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Phenoxy herbicidal ammonium ionic liquids

Roksana Kordala-Markiewicz^a, Hubert Rodak^a, Bartosz Markiewicz^a, Filip Walkiewicz^a, Agata Sznajdrowska^a, Katarzyna Materna^a, Katarzyna Marcinkowska^b, Tadeusz Praczyk^b, Juliusz Pernak^{a,*}

^a Department of Chemical Technology, Poznan University of Technology, Poznan 60-965, Poland ^b Institute of Plant Protection—National Research Institute, Poznan 60-318, Poland

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ABSTRACT

Ammonium ionic liquids with the 4-chloro-2-methylphenoxyacetate anion were synthesized and characterized. Physicochemical properties, such as thermal stability, phase transition temperatures, viscosity, density, refractive index, as well as surface activity and herbicidal activity were determined. Improved physicochemical properties suggest a reduced environmental impact of newly formed group of herbicidal ionic liquids (HILs). HILs with a longer substituent can be characterized with better herbicidal activity in comparison with commercial products.

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1. Introduction

Chemicals in agriculture are used to eliminate or control a variety of agricultural pests that can damage crops and livestock and reduce farm productivity. Among the most popular are phenoxy acid based herbicides, especially with 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid), which due to low cost and high effectiveness, have been widely applied for many years.¹ Although industry provides more safer chemicals for crop protection, it is still an urgent need to develop new opportunities to reduce the negative impact of these compounds on the environment and human health.² Herbicides have been linked to a number of health problems, including neurologic and endocrine (hormone) system disorders, birth defects, cancer, and other diseases.³ Therefore, there is an increasing requirement for improving existing herbicides, their modification or new forms to reduce environmental impact and growth of their efficacy. Regulations of the European Parliament states that low-risk plant protection products should be identified and placed on the market.⁴ In the view of these facts, it is extremely important to find an alternative to conventional herbicides. Herbicidal ionic liquids (HILs) seem to be an interesting proposal. HILs are phytopharmaceuticals enriching the third generation of ionic liquids (targeted biological properties with chosen physical and chemical properties).⁵

HILs, defined as ionic compounds with melting temperature below 100 °C, where one of the ions possesses herbicidal activity were first described by us in 2011.⁶ In our previous papers, HILs with one herbicidal ion (MCPA,⁶ 2,4-D,^{7,8} dicamba—3,6-dichloro-2methoxybenzoate,^{9,10} mecoprop—2-(4-chloro-2-methylphenoxy) propionate,¹⁰ and glyphosate¹⁰) or two herbicidal ions (2chloroethyltrimethylammonium cation with MCPA¹¹ or 2,4-D anion¹²) were studied.

2,4-D- and MCPA-ammonium salts are already known and used as herbicides. The structures of commercial primary, secondary, and tertiary ammonium cations are shown in Fig. 1, along with their abbreviations and melting temperatures. Two of them may be classified as the protic ILs (diolamine and triisopropanolammonium), which contain secondary and tertiary 2,4-D-ammonium salts. Recently, Dow Agrosciences LLC patent¹³ describes seven quaternary 2,4-D-ammonium salts (inter alia 2,4-D-tetraalkylammonium, 2,4-D-benzyltrimethylammonium, and 2,4-Dhexadecyltrimethylammonium).

The use of HILs gives more advantages as compared with conventional herbicides. Firstly, HILs allow the reduction of the herbicide dose per hectare, while controlling its toxicity (toxic phenoxy herbicide may become nontoxic as the HIL⁶), and possessing unique physicochemical properties (thermal stability, low volatility). Reduced the volatility of the described compounds makes usage safer for the operators and reduces the overall





^{*} Corresponding author. Tel.: +48 61 665 3682; fax: +48 61 665 3649; e-mail address: juliusz.pernak@put.poznan.pl (J. Pernak).



Fig. 1. Structures of cations of commercial primary, secondary, and tertiary 2,4-Dammonium and MCPA-ammonium salts.

environmental impact of the herbicide.⁹ Commercial products are a combination of many different substances. HILs are multifunctional compounds, not mixtures, and do not overload the environment. The use of them can decrease the non-profitable effect of chemical weed control.

The earlier described HILs^{6–9} are quaternary ammonium, pyridinium or imidazolium ILs with 2,4-D, MCPA, MCPP, and dicamba anions. HILs anion is responsible for the herbicidal activity, while the role of a cation is recognized for its surface activity, toxicity, and ecotoxicity of the entire compound.

Here we compare the alkylcyclohexyldimethylammonium salts of the phenoxy herbicide anion (MCPA) with the analogous salts of alkoxymethylcyclohexyldimethylammonium cations.

The addition of functional groups (e.g., ether oxygens) to the ions may change the properties of salts. Zhou and co-workers demonstrated that the replacement of a methylene group in various cations by an oxygen atom significantly decreases the melting point and viscosity for ILs.¹⁴ The effects of an alkoxy group on the properties of ILs have been studied from the aspects of crystallog-raphical,^{15a} thermal,¹⁵ and theoretical investigation.¹⁶ Thus, a study of our salts represents an excellent opportunity to examine how structural changes affects the properties of HLs. It was previously described that ammonium ILs with alkyl or alkoxymethyl chains from eight to sixteen carbon atoms have high anti-microbial activity.^{17,18} At present, we would like to investigate how long must a substituent be to obtain the optimal conditions for herbicidal action HILs, and whether there is a correlation between surface and herbicidal activity.

2. Results and discussion

Alkylcyclohexyldimethylammonium 4-chloro-2-methylpheno xyacetate (**10–18**) were synthesized in acid–base reactions (method A) and alkoxymethylcyclohexyldimethylammonium 4-chloro-2-methylphenoxyacetate (**19–24**) in metathesis reactions (method B), according to Scheme 1.

Acid—base reactions were conducted in methanol and took place immediately with high yields. Metathesis reactions were carried out in water over 24 h. The used herbicide—MCPA, represents the group of phenoxy herbicides.

Purity of the obtained acetates in water solution with a chain of eight or more carbon atoms was determined by a direct two-phase



Scheme 1. Synthesis of 4-chloro-2-methylphenoxyacetates (10-24).

titration technique (EN ISO 2871-1,2:2010) as surfactant content. All of the obtained salts were liquids at room temperature, except for **10** and **11**, which were waxes. The melting temperatures are below 100 °C, so new ionic liquids were synthesized. They were stable in air as well as in contact with water and popular organic liquids. Alkyl-based ILs **10–18** are hygroscopic and alkoxymethylbased ILs **19–24** are highly hygroscopic. They require drying under reduced pressure at elevated temperature. For dried ILs the water contents were determined by Karl-Fischer method and found to be less than 500 ppm.

The synthesized 4-chloro-2-methylphenoxyacetates (**10–24**), their yields and surfactant content are presented in Table 1.

 Table 1

 Synthesized 4-chloro-2-methylphenoxyacetates

Salt	R	Yield [%]	Surfactant content [%]
10	C_2H_5	97	—
11	C_4H_9	98	_
12	C ₆ H ₁₃	98	_
13	C ₈ H ₁₇	97	98
14	C ₁₀ H ₂₁	98	99
15	C ₁₂ H ₂₅	99	98
16	C14H29	97	98
17	C ₁₆ H ₃₃	98	99
18	C ₁₈ H ₃₇	98	98
19	CH ₂ OC ₄ H ₉	94	_
20	CH ₂ OC ₆ H ₁₃	93	_
21	CH ₂ OC ₈ H ₁₇	90	92
22	CH ₂ OC ₁₀ H ₂₁	98	89
23	CH ₂ OC ₁₂ H ₂₅	94	90
24	CH ₂ OC ₁₄ H ₂₉	86	90

Thermal transitions for selected compounds were determined using differential scanning calorimetry (DSC), while the decomposition temperatures (T_{onset5} , onset for 5% decomposition and $T_{onset50}$, onset for 50% decomposition) were determined using thermal gravimetric analysis (TGA). All data are presented in Table 2. The melting points or glass transitions for all obtained ILs were below $-60 \,^{\circ}$ C. In case of acetates **23** and **24**, the crystallization and melting temperatures were observed and valued: -15.6 and $-9.6 \,^{\circ}$ C for crystallization, and -26.0 and $-3.2 \,^{\circ}$ C for melting temperature, respectively. Decomposition temperatures T_{onset5} for all tested alkyl-based ILs (**10–18**) were at least around 190 $^{\circ}$ C, up to 214 $^{\circ}$ C for **18**. For the ILs with an alkoxymethyl substituent (**19–24**) decomposition temperatures T_{onset5} were lower to about 160 $^{\circ}$ C. In case of ILs with long alkyl (**16–18**) and alkoxymethyl substituents **23** and **24**, a two-step decomposition was observed.

Viscosity of the prepared ILs (Table 2) was relatively low compared to most known ILs. Values of viscosity for alkyl-based ILs

Table 2								
Viscosity density	refractive index	thermal	transitions	and decomr	osition tem	peratures of	synthesized II	s

IL	R	Density [g cm ⁻³] ^a	Viscosity [Pa s] ^a	Refractive index ^a	$T_{\rm g} [^{\circ} {\rm C}]^{\rm b}$	$T_{\text{onset5}} [^{\circ}C]^{c}$	$T_{\text{onset50}} [^{\circ}C]^{d}$
10	C ₂ H ₅	_	_	_	-61.3	202	243
11	C ₄ H ₉	_	_	_	-60.0	198	226
12	C ₆ H ₁₃	1.1381	0.4062	1.5199	-62.6	187	222
13	C ₈ H ₁₇	1.1269	0.6318	1.5176	-61.7	190	239
14	C ₁₀ H ₂₁	1.1122	0.5782	1.5150	-60.4	189	242
15	C ₁₂ H ₂₅	1.0789	0.3463	1.5112	-60.9	203	267
16	C ₁₄ H ₂₉	1.0678	0.8837	1.5100	-61.4	206	278, 268 ^e
17	C ₁₆ H ₃₃	1.0577	0.6447	1.5074	-59.9	206	298, 278 ^e
18	C ₁₈ H ₃₇	1.0416	0.7224	1.4983	-60.8	214	332, 298 ^e
19	CH ₂ OC ₄ H ₉	1.1376	0.3473	1.5129	-62.1	152	210
20	CH ₂ OC ₆ H ₁₃	1.1155	0.1550	1.5088	-64.7	175	215
21	CH ₂ OC ₈ H ₁₇	1.1019	0.3789	1.5061	-70.5	150	222
22	CH ₂ OC ₁₀ H ₂₁	1.0542	0.0734	1.4988	-72.5	168	214
23	CH ₂ OC ₁₂ H ₂₅	1.0431	0.1160	1.4972	-57.0	175	250, 230 ^e
24	CH2OC14H29	1.0372	0.1173	1.4969	-49.5	164	268, 220 ^e

^a At 25 [°C].

^b *T*_g—glass transition.

^c T_{onset5} —decomposition of 5% of the sample.

^d *T*_{onset50}—decomposition of 50% of the sample.

^e Two-stage decomposition.

12–18 differ from 0.3463 to 0.8837 Pa s, while for the alkoxymethyl-based ILs **19–24**, the viscosity valued from 0.0734 to 0.3789 Pa s. The oxygen presence in the alkyl chain in the case of ILs **19–24** causes lowering of the viscosity. In the temperature range of 20–60 °C a strong dependence of viscosity on temperature is observed (Figs. S1–S2 in Supplementary data). For all studied ILs the viscosity values were determined to be approximately 0.01–0.02 Pa s at 60 °C.

Density of the studied ILs (Table 2) decreases with elongation of the alkyl or alkoxymethyl chain. For alkyl-based ILs, the density values lower from 1.1381 for **12** to 1.0416 g cm⁻³ for **18**, and in the case of alkoxymethyl-based ILs, values of density differ from 1.1138 for **19** to 1.0372 g cm⁻³ for **24**. The values of density of the ILs are temperature dependent, with an increase in temperature, the density values decrease (Fig. S3 in Supplementary data).

Refractive indices for the ILs vary in the range 1.5199-1.4969 (Table 2). The substituent elongation caused a decrease of index values. In case of temperature, the dependence between the refractive index and temperature is linear; with the increase of temperature, the refractive index values decrease. For example, in the case of butoxymethylcyclohexyldimethylammonium 4-chloro-2-methylphenoxyacetate (**19**) the refractive index is equal to 1.5129 at 20 °C, while this value is 1.4991 at 60 °C.

The surface activity parameters are summarized in Table 3. The length of the alkyl or alkoxymethyl substituent was, as expected, decisive for the critical micelle concentration (CMC) of an aqueous

Table	3
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Surface	activity	narameters	of	synthesized	bromides	(4 - 9)	and IIs
Surface	accivicy	parameters	01	Synthesized	bronnacs	(10)	und ins

Salt	CMC [mmol dm ⁻³]	^γ смс [mN m ⁻¹]	pC ₂₀	$\Gamma_{\rm max} \times 10^6$ [mol m ⁻²]	$A_{\min} \times 10^{19}$ [m ²]	CA [°]
4	100.0	37.7	1.50	0.02	7.16	66.9
5	46.8	38.3	2.00	6.98	2.38	64.8
6	10.7	37.2	2.60	1.84	9.03	59.1
7	2.19	38.8	3.35	2.27	7.32	58.3
8	0.37	40.5	3.95	3.78	4.39	64.5
9	0.10	41.4	4.25	0.07	2.37	65.5
13	14.8	33.7	2.60	1.70	9.75	50.1
14	3.98	31.9	3.35	1.30	1.33	55.1
15	1.18	33.2	3.65	5.55	2.99	58.2
16	0.44	35.1	4.00	8.81	1.88	57.3
17	0.12	36.3	4.30	6.82	2.43	56.3
18	0.05	39.4	4.50	5.20	3.20	52.7
21	7.33	32.1	3.30	3.77	4.40	73.0
22	2.10	31.2	3.70	4.39	3.78	40.5
23	0.46	31.2	4.15	5.55	2.99	52.7
24	0.19	31.6	4.40	4.28	3.88	41.1

solution of the ILs. The elongation of alkyl chain length caused a decrease from 100 to 0.1 mmol dm⁻³ for bromides **4–9**, and 15 to 0.05 for alkyl-based ILs **13–18**. In case of the same cation, the anion exchange caused a decrease in CMC value, e.g., for cyclohexyldimethyloctylammonium from 100 mmol dm⁻³ for bromide **4** to 15 mmol dm⁻³ for phenoxyacetate **18**. A comparison of CMC for a homologous series of alkylcyclohexyldimethylammonium salts demonstrates lowering the concentration in parallel with alkyl chain elongation due to enhanced hydrophobic interaction between the counter ion and micelle. Surface activity of the synthesized bromides and acetates can be judged by the surface tension (γ CMC).

The surface tension of aqueous solutions of the studied salts decreased from water value to a minimum located from 30 to 42 mN m^{-1} , where it reached a plateau. All of the synthesized salts, with the alkyl substituent longer than eight carbon atoms were active compounds with surface tension generally increasing in parallel with the substituent elongation (Fig. 2).



Fig. 2. Relationship between logCMC and the chain length of the alkyl bromides (4–9), alkyl-based ILs (13–18), and alkoxymethyl-based ILs (21–24).

Surface excess concentrations at the saturated interface (Γ_{max}), the minimum surface occupied by a molecule at the interface (A_{min}), and the adsorption efficiency, pC₂₀ were calculated. The pC₂₀ is defined as the negative logarithm of the surfactant concentration in the bulk phase required to reduce the surface tension of the water by 20 mN m⁻¹, which represents efficiency of surface adsorption on an air–water interface. The larger the value of pC₂₀, the more efficiently ILs are adsorbed at the interface and the more

efficiently it reduces surface tension. The efficiency of adsorption of a surfactant at the surface, as measured by the pC_{20} value, is increased linearly with an increase in the number of carbon atoms in the hydrophobic chain, reflecting the negative free energy of adsorption of a methylene group at these interfaces.

High surface activity allowed the reduction of the contact angle of a drop of alkyl-based ILs solution, from 58 to 67 for alkylcyclohexyldimethylammonium bromides from 50 to 58 for 4-chloro-2methylphenoxyacetates, as evident in Table 3. Better wettability of the paraffin surface, which resembles the real surface of plants, observed for MCPA salts may be useful in future application of these HILs as herbicides.

Growth chamber experiments were performed under controlled environmental conditions (20 °C, humidity 60%, 16/8 h day night photoperiod) to determine the biological activity of the selected HILs. The fresh mass reduction of cornflower, white mustard, and rapeseed (*Centaurea cyanus, Sinapis alba*, and *Brasica napus*, respectively) as compared to control was measured, and the results are presented in Fig. 3. The elongation of alkyl chain length in alkylbased ILs (**10–18**) caused an increase in the fresh mass reduction of every tested plant. The best results of efficacy (76%) were observed for cyclohexyldodecyldimethylammonium 4-chloro-2-methylphenoxyacetate (**15**) in the case of cornflower. The commercial product (Chwastox), with efficacy equal to 14%, is more than five times less effective.



Fig. 3. Values of efficacy for alkyl-based ILs (10-18).

Mean values of fresh mass reduction of three tested plants for ILs **10–15** indicate that starting from cyclohexylhexyldimethylammonium 4-chloro-2-methylphenoxyacetate (**12**), with the alkyl chain composed of six carbon atoms, the ILs manifest better herbicidal activity than the commercial product, and are very effective against cornflower, rapeseed, and white mustard (Fig. S4 in Supplementary data). Obtained results show that the most effective alkyl-based ILs are 4-chloro-2-methylphenoxyacetates with the alkyl chain composed of 12 or more carbon atoms. It was previously described that ammonium ILs with alkyl or alkoxymethyl chains from eight to sixteen carbon atoms manifest high antimicrobial activity.¹⁸

Alkylcyclohexyldimethylammonium ILs with an acetate anion dissolve cellulose and show anti-microbial activity. The biological activity against microbes begins when a length of the alkyl substituent begins to block cellulose solubility.¹⁷ In this case, not only the acetate anion (and its analogues) but also the cyclohexyl substituent simplify the cellulose dissolution. Alkyl-based ILs with a 4-chloro-2-methylphenoxyacetate anion and a cyclohexyl substituent in the cation structure preserve the biological activity, but did not dissolve the cellulose chain.

In Fig. 4, the herbicidal activity as a function of the pC_{20} is shown. The bulk liquid phase concentration of surfactant required to depress the surface tension of the solvent by 20 mN m⁻¹ is



Fig. 4. Relationship between the herbicidal efficacy and pC_{20} for alkylcyclohexyldimethylammonium 4-chloro-2-methylphenoxyacetates **13–18** (white mustard).

a good measure of the efficiency of adsorption of ILs. The efficiency with which the IL is adsorbed at the surface can be related to its herbicidal efficacy. In case of white mustard we obtained a linear correlation.

Because of the weak herbicidal activity of commercial products in low temperatures, we decided to investigate the activity of synthesized alkyl-based HILs on selected weeds. The growth chamber experiments were conducted at different temperatures: 6 and 20 °C (Table S1 in Supplementary data). The alkyl-based ILs with the alkyl substituent longer than 10 carbon atoms is active against white mustard. The most effective at 6 °C is 4-chloro-2methylphenoxyacetate **18** with an octadecyl substituent, with the efficacy value of 13%. HILs possess herbicidal activity even at low temperatures, and their activity is linked to the alkyl substituent length. HILs activity becomes less dependent on temperature variations, which affects the extended period of their application.

For alkoxymethyl-based ILs **19–24**, the mass reduction of fresh white mustard and lamb's quarters (*S. alba* and *Chenopodium album*) with comparison to control was measured. The results are shown in Fig. 5.



Fig. 5. Values of efficacy for alkoxymethyl-based ILs (19-24).

In this case, the elongation of the alkoxymethyl chain resulted in an increase of efficacy, reaching the maximum of 47% for cyclohexyldodecyloxymethyldimethylammonium 4-chloro-2-methylphenoxyacetate (**22**). After that point, further chain elongation caused a decrease of efficacy, while still remaining higher than the commercial product. For alkoxymethyl-based ILs we can observe a maximum value of herbicidal activity for the dodecy-loxymethyl substituent. It is clear that the substituent length in the HILs' cation is very important.

The alkoxymethyl chain is flexible, resulting in a higher surface and herbicidal activity. In the area or high herbicidal activity, observation of maximal effectiveness for one substituent is a very valuable indication in the design of the HILs.

3. Conclusion

In summary, the obtained results allow us to categorize newly synthesized 4-chloro-2-methylphenoxyactate ILs as herbicidal ionic liquids. We demonstrated that the choice of the cation determines the herbicidal effectiveness. In addition, for the first time, the efficiency of surface tension reduction (pC_{20}) for these HILs was correlated with the herbicidal activity. In conclusion, the synthesized HILs with longer substituents are very promising herbicidal agents, with better herbicidal activity in comparison with commercial products.

4. Experimental section

4.1. Materials

Cyclohexyldimethylamine, bromoalkanes, potassium, and sodium hydroxide as well as all the solvents were purchased from commercial suppliers (Merck, Aldrich, POCh) and used without further purification. 4-Chloro-2-methylphenoxyacetic acid was purchased from Organika-Sarzyna S.A. Poland. Water for surface activity measurements was deionized with the conductivity below 0.1 μ S cm⁻¹ from demineralizer HLP Smart 1000 (Hydrolab). Chloromethylalkyl ethers were synthesized by passing HCl through a mixture of formaldehyde and the appropriate alcohol, and their purities were above 85%.

4.2. General

¹H NMR spectra were recorded on an NMR Varian VNMR-S spectrometer operating at 400 MHz with TMS as the internal standard. ¹³C NMR spectra were obtained with the same instrument at 100 MHz. CHN elemental analyses and IR spectra were performed at the Adam Mickiewicz University, Poznan (Poland).

The water content was determined by using an Aquastar volumetric Karl-Fischer titration with Composite 5 solution as the titrant and anhydrous methanol as a solvent.

Density was measured with Automatic Density Meter DDM2911 with mechanical oscillator method. Density of the samples (ca. 2.0 cm^3), was measured with respect to temperature controlled via Peltier, from 20 to 60 °C. The apparatus was calibrated using deionized water and air as reference substances. After each series of measurements, the densimeter was washed with methanol or acetone and dried. The uncertainty of measurements was estimated to be less than $10^{-5} \text{ g cm}^{-3}$.

Viscosity was determined using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosity of the samples, about 1.5 cm³ was measured with respect to temperature, from 20 to 100 °C. The uncertainty of the viscosity measurement was estimated to be less than 10^{-4} Pa s.

Refractive index was determined using an Automatic Refractometer J357 with electronic temperature control from 20 to 60 °C. The uncertainty of measurements was estimated to be less than 10^{-5} .

4.3. Preparation

4.3.1. Alkylcyclohexyldimethylammonium salts (method A). Alkylcyclohexyldimethylammonium bromides (1-9) were synthesized according to methods described earlier.¹⁷ Alkylcyclohexyldimethylammonium bromide (0.05 mol) was dissolved in methanol and after addition of a stoichiometric amount of a saturated methanolic solution of KOH, the solution was stirred at room temperature for 5 min, after which the partially precipitated KBr was filtered. Then a stoichiometric amount of a saturated methanolic solution of 4-chloro-2-methylphenoxyacetic acid was added. The solution was stirred at room temperature for 15 min and after evaporation of the solvent, the product was washed with acetone. The inorganic salt was separated and acetone was evaporated to give the product, which was finally dried under reduced pressure at 60 °C for 24 h.

4.3.2. Alkoxymethylcyclohexyldimethylammonium salts (method *B*). Sodium 4-chloro-2-methylphenoxyacetate was synthesized by reaction of 4-chloro-2-methylphenoxyacetic acid and sodium hydroxide. Alkoxymethylcyclohexyldimethylammonium chloride (0.05 mol) was dissolved in 30 cm³ of deionized water and stoichiometric amount of sodium 4-chloro-2-methylphenoxy-acetate was added. The solution was stirred at room temperature for 24 h. Water was evaporated, and anhydrous acetone was added. The precipitate (NaCl) was filtered and the filtrate concentrated in a vacuum evaporator. Finally, the product was dried under reduced pressure at 40 °C for 24 h.

4.3.3. Cyclohexyldecyldimethylammonium 4-chloro-2-methylphen oxyacetate (14). δ_H (DMSO-d₆, 298 K, 402.645 MHz): 0.87 (t, J=6.5 Hz, 3H, N⁺-CH₂CH₂(CH₂)₇CH₃); 1.11 (m, 1H, cyclohexyl C4 axial); 1.26-1.32 (m, 16H, cyclohexyl C3 and C5 axial, N⁺–CH₂CH₂(CH₂)₇CH₃); 1.43 (m, 2H, cyclohexyl C2 and C6 axial); 1.58-1.64 (m, 3H, cyclohexyl C4 equatorial, N⁺-CH₂CH₂(CH₂)₇CH₃); 1.85 (m, 2H, cyclohexyl C3 and C5 equatorial); 2.05 (m, 2H, cyclohexyl C2 and C6 equatorial); 2.14 (s, 3H, C=CCH₃-C); 2.98 (s, 6H, $N^{+}-(CH_{3})_{2}$; 3.29-3.34 (m, 2H, $N^{+}-CH_{2}CH_{2}(CH_{2})_{7}CH_{3}$); 3.36 (m, 1H, cyclohexyl C1); 4.25 (s, 2H, $O-CH_2-COO^-$); 6.71 (d, J=6.9 Hz, 1H, CO-CH=CH); 7.05 (d, J=4.2 Hz, 1H, CH=CH-CCI); 7.10 (s, 1H, CCH₃-CH=CCl). δ_C (DMSO-d₆, 298 K, 101.254 MHz): 13.92; 15.90; 21.57; 22.09; 24.81; 25.31; 28.51; 28.70; 28.92; 29.00; 29.05; 29.09; 31.30; 47.62; 61.57; 67.77; 70.45; 112.81; 122.77; 125.89; 127.77; 129.23; 155.89; 170.42. Elemental analysis for C₂₇H₄₆ClNO₃ (M=468.11) requires (%): C 69.28; H 9.90; N 2.99; found: C 69.59; H 9.68; N 2.63. *v*_{max} (KBr): 3600–3100 (br), 2930, 2858, 1616, 1492, 1297, 1233, 1052, 879, 803, 648 cm⁻¹.

4.3.4. Butoxymethylcyclohexyldimethylammonium 4-chloro-2methylphenoxyacetate (**19**). $\delta_{\rm H}$ (DMSO-d₆, 298 K, 402.645 MHz): 0.89 (t, *J*=6.8 Hz, 3H, N⁺–CH₂OCH₂(CH₂)₂CH₃); 1.10–1.15 (m, 1H, cyclohexyl C4 axial); 1.29–1.40 (m, 6H, cyclohexyl C3 and C5 axial, N⁺–CH₂OCH₂(CH₂)₂CH₃); 1.56 (m, 2H, cyclohexyl C2 and C6 axial); 1.67 (d, *J*=11.0 Hz, 1H, cyclohexyl C4 equatorial); 1.95 (d, *J*=12.0 Hz, 2H, cyclohexyl C3 and C5 equatorial); 2.04 (d, *J*=9.8 Hz, 2H, cyclohexyl C2 and C6 equatorial); 2.25 (s, 3H, C=CCH₃–C); 3.02 (s, 6H, N⁺–(CH₃)₂); 3.30 (m, 1H, cyclohexyl C1); 3.70 (t, *J*=6.8 Hz, 2H, N⁺–CH₂OCH₂(CH₂)₂CH₃); 4.44 (s, 2H, O–CH₂–COO⁻); 4.74 (m, 2H, N⁺–CH₂OCH₂(CH₂)₂CH₃); 6.71 (d, *J*=8.8 Hz, 1H, CO–CH=CH); 7.01 (d, *J*=6.4 Hz, 1H, CH=CH–CCI); 7.06 (d, *J*=3.4 Hz, 1H, CCH₃–CH= CCI); $\delta_{\rm C}$ (DMSO-d₆, 298 K, 101.254 MHz): 13.67; 16.18; 22.29; 25.12; 25.70; 29.28; 31.24; 44.75; 67.79; 69.27; 72.76; 112.59; 124.30; 125.93; 128.46; 129.87; 130.58; 155.76; 173.46.

Elemental analysis for $C_{22}H_{36}CINO_4$ (*M*=413.98) requires (%): C 63.83; H 8.77; N 3.38; found: C 63.66; H 8.58; N 3.15. ν_{max} (KBr): 3600–3100 (br), 2936, 2863, 1615, 1491, 1296, 12,323, 1054, 880, 804, 648 cm⁻¹.

All of the prepared ILs were characterized by ¹H NMR and ¹³C NMR, and elemental analysis—details can be found in Supplementary data.

4.4. Thermal analysis

Thermal transitions of the prepared salts were determined by DSC, with a Mettler Toledo Star^e TGA/DSC1 (Leicester, UK) unit, under nitrogen. Samples between 5 and 15 mg were placed in aluminum pans and heated from 25 to 120 °C at a heating rate of

10 °C min⁻¹ and cooled with an intracooler at a cooling rate of 10 °C min⁻¹ to -100 °C. Thermogravimetric analysis was performed using a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples between 2 and 10 mg were placed in aluminum pans and heated from 30 to 450 °C at a heating rate of 10 °C min⁻¹.

4.5. Herbicidal activity

The biological activity of the alkyl-based ILs was examined on white mustard (S. alba L.), cornflower (C. cyanus L.), and rapeseed (B. napus) plants. In case of alkoxymethyl-based ILs the biological tests were conducted on common lamb's quarters (C. album L.) and white mustard plants. The seeds were sown into soil-filled pots to a depth of 1 cm. After emergence the plants were thinned to five plants in each pot. The treatment was applied at four leaf stage with the application of a spray chamber with Tee Jet 1102 flat-fan nozzles delivering 200 dm³ of spray solution per 1 ha at 0.2 MPa pressure. The distance from the nozzles to the tips of the plant was 40 cm, and the sprayer was moving above the plants, at a constant speed of 3.1 m s^{-1} . ILs and commercial herbicide were dissolved in a mixture of water and ethanol (1/1). All treatments were applied at a rate of 400 g of MCPA in calculation for 1 ha. The standard herbicide was commercial product (Chwastox 300 SL®) that contains 300 g of sodium and potassium salts of MCPA in 1 dm³. The plants were treated once with a solution of tested ILs and further placed in a growth chamber at a temperature of 20±2 °C, humidity of 60%, and photoperiod (day/night hours) 16/8.

In the case of experiments concerning the influence of temperature on herbicidal activity, a temperature of 6 °C was also used in growth chamber. After 4 weeks, the plants were cut to soil level and weighed with an accuracy of 0.01 g. The efficacy of the herbicides was calculated on the basis of the reduction of plant fresh weight as compared to control (no sprayed plants).

The study was carried out in four replications in a randomized setup.

4.6. Surface activity

The surface tension was determined using the shape drop method. The measurements were carried out by the use of a DSA 100 analyzer (Krüss, Germany, the accuracy of 0.01 mN m⁻¹) at 25 °C (temperature controlled using a Fisherbrand FBH604 thermostatic bath—Fisher (Germany), with the accuracy of 0.1 °C). 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 (3 cm³) from a CCD camera was taken and digitized. The surface tension (γ CMC, mN m⁻¹) is calculated by analyzing the profile of the drop according to the Laplace equation. The values of the critical micelle concentration (CMC) and the surface tension at the CMC (γ CMC) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension analysis method.

The basis for the determination of the contact angle is the image of the drop on the examined surface (paraffin). After determination of actual drop shape and the contact line, the drop shape is adapted to fit a mathematical model used to calculate the contact angle. The most exact method to calculate this value is Young–Laplace fitting (sessile drop fitting). Complete drop contour is evaluated. After successful fitting of the Young–Laplace equation, the contact angle is determined as the slope of the contour line at the 3-phase contact point (solid–liquid and liquid–air). The measurements were carried out by the use of DSA 100 analyzer, Krüss (Germany).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.05.041.

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