400. Then, the methanol was evaporated in a rotary evaporator and the product was dried under reduced pressure at 50°C for 48 h.

Subsequently, in a 50 cm<sup>3</sup> round-bottom flask equipped with a magnetic stirring bar, 0.01 mol of the corresponding tetraalkylammonium chloride (didecyldimethylammonium chloride) was dissolved in 10 cm<sup>3</sup> of methanol (2). Then, an equimolar amount of the potassium salt of chlorsulfuron herbicide (2-chloro-*N*-((4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoyl)

benzenesulfonamide) was added to the flask. The obtained mixture was stirred for 1 h at  $40^{\circ}$ C temperature, and the solvent was removed using a rotary evaporator. Then,  $20~\text{cm}^3$  of anhydrous acetone was added. After filtration of the precipitated sediment of inorganic byproduct, the solvent was evaporated from the filtrate. Finally, the product (2) was dried under reduced pressure at  $50^{\circ}$ C for 48~h and stored over  $P_4O_{10}$ .

## 2.4 Spectroscopic data

#### 2.4.1 Tetramethylammonium chlorsulfuron (1)

<sup>1</sup>H NMR (401.13 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 2.26 (s, 3H, CC<u>H</u><sub>3</sub> e), 3.08 (s, 12H,  ${}^{+}$ NC<u>H</u><sub>3</sub>), 3.81 (s, 3H, OC<u>H</u><sub>3</sub>), 7.33–7.44 (m, 3H, CHC<u>H</u>C<u>H</u>C<u>H</u>C), 7.95–8.00 (m, 1H, CClC<u>H</u>CH), 8.99 (s, 1H, CN<u>H</u>CO).

<sup>13</sup>C NMR (100.87 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 25.1, 54.1, 54.4(3), 126.2, 130.40, 130.6, 130.8, 131.2, 143.5, 154.6, 165.6, 170.6, 177.5.

IR  $v_{\text{max}}$  [cm<sup>-1</sup>] = 764, 792, 825, 861, 945, 1,038, 1,084, 1,109, 1,025, 1,135, 1,156, 1,221, 1,256, 1,308, 1,364, 1,392, 1,418, 1,480, 1,562, 1,655.

#### 2.4.2 Didecyldimethylammonium chlorsulfuron (2)

<sup>1</sup>H NMR (300.41 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 0.82–0.92 (m, 6H, CH<sub>2</sub>–C<u>H</u><sub>3</sub>), 1.16–1.36 (m, 28H, C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<sub>H</sub><sub>2</sub>C<sub>H</sub><sub>2</sub>C<sub>H</sub><sub>3</sub>), 1.54–1.69 (m, 4H, <sup>+</sup>NCH<sub>2</sub>C<u>H</u><sub>2</sub>C<sub>H</sub><sub>2</sub>), 2.27 (s, 3H, CC<u>H</u><sub>3</sub>), 2.99 (s, 6H, <sup>+</sup>NC<u>H</u><sub>3</sub>), 3.17–3.27 (m, 4H, <sup>+</sup>NC<u>H</u><sub>2</sub>CH<sub>2</sub>), 3.82 (s, 3H, OC<u>H</u><sub>3</sub>), 7.32–7.44 (m, 3H, CHC<u>H</u>C<u>H</u>C<u>H</u>C<u>H</u>C), 7.96–8.02 (m, 1H, CClC<u>H</u>CH), 8.97 (s, 1H, CN<u>H</u>CO).

<sup>13</sup>C NMR (75.55 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 14.0, 21.7, 22.1, 25.1, 25.8, 28.5, 28.7, 28.8, 28.9, 31.3, 50.0, 54.1, 62.8, 126.1, 130.4, 130.5, 130.9, 131.1, 143.5, 154.5, 165.6, 170.6, 177.4.

IR  $v_{\text{max}}$  [cm<sup>-1</sup>] = 758, 818, 881, 956, 1,040, 1,086, 1,105, 1,122, 1,142, 1,200, 1,234, 1,357, 1,467, 1,508, 1,554, 1,670, 1,711, 2,853, 2,925.

#### 2.4.3 Benzyltrimethylammonium chlorsulfuron (3)

<sup>1</sup>H NMR (399.91 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 2.27 (s, 3H, CC<u>H</u><sub>3</sub>), 3.03 (s, 9H, <sup>+</sup>NC<u>H</u><sub>3</sub>), 3.81 (s, 3H, OC<u>H</u><sub>3</sub>), 4.54 (s, 2H, <sup>+</sup>NC<u>H</u><sub>2</sub>C), 7.33–7.44 (m, 3H, CHC<u>H</u>C<u>H</u>C<u>H</u>C), 7.46–7.57 (m, 5H, CC<sub>6</sub><u>H</u><sub>5</sub>, 7.99–8.04 (m, 1H, CClC<u>H</u>CH), 9.05 (s, 1H, CNHCO).

<sup>13</sup>C NMR (100.57 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 25.1, 51.7, 54.1, 67.7, 126.2, 128.4, 128.8, 130.2, 130.4, 130.5, 130.9, 131.2, 132.8, 143.4, 154.7, 165.7, 170.6, 177.4.

IR  $v_{\text{max}}$  [cm<sup>-1</sup>] = 760, 818, 885, 954, 982, 1,040, 1,101, 1,107, 1,124, 1,200, 1,230, 1,342, 1,360, 1,366, 1,452, 1,470, 1,508, 1,552, 1,662.

#### 2.4.4 Choline chlorsulfuron (4)

<sup>1</sup>H NMR (402.65 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 2.29 (s, 3H,  $CCH_3$ ), 3.12 (s, 9H,  ${}^+NCH_3$ ), 3.37–3.35 (m, 2H,  ${}^+NCH_2CH_2$ ), 3.79–3.88 (m, 5H, CH<sub>2</sub>CH<sub>2</sub>OH, OCH<sub>3</sub>), 5.32 (br.s, 1H, CH<sub>2</sub>OH), 7.35-7.47 (m, 3H, CHCHCHCHC), 7.97-8.04 (m, 1H, CClCHCH), 9.01 (s, 1H, CNHCO).

<sup>13</sup>C NMR (101.25 MHz, DMSO-d<sub>6</sub>)  $\delta$  [ppm] = 25.5, 53.6(2), 53.7, 54.6, 55.7, 67.4, 126.7, 130.9, 131.0, 131.3, 131.7, 143.7, 155.0, 166.0, 171.0, 177.9.

IR  $\nu_{\text{max}}$  [cm<sup>-1</sup>] = 759, 773, 812, 897, 958, 1,030, 1,040, 1,092, 1,105, 1,120, 1,193, 1,228, 1,280, 1,146, 1,340, 1,370, 1,414, 1,457, 1,508, 1,570, 1,680.

## 2.5 Differential scanning calorimetry (DSC)

Mettler Toledo Star<sup>e</sup> DSC1 (Mettler Toledo) unit was utilized to analyze thermal transition temperatures of the synthesized salts. In the experiment, samples of products in a range from 4.5 to 7.0 mg were placed in aluminum pans and heated under nitrogen at a heating rate of 10°C min<sup>-1</sup> from 25 to 120°C. Subsequently, pans were cooled at a cooling rate equal to 10°C min<sup>-1</sup> to the temperature of -100°C and then heated again to 120°C.

## 2.6 Thermal gravimetric analysis (TGA)

Samples (approx. 4.0-5.0 mg) were weighed in aluminum pans and introduced into Mettler Toledo Stare TGA/DSC1 unit (Mettler Toledo). In the experiment, pans were heated under nitrogen at a constant heating rate (10°C min<sup>-1</sup>) starting from 30 to 450°C and the instrument recorded the mass loss during the process of heating.

## 2.7 Solubility

The following solvents, arranged in the order of decreasing Snyder polarity index: water, 9.0; methanol, 6.6; DMSO, 6.5; acetonitrile, 6.2; acetone, 5.4;

chloroform, 4.4; isopropanol, 4.3; ethyl acetate, 4.3; toluene, 2.3; and hexane, 0.0, were selected for the test which was performed according to the methodology described in Vogel's Textbook of Practical Organic Chemistry. The sample of ILs  $(0.1 \pm 0.0001 \,\mathrm{g})$  was weighed in a vial and then a specific volume of solvent was introduced at 25°C. Compounds that dissolved in 1 cm<sup>3</sup> of the solvent (>10.0% m/v) were marked with a term "good solubility," whereas "medium solubility" was applied for compounds that dissolved in 3 cm<sup>3</sup> of the solvent (between 3.33 and 10.0% m/v). The term "low solubility" was utilized in the case of products that did not dissolve in  $3 \text{ cm}^3$  of the solvent (<3.33% m/v).

#### 2.8 Field studies

The biological activity of new IL forms of chlorsulfuron was examined under field conditions in the fiber flax. The plots were located at the experimental station of Institute of Natural Fibres and Medicinal Plants in Petkowo, Poland (DMS: 52°12'N, 17°15'E). The target weeds are the following two species: common lambsquarters (Chenopodium album L.) and common barnyard grass (Echinochloa crus-galli L.). The experiment was established on 13.5 m<sup>2</sup> plots arranged in a completely randomized setup with three replications. Fiber flax variety Modran has been sown in a quantity of 120 kg ha<sup>-1</sup> with a row distance of 15 cm. HILs and reference product (Glean 75 WG, 75% of chlorsulfuron; Cheminova Polska, Warszawa, Poland) were applied at the dose of 10 g ha<sup>-1</sup>. A knapsack sprayer equipped with a TeeJet 1102 flat-fan nozzle delivering 200 L ha<sup>-1</sup> of spray solution at 0.2 MPa operating pressure was utilized for all the treatments. The plots were sprayed when flax plants were 8-12 cm tall and the weeds reached 4-6 leaves. The efficacy of herbicides was assessed visually 4 weeks after application and demonstrated as percent of weed control in comparison to control (non-treated plants) using a scale of 0 (no herbicide effects) to 100% (complete weed destruction). The influence of the tested compounds on the growth of flax plants was evaluated twice, 2 and 4 weeks after spraying. The assessment of herbicide selectivity for flax plants consisted of a visual comparison of the growth of herbicide-treated plants with plants from control plots (non-treated). After harvesting, the influence of the used substances on yielding was also determined. For this purpose, 20 randomly selected flax plants from each experimental plot were harvested. The mass of straw

after ginning and root removal was assumed as the straw yield. The mass of seeds after extracting from seed bolts was assumed as the seed yield.

In order to study the effect of applied forms of chlorsulfuron on the yield of fiber flax and the weed reduction, a one-way analysis of variance (ANOVA) was performed. The analysis was preceded by the Fligner–Killeen test of homogeneity of variances. If the null hypothesis of ANOVA was rejected, multiple Tukey's post hoc test ( $\alpha = 0.05$ ) was applied to compare the studied treatments.

**Ethical approval:** The conducted research is not related to either human or animal use.

## 3 Results and discussion

In this research, four new quaternary ammonium salts of chlorsulfuron were synthesized via acid-base reaction or

by ion exchange reaction in methanol or methanolwater solution. The new salts with chlorsulfuron contained the following cations: tetramethylammonium (1), didecyldimethylammonium (2), benzyltrimethylammonium (3) and cholinium (4) (Figure 1 and Table 1). All products were synthesized with high yields exceeding 90%, with the use of environment-friendly solvents, which can be easily regenerated by distillation and reused in the process. Additionally, all reactions were carried out in mild conditions, wherein the temperature was equal to 40°C or slightly lower. It should also be emphasized that salt 4 comprises a cation of natural origin, which directly participates in the metabolism of living organisms, including plants and humans. Interestingly, compounds comprising smaller cations (1, 3 and 4) turned out to possess a glassy appearance at room temperature, while one compound with two long alkyl chains present in the cation (2) turned out to be a liquid.

The water content in the dried products, examined by Karl Fischer titration, was less than 2,000 ppm.

Figure 1: Synthesis of new salts comprising various tetraalkylammonium cations and chlorsulfuron as the anion (1-4).

Table 1: Obtained chlorsulfuron-based salts (1-4)

Salt	Code	R <sup>1</sup>	R <sup>2</sup>	State at 25°C	Method of synthesis	Yield (%)
1	[TMA[CHS]	CH₃	CH <sub>3</sub>	Glass	Α	95
2	[DDA][CHS]	$C_{10}H_{21}$	$C_{10}H_{21}$	Liquid	В	94
3	[BTMA][CHS]	CH <sub>3</sub>	Ph-CH <sub>2</sub>	Glass	Α	99
4	[CHOL][CHS]	CH <sub>3</sub>	HOCH <sub>2</sub> CH <sub>2</sub>	Glass	Α	90

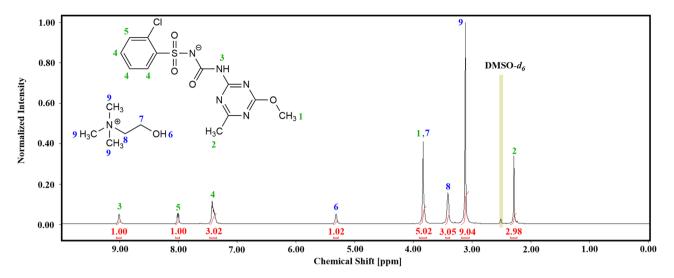


Figure 2: 1H NMR spectrum of salt comprising cholinium cation and chlorsulfuron as the anion (4).

Additionally, all the products were found to be stable in contact with water and tested organic solvents as well as during storage in air. FT-IR and NMR spectra descriptions for compounds **1–4** are provided in the Supporting Information (Figures S1–S12).

The NMR analysis revealed that all characteristic peaks originating from the chlorsulfuron anion were present in the collected  $^1$ H NMR spectra. Hence, in the  $^1$ H NMR spectrum of cholinium chlorsulfuron (4) (Figure 2), we can distinguish three singlets at 2.27 ppm (2) (protons from the methyl group), 3.81 ppm (1) (protons from the methoxyl group) and 9.05 ppm (3) (proton from the amide group), one multiplet at 7.39 ppm (4) (three protons from the aromatic ring) and one doublet at 8.01 ppm (5) (one proton from the aromatic ring,  $J = 6.9 \, \text{Hz}$ ) for this particular herbicide. Interestingly, detachment of the proton from the nitrogen atom of the sulfonamide group decreased the peak shift from the second proton from the urea group from 11 ppm to

approximately 9 ppm. The signals originating from three methyl groups of the cholinium cation appeared at 3.12 ppm (9), whereas peaks from two methylene groups occurred at 3.41 ppm (8) and 3.84 ppm (7) (overlapping with protons from the methyl group of the anion), respectively. Additionally, we can find a broad singlet at 5.32 ppm (6), which was attributed to the hydroxyl substituent present in the cation.

Direct comparison of FT-IR spectra of the potassium salt of chlorsulfuron [K][CHS] and IL comprising a didecyldimethylammonium cation (2) is presented in Figure 3. The most distinctive bands for the chlorsulfuron occurred in the range  $1,720-750~\text{cm}^{-1}$ . Therefore, in both spectra we can distinguish a strong peak from the amide group ( $\nu \sim \text{C=O}$ ) at  $1,670~\text{cm}^{-1}$  (2), which overlapped with peak originating from in-plane stretching vibrations from C=C conjugated bonds [32]. We can also observe a characteristic peak originating from a sulfonamide group [32] ( $\nu$  (as)  $\sim$  S=O) at  $1,357~\text{cm}^{-1}$  (3), which occurred at

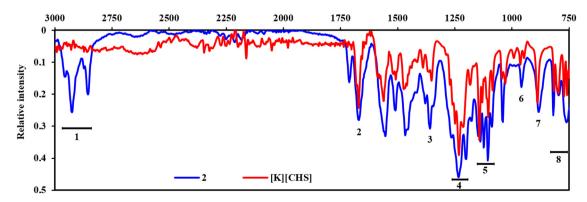


Figure 3: FT-IR spectra of IL comprising a didecyldimethylammonium cation (2) and potassium salt of chlorsulfuron [K][CHS].

slightly shorter values of wavelength for both analyzed salts compared to chlorsulfuron in the non-ionized form [33]. Moreover, both salts exhibited very strong signals at 1,200 and 1,234 cm<sup>-1</sup> (4), which may be assigned to stretching vibrations from the aryl-methyl ether group. A group of peaks between 1,150 and 1,080 cm<sup>-1</sup> (5) originate from the following vibrations: S=O symmetrical stretching [32], C-H aromatic in-plane bending [32] and C-N stretching from the triazine ring [34]. In Figure 3, we can also note a characteristic peak for sulfonamides [32,35], which occurred at  $881 \, \text{cm}^{-1}$  ( $\nu$  (s) ~ C–N) (7). Bands appearing at 818 and 758 cm<sup>-1</sup> (8) are due to C-H out ofplane bending vibrations from aromatic rings [32]. All the aforementioned peaks that originate from chlorsulfuron anion are also clearly visible in the FT-IR spectra of the other salts (1, 3 and 4), which serves as a proof of the presence of this herbicide in the structure of the obtained products. It should also be stressed that in the spectrum of IL 2 there are two broad, strong peaks at 2,925 and 2,853 cm<sup>-1</sup> (1), which can be attributed to alkyl chains in didecyldimethylammonium cation ( $\nu \sim \text{CH}_2$ ). Furthermore, additional asymmetric stretching vibrations of the C-N group ( $\nu$  (as) ~ C-N) present in the utilized quaternary ammonium cation caused the increase in intensity of signal at 881 cm<sup>-1</sup> (**6**) [36].

#### 3.1 Thermal properties

The thermal properties of products (**1–4**) are demonstrated in Table 2 and Figure 4. The lack of melting or crystallization events within the analyzed temperature range allows us to classify all salts as ILs. However, all of them exhibited a glass transition temperature ( $T_{\rm g}$ ) ranging from –3.7°C (for **2**) to 74.8°C (for **1**). Glass transition temperature noted for product with cholinium cation (47.4°C) (**4**) was much higher than glass transition temperature of structurally similar HIL containing a

metsulfuron-methyl anion ( $T_{\rm g}=4^{\rm o}{\rm C}$ ) [16]. IL with longest alkyl chain ( $-3.7^{\rm o}{\rm C}$ ) (2) possessed the lowest glass transition temperature, whereas the highest value (74.8°C) was demonstrated by HIL with shortest possible alkyl chain – methyl group (1), which complies with available data [16].

According to thermogravimetric analysis, simple thermal decomposition with a single decomposition step was noted only for two of the examined salts (1 and 3) (Figure 4). On the other hand, products containing didecyldimethylammonium (2) and cholinium (4) cations exhibited a two-step decomposition characteristics. Such differences may be caused by the partial fragmentation of long alkyls (in the case of 2) [8] or the presence of functional (hydroxyl) group (in the case of 4) that are known to alter the thermal stability of HILs comprising tetraalkylammonium cation [19]. As shown in Table 2, choline salt (4) possessed the lowest initial decomposition temperature ( $T_{5\%}$  = 188°C), whereas products **1** and **3** ( $T_{5\%} = 204$  °C) exhibited the greatest value. Salt 2 possessed initial decomposition temperature equal to approx. 200°C. Interestingly, 4 proved to be more resistant to thermal decomposition

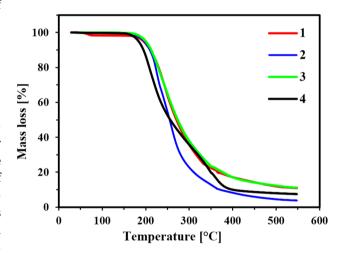


Figure 4: Thermal stability of the obtained salts (1-4).

Table 2: Thermal properties of the obtained salts (1-4)

Salt	Tg a (°C)	<i>T</i> <sub>m</sub> <sup>b</sup> (°C)	<i>T</i> <sub>c</sub> (°C)	Steps of degradation	7 <sub>5%</sub> <sup>d</sup> (°C)	7 <sub>50%</sub> e (°C)
1	74.8	_	_	1	204	276
2	-3.7	_	_	2	200	258
3	55.6	_	_	1	204	277
4	47.4	_	_	2	188	260

 $<sup>^{</sup>a}T_{g}$  – glass transition temperature.  $^{b}T_{m}$  – melting point.  $^{c}T_{c}$  – temperature of crystallization.  $^{d}T_{5\%}$  – decomposition temperature of 5% sample.  $^{e}T_{50\%}$  – decomposition temperature of 50% sample.

than HIL containing the same cholinium cation and metsulfuron-methyl as the anion, which showed a decomposition of 5% at 150°C [16]. Molecule of metsulfuron-methyl differs from chlorsulfuron in the presence of methoxycarbonyl group instead of chlorine atom. Hence, we may conclude that the structure of sulfonylurea anion plays a crucial role in susceptibility of this group of HILs on thermal decomposition and glass transition temperature.

According to data in Table 2, the decomposition temperatures of 50% sample  $(T_{50\%})$  were found to be higher for products comprising the shortest alkyl or alkylaryl substituents in the cation (1, 3), for which the decomposition temperature exceeded 275°C. Salts with decyl and 2-hydroxyethyl substituents (2 and 4) exhibited slightly lower temperature of decomposition (approx. 260°C). Additionally, notably greater mass loss of 2 in a temperature range of 250-350°C may be explained by a successive degradation of long alkyl groups and evaporation of volatile products of their decomposition. This assumption can be supported by literature data, according to which didecyldimethylammonium-based ILs exhibited very similar values of thermal stability parameters [37,38].

#### 3.1.1 Solubility

The procedure described by Vogel was used to examine the solubilities of chlorsulfuron, its potassium salt as well as the prepared chlorsulfuron-based quaternary ammonium salts (1-4) [39]. As shown in Table 3, solvents characterized by diverse polarity were selected for the analysis. The collected data revealed that chlorsulfuron ([H][CHS]) was found to be soluble in DMSO, acetonitrile and chloroform, while its potassium salt ([K][CHS]) was characterized with good affinity only

with water and DMSO. Interestingly, HIL comprising didecyldimethylammonium cation (2) was characterized by exceptionally good affinity with the majority of utilized solvents. This can be attributed to the presence of two long alkyl chains in the cation, which leads to the enhancement of compound's surface activity and amphiphilicity. In effect, 2 turned out to be insoluble only in the most polar (water) and most non-polar (hexane). On the contrary, the other synthesized salts were found to be soluble in solvents possessing the highest polarity such as methanol, DMSO and water. Additionally, salts comprising the most polar cations (1 and 4) were found to be soluble only in these three solvents, while 3 exhibited affinity with semi-polar solvents as well. Regarding the less polar solvents, two of the obtained salts (2 and 3) were soluble in chloroform, while only one (2) was miscible with toluene and none dissolved in hexane. The explanation of this observation lies in the fact that solvents with low dielectric constants are generally poorly miscible with ILs (which are equal to 4.4 for chloroform, 2.3 for toluene and 0.0 for hexane) [40,41]. Generally, the differences between solubility of the synthesized chlorsulfuron-based salts lead to conclusion that it is possible to influence this parameter by simple modification of particular substituents in the cation.

## 3.2 Herbicidal effectiveness

The efficiency of four synthesized HILs (1-4) has been studied under field conditions in the cultivation of flax variety Modran. This variety has a dominate structure of flax fiber in Poland. Generally, it can be concluded that all tested HILs demonstrated herbicidal activity, but their efficiency was highly influenced by the structure of each cation as well as weed species. The one-way ANOVA has

Table 3: Solubility of the prepared chlorsulfuron-based HILs (1-4) at 25°C

Salt	Water 9.0ª	Methanol 6.6	DMSO 6.5	Acetonitrile 6.2	Acetone 5.4	Chloroform 4.4	Isopropanol 4.3	Ethyl acetate 4.3	Toluene 2.3	Hexane 0.0
1	+	+	+	_	_	_	=	_	_	_
2	_	+	+	+	+	+	+	+	+	-
3	+	+	+	+	+	+	_	_	_	-
4	+	+	+	_	_	_	_	_	_	_
[H][CHS] <sup>b</sup>	_	_	+	±	_	+	_	_	_	_
$[K][CHS]^c$	+	_	+	_	_	_	_	_	_	_

<sup>&</sup>lt;sup>a</sup> Snyder polarity index [41]; "+": good solubility; "±": medium solubility; "-": low solubility. <sup>b</sup>Chlorsulfuron. <sup>c</sup>Potassium salt of chlorsulfuron.

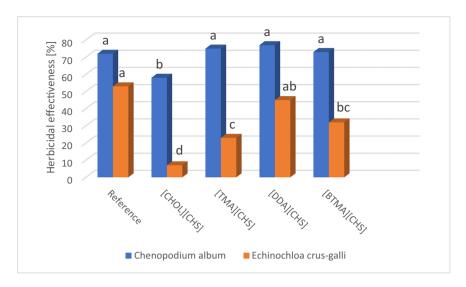


Figure 5: Herbicidal effectiveness of the tested HILs (1-4).

shown the significant differences in mean effects of the action of the tested HILs toward both common lambsquarters (see F = 7.194; p-value = 0.00537 in Table S2) and common barnyard grass (see F = 39.61; p-value =  $4.2 \times 10^{-6}$  in Table S2). The most active turned out to be HILs with didecyldimethylammonium (2) and benzyltrimethylammonium (3) cations (Figure 5, Figures S13 and S14). The post hoc comparisons using the Tukey HSD test  $(\alpha = 0.05)$  indicated that the mean reduction of common barnyard grass treated with these two HILs was significantly higher from the effects of tetramethylammonium (1) and cholinium (4). There were no statistically significant differences in the effectiveness of HILs toward common lambsquarters compared to the reference herbicide, except for cholinium (4) that showed significantly lower activity. As regards barnyard grass control, only salt **2** showed similar efficacy to the reference herbicide, while the other HILs showed significantly lower efficacy (Figure 5 and Table S2).

## 3.3 Effect on crops

All tested HILs were safe for flax plants. No damage symptoms were found throughout the growing season. There were no significant differences between the effects of applied HILs on the yield of fiber flax both in terms of seed yield and straw yield (Table S3). The average yield of straw from the plot (13.5 m<sup>2</sup>) varied between 6.6 and 8 kg. Among the tested HILs, the highest yield was obtained from plots treated with didecyldimethylammonium (2) and benzyltrimethylammonium (3) (Figure 6).

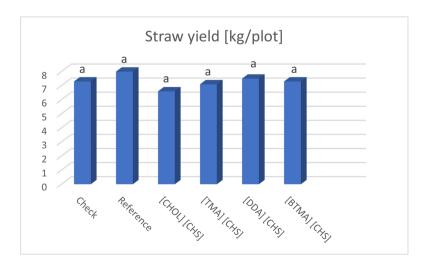


Figure 6: Influence of the tested HILs (1-4) on straw yield (kg/plot) of fiber flax.

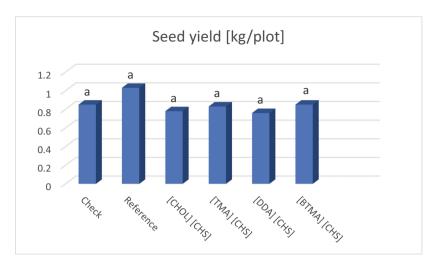


Figure 7: Influence of the tested ILs on seed yield (kg/plot) of fiber flax.

The average yield of seeds from the plot was from 0.76 to 1.03 kg, but the statistical analysis showed that these differences were not significant (Table S3). When comparing the impact of individual HILs on seed yield, it should be stated that HILs benzyltrimethylammonium (3) and tetramethylammonium (1) exhibited the most favorable impact (Figure 7).

## 4 Conclusions

In this study, four new ILs with herbicidal anion from the group of sulfonylureas-chlorsulfuron were synthesized. This is the first report describing the use of chlorsulfuron as a source of anion in ILs. Elaborated synthesis methodology allows us to synthesize products with good efficiency, exceeding 90% under mild conditions and using green solvents. Compounds comprising small tetraalkylammonium cations turned out to possess glassy appearance at room temperature, while the presence of two long chains in the cation led to a product that occurred in the form of liquid. All new ILs were identified by using spectroscopic methods, such as infrared spectroscopy (FT-IR) and nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR). Additionally, the obtained products were tested in terms of their thermal properties, solubility and biological activity. All the salts were deprived from melting or crystallization events in the analyzed temperature range; however, they all exhibited a glass transition temperature in a range from -3.7 to 74.8°C, which is in accordance with available literature [16]. Furthermore, all compounds were thermally stable, with lowest decomposition temperature equal to 188°C for salt comprising a cholinium cation. Generally, conversion of chlorsulfuron herbicide into ILs caused an increase in solubility in water and methanol. All tested ILs with chlorsulfuron anion showed herbicidal effects without causing damage to fiber flax plants. The weed control of the tested HILs depended on the weed species. Higher herbicidal effectiveness was found for Chenopodium album L., while the tested HILs were less effective in controlling Echinochloa crus-galli L. Didecyldimethylammonium salt demonstrated by the greatest effectiveness among the examined HILs for both these weed species. The studied HILs had no effect on the yields of flax plants.

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Conflict of interest: The authors declare no conflict of interest.

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