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Article

ALKYL(C,C,C)TRIMETHYLAMMONIUM BASED HERBICIDAL IONIC LIQUIDS

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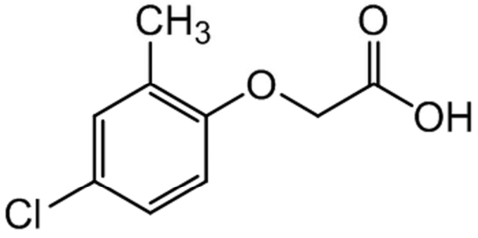
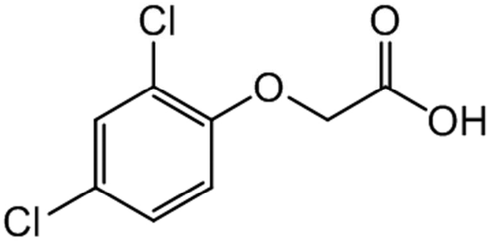
Graphic abstract



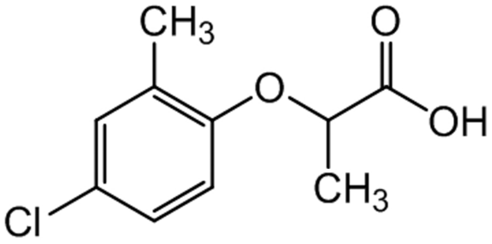
MCPA

1a-3a



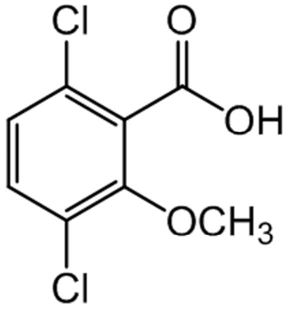
2,4-D

1b-3b



MCPP

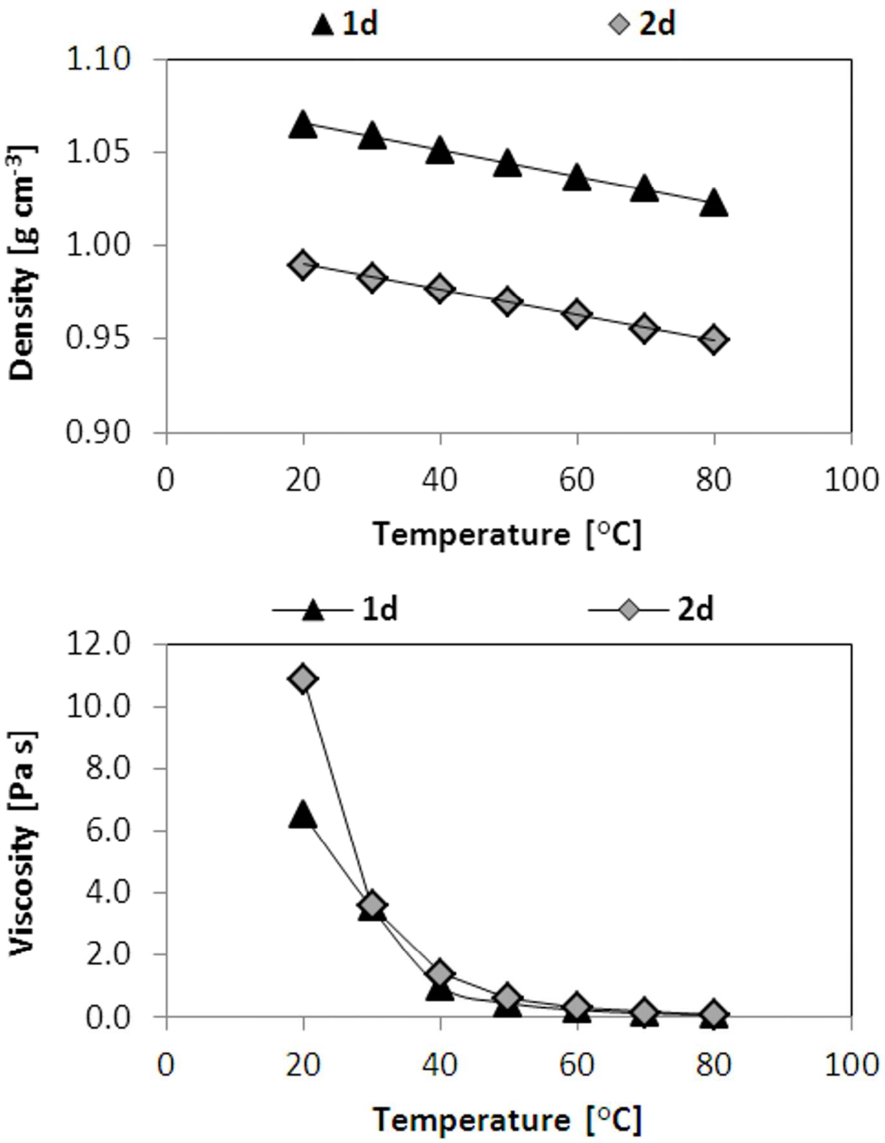
1d-3d



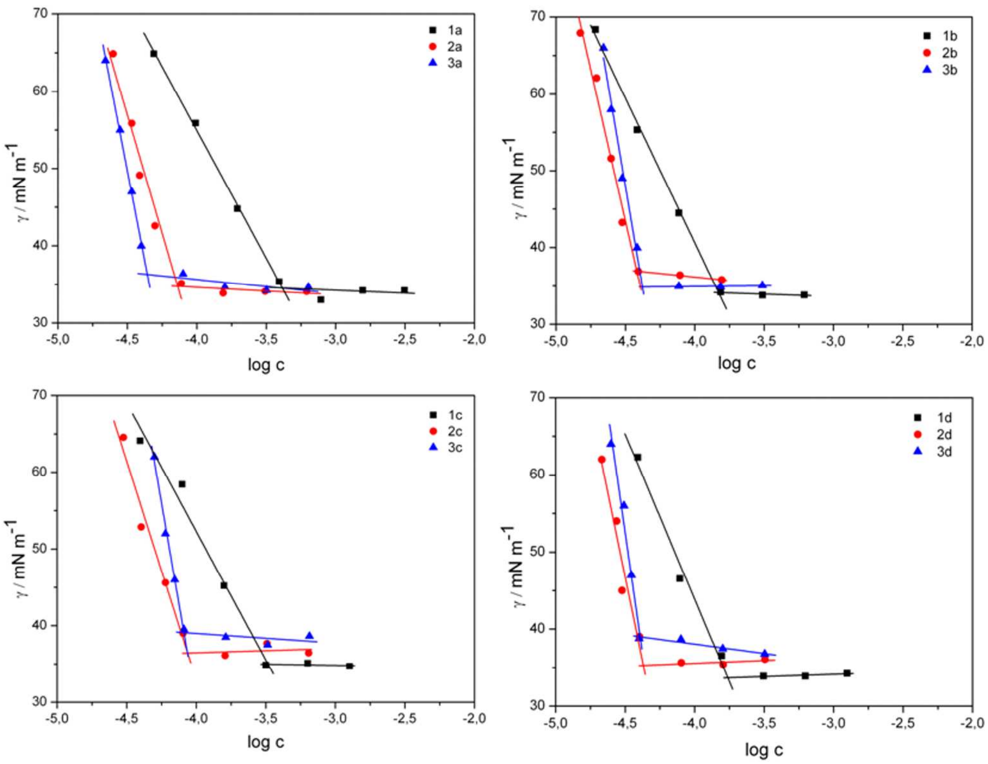
Dicamba

1c-3c

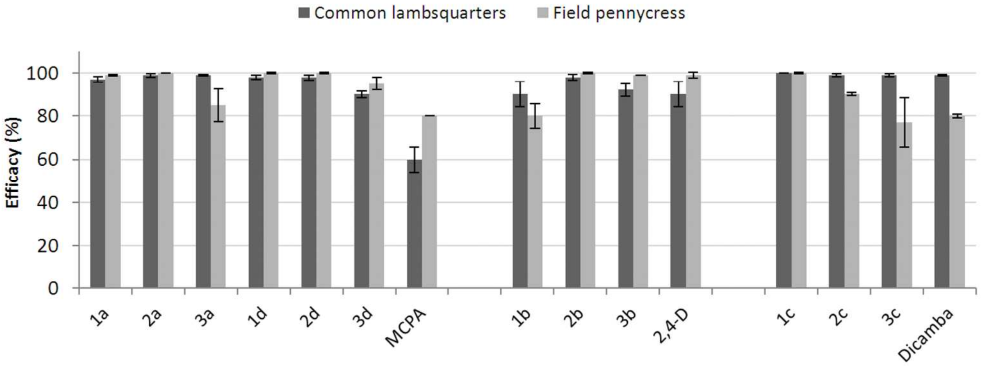
Structures of used herbicidal acids.



Viscosity and density values for **1d** and **2d**.



Surface tension of obtained salts.



Efficacy of HILs and reference products against two weed species in spring barley (Winna Gora – western part of Poland).

ALKYL(C_{16},C_{18},C_{22})TRIMETHYLAMMONIUM BASED HERBICIDAL IONIC LIQUIDS

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ABSTRACT. In the framework of this study a synthesis methodology and characterization of long alkyl herbicidal ionic liquids (HILs) based on four commonly used herbicides (2,4-D, MCPA, MCPP and dicamba) was presented. New HILs were obtained with high efficiency (>95%) using an acid-base reaction between herbicidal acids and hexadecyltrimetylamonium, octadecyltrimetylamonium and behenyltrimethylammonium hydroxides in alcoholic medium. Among all synthesized salts, only three compounds comprising the MCPP anion were liquids at room temperature. Subsequently, the influence of both the alkyl chain length and the anion structure on their physicochemical properties (thermal decomposition profiles, solubility in 10 representative solvents surface activity, density, viscosity and refractive index,) was determined. All HILs exhibited high thermal stability as well as surface activity, however, their solubility notably depended on both the length of the carbon chain and the structure of the anion. The herbicidal efficacy of the obtained salts was tested in greenhouse and field experiments. Greenhouse testing performed on common lambsquarters (*Chenopodium album* L.) and Flixweed (*Descurainia sophia* L.) as test plants indicated that HILs were characterized by similar or higher efficacy compared to commercial herbicides. The results of field trials confirmed the high activity of HILs, particularly those containing phenoxyacids as anions (MCPA, 2,4-D and MCPP).

KEYWORDS. Phenoxyacids, Growth regulators, Herbicidal Ionic Liquids, efficacy, long alkyl.

INTRODUCTION

Within the last several years, ionic liquids (ILs) have evolved from their application as solvents in synthesis towards new directions.[1] As a result, the third and most recent generation of ILs was created, which is focused on the production of ILs with biological activity, mainly in the field of pharmaceuticals.[2-5] Several studies confirm that active pharmaceutical ingredients in the form of ILs can provide new and unique properties compared to the solid pharmaceutical forms, with the possibility of improved performance, such as controlled solubility and drug delivery.[6-9] Moreover, dual-functional ILs composed of two active ions may even lead to synergistic effects.[6,10] Agrochemistry is another field where the combination of biological activity and the IL form contributes to many outstanding operational benefits. The novel fungicides with thiabendazole, imazalil, tebuconazole and propiconazole as ILs, with increased biological activity against many common plant pathogens, have already been described.[11,12] Moreover, ILs proved to be effective plant resistance inducers, which allow to stimulate the resistance system of the plant to act against pathogenic microorganisms.[13,14]

The insertion of the herbicidal anion into the structure of ionic liquids led to the development of a novel group of compounds defined as herbicidal ionic liquids (HILs).[15] This new group of ILs, described for the first time in 2011, may be applied as anti-weed agents in crop protection. HILs belong to the third generation of ILs due to the fact that they simultaneously exhibit targeted biological activity combined directly with selected physical and chemical properties.[2] There are several reports describing HILs which incorporate commonly used herbicides, such as: 2,4-D,[16,17] MCPA,[18-20] MCPP,[15,20] MCPB,[21] dicamba,[22] fomesafen,[23] glyphosate,[24] clopyralid,[25] metsulfuron-methyl,[26] and bentazone.[27] The combination of herbicidal activity of the anion with a different biological property of the cation (*e.g.*, plant growth inhibition) leads to dual-function HILs.[28] HILs can be also used in the protection of crops against pathogenic fungi – transformation of fungicides, such as tebuconazole and propiconazole, results in efficient fungicidal ILs with improved physicochemical properties.[29]

The currently available herbicidal formulations contain active ingredients mainly in the forms of sodium, potassium or ammonium salts and alkyl esters. Disadvantages of these forms are high water solubility and high vapor pressure. HILs are one of the recent discoveries in plant protection, which may bring a lot of advantages and solve many problems associated with the present agricultural practices. Due to their enhanced efficiency the required dose of active ingredient per hectare could be significantly reduced.[16,19,23] HILs could also reduce toxicity, hence a toxic herbicidal acid combined with an appropriate cation may form a nontoxic herbicide.[15] The negative influence of toxic vapors can be reduced by the extraordinary low vapor pressure of HILs – the ionic form of the pesticide does not spread to the neighboring fields and the potentially negative impact on the environment is significantly reduced.[22]

(Long alkyl)trimethylammonium chlorides and bromides are popular cationic surfactants that are commonly used mainly in the cosmetic industry.[30-32] The most representative compounds from this group possess C_{16}, C_{18} and C_{22} straight alkyl substituents attached to the nitrogen atom.[33-36] Low costs as well as good availability of hexadecyltrimethylammonium chloride (CAS 112-02-7), octadecyltrimethylammonium chloride (CAS 112-03-8) and behenyltrimethylammonium chloride (CAS 17301-53-0) are the results of a positive opinion of European Food Safety Authority (EFSA) and U. S. Food and Drug Administration (FDA), which allowed their use in cosmetic products.[37,38] Furthermore, the maximum authorized concentration of these ammonium salts should not exceed 0.1% when applied as preservatives or be in range from 0.5 to 3.0% for other, non-preservative functions. However, the possible occurrence of skin irritating issues limits their use at higher concentrations in dermal care products.[37] Nevertheless, due to their unique, multifunctional properties, alkyl(C_{16},C_{18},C_{22})trimetylamonium halides have also been successfully applied as intercalating agents for layered silicates and their nanocomposites,[39-42] drag reducing agents for anionic polymer solutions,[43] emulsion viscosity stabilizers[44] and basic hydrolysis catalysts via cationic mixed micelles.[45]

This study describes a convenient synthesis methodology of biologically active ILs possessing a long-alkyl-chain quaternary ammonium cation. Furthermore, HILs comprising an alkyl substituent longer than C_{18} in the cation – a behenyl group (C_{22} alkyl) was presented for the first time and their properties were compared with their homologues - alkyltrimethylammonium HILs with a shorter carbon chain (C_{16} and C_{18} alkyl). The source of anion were phenoxyacids (2,4-D, MCPA and MCPP) as well as dicamba, which are systemic, selective herbicides belonging to the group of growth regulators. The high, unabated popularity of these compounds is due to the fact that the risk of formation of biotypes resistant to them is relatively low compared to other classes of herbicides (*e.g.*, sulfonylureas). This study involves the evaluation of the influence of length of alkyl chain on the physicochemical properties (*i.e.* thermal stability, solubility, surface activity) as well as results of herbicidal efficiency determined in greenhouse and field experiments.

MATERIALS AND METHODS

Materials

Quaternary ammonium chlorides with long alkyl groups were purchased from Stockmeier and Brenntag. Herbicidal acids (2,4 D, MCPA, MCPP and dicamba) were supplied by Organika-Sarzyna S.A. Poland and PESTINOVA Poland. All solvents (methanol, DMSO, acetonitrile, acetone, isopropanol, ethyl acetate, chloroform, toluene, hexane) and KOH were purchased from Aldrich (European market, Poznan, Poland) and used without further purification. Water for solubility and surface activity measurements was deionized with the conductivity below 0.1 mS cm^{-1} from demineralizer HLP Smart 1000 (Hydrolab).

Synthesis of alkyltrimethylammonium salts

After evaporation of solvent from an aqueous solution of appropriate precursor, each alkyltrimethylammonium chloride (0.1 mol) was dissolved in 50 cm^3 of anhydrous methanol, and then mixed with solution of 0.1 mol of potassium hydroxide dissolved in 25 cm^3 of methanol. The reaction was conducted for 10 minutes and the precipitated inorganic by-product was removed by filtration. Next, the filtrate containing alkyltrimethylammonium hydroxide was neutralized with the selected herbicidal acid. All neutralization reactions were conducted in a Mettler Toledo semi-automated reactor system - EasyMax™. In order to prevent the degradation of intermediate products, the temperature of the reactor contents was thermostatted at 25 °C. The connected SevenMulti Mettler Toledo instrument equipped with a calibrated glass electrode allowed for precise measurement of the decrease in pH of the mixture as a result of proceeding reaction. Then, the solvent was removed under reduced pressure and the crude product was obtained. Afterwards, the residue was dissolved in 50 cm^3 of acetone and the inorganic salts (by-products) were filtered off. After the evaporation of acetone, the compound was dried under vacuum for 24 hours at the temperature 65 °C. NMR spectra descriptions, elemental analyses for all compounds are provided in the ESI.

General

The structures of obtained salts were confirmed by the analysis of the nuclear magnetic resonance spectrum (^1H and ^{13}C). ^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. ^{13}C NMR spectra were obtained with the same instruments at 75 and

100 MHz, respectively. CHN elemental analyses were performed at A. 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 measurements

Density was determined using an Automatic Density Meter DDM2911 with a mechanical oscillator method. The density of the samples (approx. 2.0 cm^3) were measured with respect to temperature controlled conditions via Peltier, from 20 to 80 °C. The apparatus used for density measurements 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.

Viscosity measurements

Viscosity was determined using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosity of the samples (approx. 1.5 cm^3) was measured with respect to temperature, from 20 to 80 °C. The uncertainty of the viscosity measurement was estimated to be less than 10^{-4} Pa·s.

Refractive index measurements

Refractive index was determined using Automatic Refractometer J357 with electronic temperature control in range from 20 to 80 °C. The accuracy of the temperature stabilization was 0.02 °C and uncertainty of the refractive index measurement was less than 0.00005.

The 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 of the ammonium salt in the water-chloroform biphasic system (or water-methanol-chloroform in the case of compounds with limited solubility in water) by a standard solution of sodium dodecylsulphate(VI) in the presence of the mixed indicator (dimidium bromide indicator (CAS: 518-67-2) is used for determination of cationic active substances, and sulfan blue indicator (CAS: 129-17-9) is employed for determination of anionic active substances.

Thermal analysis

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

Solubilities

The solubilities of the prepared salts were determined according to the protocols in Vogel's Textbook of Practical Organic Chemistry.[46] Ten representative protic and aprotic solvents with a diverse polarity range were selected for analyses and arranged in order of decreasing polarity expressed as the Snyder polarity index: water, 9.0; methanol, 6.6; DMSO, 6.5; acetonitrile, 6.2; acetone, 5.1; isopropanol, 4.3; ethyl acetate, 4.3; chloroform, 4.1; toluene, 2.3; hexane, 0.0. A 0.1 g sample of each salt was added to a certain volume of the solvent and the samples were thermostatted in Water Bath MEMMERT Model WNB 7 at 25 °C. Based on the volume of solvent used, 3 types of behaviors were recorded: ‘soluble’ applies to compounds which dissolved in 1 cm^3 of solvent, ‘limited solubility’ – applies to compounds that dissolved in 3 cm^3 of solvent, and ‘not soluble’ – applies to the compounds which did not dissolve in 3 cm^3 of solvent.

Surface activity

Surface tension measurements were carried out by the use of a DSA 100 analyzer (Krüss, Germany, accuracy 0.01 mN m^{-1}), at 25 °C. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy 0.1 °C). The surface tension was determined using the shape drop method. 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 from a CCD camera and digitized. The surface tension (in 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 (γCMC) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves (γCMC vs logC curves) using a linear regression 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 the 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.

Greenhouse experiment

The test were conducted using two species of weeds: common lambsquarters (*Chenopodium album* L.) and flixweed [*Descurainia Sophia* (L.) Webb ex Prantl]. The seeds were sown into plastic pots filled with commercial peat-based potting material. All ILs were dissolved in a mixture of water and ethanol (1:1 v/v) in an amount corresponding the dose of 400 g MCPA, MCPP, 2,4-D per 1 ha or 200 g dicamba per 1 ha. The commercial herbicides Chwastox Extra 300 SL (300 g of sodium and potassium salts of MCPA in 1 dm^3), Aminopielik Standard 600 SL (600 g dimethylammonium salts of 2,4 D in 1 dm^3) and Dikamba 480 SL (480 g dicamba in 1 dm^3) were dissolved in water at the same doses of active ingredient as in the case adequate ILs. The treatments were applied at 4-6 leaf stage using a moving sprayer occupied with Tee Jet 110/02 flat-fan nozzles delivering 200 dm^3 of spray solution per 1 ha at 0.2 MPa pressure. The plants were placed in a greenhouse at the temperature of 20 °C, humidity of 60% and photoperiod (day/night hours) of 16/8. 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 corresponding control: commercial herbicides treatments to the water treatment (control 1); ILs treatments – to the water:etanol treatment (control 2).

The linear models with only treatment were used as a fixed effect to analyze the influence of treatments on fresh weight of both investigated plants. In the next step the assumptions through inspection of diagnostic plots were checked for deviations from homoscedasticity and normality of residuals.[47,48] The post hoc pairwise comparisons were performed with Tukey’s adjustment on all possible combinations of treatments. All analyses were performed in R 3.3.2 (R Core Team 2012) with lsmeans 2.25 package.[49,50]

Field experiment

The field experiment was performed in 2015 at the Experimental Station of the Institute of Plant Protection in Winna Gora (Poland) in spring barley. The individual plot size was 16 m^2. All treatments were applied using a small plot spraying equipment with AXR 110/03 flat-fan nozzles (TeeJet Technologies, Wheaton, IL, USA) delivering 200 dm^3 ha^{-1} of spray solution at 0.3 MPa of operating pressure. The synthesized ILs were applied at the same dose as in greenhouse experiments. Weed control was evaluated visually using a scale of 0 (no effect) to 100% (complete weed destruction). The target weeds were common lambsquarters (*Chenopodium album* L.) and field pennycress (*Thlaspi arvense* L.). The study was carried out in 4 replications in a randomized blocks setup. The study was carried out in four replications in a randomized setup. Each error margin range represents standard errors of the mean (SEM). The SEM values were calculated according to equation 1:

Equation 1. Calculation of SEM values.

$$SEM = \frac{s}{n^{0.5}}$$

where:

SEM – standard error of the mean,

s – sample standard deviation,

n – number of samples.

RESULTS AND DISCUSSION

Synthesis and characterization of ILs

All salts presented in Table 1 were synthesized via the neutralization reaction between alkyltrimethylammonium hydroxides and different herbicidal acids, such as (4-chloro-2-methylphenoxy)acetic acid (MCPA), (2,4-dichlorophenoxy)acetic acid (2,4-D), 3,6-dichloro-2-methoxybenzoic (dicamba) and (±)2-(4-chloro-2-methylphenoxy)propionic acid (mecoprop - MCPP). Structures of the used herbicides are presented in Figure 1.

Figure 1. here.

Obtained compounds have been divided into four groups: group *a* refers to salt with MCPA anion, *b* to salts with 2,4-D anion, *c* to salts with dicamba anion and *d* to salts with MCPP anion. The acid-base reaction (Scheme 1) was carried out at 25°C in semi-automatic reactor EasyMax™ equipped with a glass electrode, where a decrease in pH has been controlled precisely.

Scheme 1. here.

Efficient neutralization and purification of obtained products allowed to achieve high yields between 90 and 99% (Table 1). The purity of **1-3** was determined via the direct two-phase titration technique. According to this method, the synthesized salts were characterized by high purities exceeding 98%. The selected syntheses methodology proved to be highly effective and repeatedly faster than the conventional anion exchange reaction performed in an aqueous solution. Therefore, the difficulties associated with the long time of separation of phases via two phase extraction (caused by the presence of highly surface-active cation) as well as foam formation during evaporation of the solvent have been easily eliminated. It was noted that the increase in the length of the alkyl chain did not deteriorate the reaction yields or the purity of the obtained products.

Table 1. here.

Structures of the obtained new salts were confirmed by ^{1}H and ^{13}C NMR spectroscopy. NMR spectra descriptions as well as elemental analysis results are provided in the Supporting Information. The water content of **1-3** measured *via* Karl-Fischer titration was below 0.5%. Moreover, the synthesized salts were stable in air as well as in contact with water and common organic solvents during all the performed analyses. They could be made anhydrous by heating at 70 °C in vacuum and storing them over P_4O_{10}.

All salts with MCPA (**1a**-**3a**), 2,4-D (**1b**-**3b**) and dicamba (**1c**-**3c**) anion were solids at room temperature. In case of these three groups, the length of alkyl chain did not significantly affect their state at 25 °C. Furthermore, only salts comprising the MCPP anion (**1d**-**3d**) were liquids at 25 °C, which demonstrates that additional methyl groups in the molecule of herbicide caused a considerable reduction of melting points. Moreover, concerning the low melting points (< 25 °C) of **1d**, **2d** and **3d**, they may be described as room temperature ionic liquids (RTILs).

Basic physicochemical properties

Basic physicochemical properties, such as viscosity, density and refractive index were determined for **1d** and **2d** in range from 20 to 80 °C and presented in Fig. 2 (the collected physicochemical data are provided in the Supporting Information in Table S1).

Figure 2. here.

At 20 °C the values of viscosity for **1d** and **2d** notably increased with the increase of the alkyl chain length. Therefore, the measured values for RTILs with hexadecyl (**1d**) and octadecyl (**2d**) group were equal to 10.898 Pa·s and 6.535 Pa·s, respectively. Further elongation of the alkyl chain caused a subsequent, rapid increase of this parameter. As a result, the IL with behenyl (**3d**) substituent was a grease at room temperature. Generally, the obtained data is consistent with several reports which established that the viscosity of IL would increase as the size of the non-polar part in the cation becomes larger.[51,52] It was also noted that the viscosity of both RTILs is comparable with values described in other reports regarding HILs.[18,20,21] As expected, the viscosity of the synthesized salts decreased nonlinearly with increasing temperature. Hence, an increase in the temperature from 20 to 80 °C caused a rapid reduction of the analyzed parameter, which ultimately reached 0.091 for (**1d**) and 0.103 Pa·s for (**2d**). Fig. 2 shows that the density of the RTIL with hexadecyl group

(**1d**) was higher compared to the density of pure water, however, the elongation of alkyl chain caused a reduction of this parameter for **2d**. As a result, the values at 20 °C collected were equal to 1.065 $g{\cdot}cm^{-3}$ for **1d** and 0.990 $g{\cdot}cm^{-3}$ for **2d**, respectively. The observed tendency was similar to other previously described HILs.[18,21] Moreover, the density values of the obtained ILs were temperature-dependent and decreased linearly with the increase in temperature. Hence, a temperature increase from 20 to 80 °C resulted in the reduction of this parameter by approx. 0.04 $g{\cdot}cm^{-3}$ for both analyzed salts. The linear decrease of density was expressed as the equation $y = a{\cdot}x + b$ (R^2>0.99), where a was equal to approx. -0.0007 while b was at 1.08 $g{\cdot}cm^{-3}$ for **1d** and 1.00 $g{\cdot}cm^{-3}$ for salt **2d**.

The measured refractive index values for RTILs with the MCPP anion at 20 °C were similar and amounted to 1.503 for **1d** and 1.493 for **2d**. All collected data are presented in Supporting Information (Table S1). The obtained results indicated that the elongation of the alkyl substituent from C_{16} to C_{18} caused a decrease of refractive index values. Moreover, heating both samples caused a slight, linear decrease of this parameter. This phenomenon was already observed and described in literature for many HILs.[18,21] At 80 °C the refractive indices were approx. 0.006 lower and reached values equal to 1.497 for **1d** and 1.486 for **2d**, respectively. The linear regression equations for both salts were characterized by high correlation coefficients ($R^2 > 0.99$), where a was equal to approx. -0.0001 while b amounted to 1.504 for **1d** and 1.495 for **2d**.

Thermal Properties of synthesized ILs

Thermal transitions and decomposition temperatures are presented in Table 2. All the obtained ILs with the MCPP anion (**1d-3d**) were liquids even at very low temperatures reaching -100 °C. Therefore neither melting nor crystallization events were observed for them in the analysed temperature range. The lowest melting point was noted for **2b** (T_m = 55

°C) and the highest for **1c** (T_m = 55 °C), which additionally possessed a crystallization event on cooling at 117.0 °C.

Table 2. here.

The obtained T_m values did not allow to determine the effect of the alkyl chain length on this parameter, however, the influence of the structure of the anion could be established. The ability of the anion to reduce the melting point of the synthesized salts increases in the following order:

$$\text{dicamba} > \text{2,4-D} \approx \text{MCPA} > \text{MCPP}$$

According to data presented in Table 2, all the prepared salts with the sole exception of **1c** could be classified as ILs. Furthermore, the crystallization temperatures (T_{cryst}) could not be determined for the majority of the obtained ILs. In consequence, **1a**-**1c**, **1b**-**3b**, **2c** and **3c** exhibited a supercooling behavior and a melting transition was observed on the first heating but it could not be reproduced within several heating/cooling cycles. Similar findings were reported for other tetraalkyl ammonium HILs with phenoxyacids as anions.[17,22,26] The glass transition temperatures (T_g) were not determined in the analyzed temperature range for all synthesized ILs. The measured $T_{onset5\%}$ values occurred at a range from 181 °C for **1c** to 199 °C for **3b**. ILs comprising the behenyl (C_{22}) substituent (**3a-d**) exhibited a higher thermal stability, since their $T_{onset5\%}$ values were higher by 2 to 5 °C compared to ILs with the hexadecyl (C_{16}) group (**1a-d**). These differences mean that enhancement of the thermal stability slightly depends on the elongation of the alkyl chain. Therefore, values collected for ILs with the octadecyltrimethylammonium cation (**2a-d**) were similar and varied from 186 to 197 °C. The influence of the anion on the decrease of $T_{onset5\%}$ may be described by the following order:

$$\text{2,4-D} > \text{MCPA} > \text{MCPP} > \text{dicamba}$$

The phenoxy acids (2,4-D, MCPA and MCPP) increased the thermal stability of the obtained salts compared to dicamba. This observation corresponds well with the previous reports regarding other HILs.[19,20] The temperature values which caused a 50% decomposition of the sample ranged from 214 °C for **1a** to 232 °C for **3a**. Similarly as in case of the $T_{onset5\%}$ parameter, the lowest values were generally observed for salts comprising the hexadecyl group (**1a**-**d**), whereas the highest were observed for ILs with the behenyl substituent (**3a**-**d**). The extension of the alkyl chain by six carbon atoms resulted in a slight increase of the T_{onset} parameter form approx. 6 °C for MCPP-based ILs (**1d**-**3d**) to approx. 18 °C for 2,4-D-based ILs (**1a**-**3a**). Although the influence of the anion structure on the T_{onset} values was small, the increase of thermal stability caused by the alkyl chain elongation is consistent with data regarding homologous series of HILs.[18,21]

Solubilities

The solubility of obtained salts (Table 3) was determined in selected solvents, such as water, DMSO, acetonitrile, acetone, 2-isopropanol, ethyl acetate, chloroform, toluene and hexane, according to Vogel's Textbook of Practical Organic Chemistry.[46]

Table 3. here.

Due to the presence of an ionic bond and apolar long alkyl chain, the ILs were soluble in some polar protic solvents as well as aprotic solvents. Thus, all tested compounds were soluble in methanol and chloroform. Moreover, the majority of them were poorly soluble in solvents characterized by the highest polarity - water and DMSO. Interestingly, the elongation of alkyl chain caused a deterioration of ILs solubility. Therefore, ILs with the hexadecyl substituent (**1a**, **1b** and **1d**) exhibited good affinity for both solvents, in contrast to ILs with behenyl group (**3a**-**3d**).

It was also noted that the dicamba anion notably decreased the solubility in both water and DMSO in comparison to other anions (MCPA, 2,4-D and MCPP), which represent phenoxyacids derivatives. Only **1d** was soluble in acetonitrile, whereas slightly less polar acetone dissolved all ILs with the MCPA anion (**1a**-**3a**) as well as two ILs (**1d** and **2d**) with MCPP as the anion. Isopropanol, similarly as methanol, dissolved all salts except **1a** and **1c**, which comprised the shortest alkyl substituent. Hence, the chain extension may improve the affinity for this solvent. In case of nonpolar solvents, all tested compounds with 2,4-D (**1b**-**3b**) and dicamba (**1c**-**3c**) anions were insoluble in toluene and hexane. The substitution of the aromatic ring with a methyl group in MCPA-based salts (**1a**-**3a**) and MCPP-based salts (**1d**-**3d**) may improve the affinity for these solvents. Among all selected solvents, only ethyl acetate and hexane did not dissolve all tested salts.

Surface properties

The surface activity parameters of ILs: critical micelle concentration (CMC), surface tension at CMC (γCMC), efficiency of surface adsorption on an air-water interface (pC_{20}), maximum surface excess concentration (Γ_{max}), surface area occupied by salt molecules (A_{min}) and contact angle (CA) were determined and presented in Table 4.

Table 4. here.

The relations between the surface tension values of aqueous solutions of the synthesized salts and the log of concentration were plotted in Fig. 3.

Figure 3. here.

It can be observed that the surface tension of the aqueous solutions of ILs showed a progressive decrease with increasing concentration and remained constant above the CMC. The CMC value is a break point of surface tension curve and the plateau zone reflects the formation of micelles. Based on these plots, the surface active parameters were calculated for the obtained salts and the corresponding chlorides. Moreover, the results obtained for halides were compared with the literature data. The measured CMC values for hexadecyltrimethylammonium chloride and octadecyltrimethylammonium chloride were 1.412 and 0.338 mmol·dm^{-3}, respectively. Similar values were presented by Cepeda et al. and were at 1.6 mmol·dm^{-3} for hexadecyltrimethylammonium chloride and 0.3 mmol·dm^{-3} for octadecyltrimethylammonium chloride (obtained by conductivity method).[49]

As the derivatives of cationic surfactants – all the obtained salts were characterized by good surface-active and wetting properties. A decrease of the CMC value was observed with the increase in the alkyl chain length. For example, in case of ILs with the MCPA anion the increase of the alkyl chain length resulted in the decrease of the measured CMC value from 0.459 mmol·dm^{-3} for **1a** to 0.043 mmol·dm^{-3} for **3a**. An interesting aspect of obtained results in the present study, which should be remarked, was the lowest values of CMC in case of ILs containing the longest alkyl chain (**3a-3d**). However these ILs were characterized by significantly higher values of the contact angle than the other tested ILs. The contact angle value ranged from 77.5° for **3a** to 96.7° for **3b**. Among all the synthesized salts, the lowest observed value of contact angle was equal to 55.7° for **2a**. Generally, the results obtained for salts **1a-1d** and **2a-2d** are similar to the results obtained for HILs comprising C_{16} and C_{18} alkyl groups.[18,21]

Moreover, the area per molecule values (A_{min}) presented in Table 4 were lowest for ILs comprising the C_{22} substituent (**3a-3d**). The obtained data indicate that alkyl chain elongation facilitates a more tightly packed arrangement of the synthesized ILs at the water–air interface. Analysis of the obtained results indicates that the influence of the structure of the anion on the surface-active properties of ILs is notable only in case of salts belonging to group 1. In this case the CMC was decreased in the following order:

MCPA > dicamba > MCPP > 2,4-D

Comparison of surface activity of salt **1a** (with the MCPA anion) and salt **1b** (with the 2,4-D anion) suggests that the CMC value was decreased by approx. 4 times. However, the influence of the anion is notably lower in case of ILs comprising shorter alkyl groups (**2a-2d** and **3a-3d**), since the obtained results are similar.

Herbicidal Activity

The herbicidal effect of **1-3** on two weed species was tested both under greenhouse and field conditions. The results of greenhouse experiments are shown in Tables 5-7. ILs with MCPA (**1a-3a**), MCPP (**1d-3d**), 2,4-D (**1b-3b**) and dicamba (**1c-3c**) anions showed varying effectiveness.

Table 5. here.

The efficacy against common lambsquarter ranged from 38% to 82%. Flixweed demonstrated a greater sensitivity to the tested compounds (69-82%). In most cases the tested ILs were more active compared to the reference herbicide. The herbicidal effect was lower in case of ILs containing the 2,4-D anion, especially in case of common lambsquarters which (efficacy at 33-42%).

In case of salts **1c-3c** with the dicamba anion the obtained results indicated that their herbicidal efficacy was similar to the reference herbicide was similar (in case of flixweed) or notably higher. The obtained results suggest that the synthesized ILs display a similar or better efficacy compared to commercial herbicidal products. It is worth noticing that the length of the aliphatic alkyl chain in the cation did notably influence the herbicidal activity of ILs in the tested range of C_{16} to C_{22}.

Visual inspection of diagnostic plots did not reveal any obvious deviations from homoskedascity or normality in the case of both plant species. Both models were statistically significant ($F(16,34) = 4.671$, $p < 0.001$ in the case of common lambsquarters and $F(16,34) = 8.272$, $p < 0.001$ in the case of significant flixweed), and presented moderately high values of adjusted R squared – 0.5402 and 0.6994 (for common lambsquarters and flixweed respectively). Significant differences ($p < 0.05$) between treatments pairs are provided in Table 6 for common lambsquarters and Table 7 for flixweed.

Table 6. and 7. here.

The synthesized ILs may be classified as ammonium HILs with surface activity, which is associated with the presence of the long alkyl group in the cation (with 16, 18 or 22 carbon atoms). No significant correlations between the surface activity (reflected by the pC_{20} parameter given in Table 4) and the herbicidal activity could be established, in contrast to the previously reported homologues of HILs comprising shorter alkyl substituents.[18,21] The general values of the pC_{20} parameter were at 3.9-4.0 (Table 4) contributed to an enhancement of the herbicidal activity in comparison to the commercial herbicide. This is also confirmed by literature data,[18,21] which suggest that an increase of the efficacy of HILs occurred at pC_{20} values > 3.0. An additional advantage of the employed cations is associated with the fact, that they can be obtained from cheap and commercially available alkyl(C_{16},C_{18},C_{22})trimethylammonium chlorides and bromides. Furthermore, most of the obtained HILs (with the exception of **1a**, **1b** and **2d**) displayed hydrophobic properties, which may reduce their mobility in the terrestrial environment and minimize the risk of groundwater contamination. Since positive results were obtained under greenhouse conditions, additional field studies were carried out.

The field studies focused on the evaluation of herbicidal efficacy based on the visual method. The results are presented in Figure 4. HILs with MCPA (**1a**-**3a**), 2,4-D (**1b**-**3b**), dicamba (**1c**-**3c**) and MCPP (**1d**-**3d**) anions exhibited a very high herbicidal efficacy against common lambsquarters and field pennycress. HILs with the behenyl group (**3**) and MCPA, MCPP or dicamba anions exhibited lower herbicidal efficacy compared to HILs with shorted alkyl substituents.

Figure 4. here.

HILs with the 2,4-D anion and the reference herbicide exhibited a very high efficacy in the range of 80-100 % in case of common lambsquarters and 90-98% in case of field pennycress. HILs with the dicamba anion exhibited a similar efficacy to the reference herbicide against common lambsquarters, while the results against field pennycress were more diversified. In this case only HIL **3c** displayed a slightly lower efficacy compared to the reference herbicide. The results obtained during field studies confirm the high herbicidal efficacy of ammonium HILs with long alkyl substituents (hexadecyl, octadecyl or even behenyl). To the best of our knowledge, this is the first report regarding HILs with the behenyl (C_{22}) group.

ABBREVIATIONS

C_{16}	Hexadecyl substituent;
C_{18}	Octadecyl substituent;
C_{22}	Behenyl substituent;
MCPA	(4-Chloro-2-methylphenoxy)acetic acid;
2,4-D	(2,4-Dichlorophenoxy)acetic acid;
Dicamba	3,6-Dichloro-2-methoxybenzoic acid;
MCPP	2-(4-Chloro-2-methylphenoxy)propionic acid;
IL	Ionic liquids;
HILs	Herbicidal ionic liquids;
pH	Acidity of solution;
NMR	Nuclear Magnetic Resonance Spectroscopy;
TGA	Thermal Gravimetric Analysis;
DSC	Differential Scanning Calorimetry;
T_g	Glass transition temperature;

$T_{onset5\%}$	Decomposition temperature of 5% of the sample;
T_{onset}	Decomposition temperature of 50% of the sample;
T_m	Melting point;
CMC	Critical micelle concentration;
γCMC	Surface tension at CMC;
pC_{20}	Efficiency of surface adsorption on an air-water interface;
Γ_{max}	Maximum surface excess concentration;
CA	Contact angle;
EN ISO	International Standard, in English;

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SUPPORTING INFORMATION. ^{1}H and ^{13}C NMR spectra, elemental analyses results of all the compounds as well as results of density, viscosity and refractive index values for ILs with MCPP anion are provided in Electronic Supporting Information.

REFERENCES

(1) Smiglak, M.; Pringle, J. M.; Lu, X.; Han, L.; Zhang, S.; Gao, H.; MacFarlane, D. R.; Rogers, R. D. Ionic liquids for energy, materials, and medicine. *Chem. Commun.* **2014**, 50, 9228-9250.

(2) Hough, W. L.; Smiglak, M.; Rodriguez, H.; Swatloski, R. P.; Spear, S. K.; Daly, D. T.; Pernak, J.; Grisel, J. E.; Carliss, R. D.; Soutullo, D. M.; Davis J. H.; Rogers, R.D. The third

evolution of ionic liquids: active pharmaceutical ingredients. *New J. Chem.* **2007**, 31, 1429-1436.

(3) Frizzo, C. P.; Gindri, I. M.; Tier, A. Z.; Buriol, L.; Moreira, D. N.; Martins, M. A. P. Pharmaceutical Salts: Solids to Liquids by Using Ionic Liquid Design in *Ionic Liquids—New Aspects for the Future*; Kadokawa, J., Ed.; InTech: Rijeka, Croatia, **2013**, Chapter 21, 557-579.

(4) Bica, K.; Rijksen, C.; Nieuwenhuyzen, M.; Rogers, R. D. In search of pure liquid salt forms of aspirin: ionic liquid approaches with acetylsalicylic acid and salicylic acid. *Phys. Chem. Chem. Phys.* **2010**, 12, 2011-2017.

(5) Cojocaru, O. A.; Bica, K.; Gurau, G.; Narita, A.; McCrary, P. D.; Shamshina, J. L.; Barber, P. S.; Rogers, R. D. Prodrug ionic liquids: functionalizing neutral active pharmaceutical ingredients to take advantage of the ionic liquid form. *MedChemComm.* **2013**, 4, 559-563.

(6) Bica, K.; Rodríguez, H.; Gurau, G.; Cojocaru, O. A.; Riisager, A.; Fehrmann, R.; Rogers, R. D. Pharmaceutically active ionic liquids with solids handling, enhanced thermal stability, and fast release. *Chem. Commun.* **2012**, 48, 5422-5424.

(7) Shamshina, J. L.; Kelley, S. P.; Gurau, G.; Rogers, R. D. Develop ionic liquid drugs. *Nature* **2015**, 528, 188-189.

(8) Bica, K.; Rogers, R. D. Confused ionic liquid ions - a "liquification" and dosage strategy for pharmaceutically active salts. *Chem. Commun.* **2010**, 46, 1215-1217.

(9) Pinto, P. C. A. G.; Ribeiro, D. M. G. P.; Azevedo, A. M. O.; Dela Justina, V.; Cunha, E.; Bica, K.; Vasiloiu, M.; Reis, S.; Saraiva, M. L. M. F. S. Active pharmaceutical ingredients based on salicylate ionic liquids: insights into the evaluation of pharmaceutical profiles. *New J. Chem.* **2013**, 37, 4095-4102.

(10) Hough-Troutman, W. L.; Smiglak, M.; Griffin, S.; Reichert, W. M.; Mirska, I.; Jodynis-Liebert, J.; Adamska, T.; Nawrot, J.; Stasiewicz, M.; Rogers. R. D.; Pernak, J. Ionic liquids with dual biological function: sweet and anti-microbial, hydrophobic quaternary ammonium-based salts. *New J. Chem.* **2009**, 33, 26-33.

(11) Bica, K.; Cooke, L. R.; Nugent, P.; Rijksen, C.; Rogers, R. D. Toxic on purpose: ionic liquid fungicides as combinatorial crop protecting agents. *Green Chem.* **2011**, 13, 2344-2346.

(12) Pernak, J.; Markiewicz, B.; Łęgosz, B.; Walkiewicz, F.; Gwiazdowski, R.; and Praczyk, T. Known triazole fungicides – a new trick. *RSC Adv.* **2015**, 5, 9695-9702.

(13) Smiglak, M.; Kukawka, R.; Lewandowski, P.; Pospieszny, H. Cationic derivatives of the plant resistance inducer benzo[1,2,3]thiadiazole-7-carbothioic acid S-methyl ester (BTH) as bifunctional ionic liquids. *Tetrahedron Lett.* **2014**, 55, 3565-3568.

(14) Lewandowski, P., Kukawka, R.; Pospieszny, H.; Smiglak M. Bifunctional quaternary ammonium salts based on benzo[1,2,3]thiadiazole-7-carboxylate as plant systemic acquired resistance inducers. *New J. Chem.* **2014**, 38, 1372-1375.

(15) Pernak, J.; Syguda, A.; Janiszewska, D.; Materna, K.; Praczyk, T. Ionic liquids with herbicidal anions. *Tetrahedron* **2011**, 67, 4838-4844.

(16) Praczyk, T.; Kardasz, P.; Jakubiak, E.; Syguda, A.; Materna K.; Pernak, J. Herbicidal Ionic Liquids with 2,4-D. *WeedSci.* **2012**, 60, 189-192.

(17) Pernak, J.; Syguda, A.; Materna, K.; Janus, E.; Kardasz, P.; Praczyk, T. 2,4-D based herbicidal ionic liquids. *Tetrahedron* **2012**, 68, 4267-4273.

(18) Kordala-Markiewicz, R.; Rodak, H.; Markiewicz, B.; Walkiewicz, F.; Sznajdrowska, A.; Materna, K.; Marcinkowska, K.; Praczyk, T.; Pernak, J. Phenoxy herbicidal ammonium ionic liquids. *Tetrahedron* **2014**, 70, 4784-4789.

(19) Niemczak, M.; Giszter, R.; Czerniak, K.; Marcinkowska K.; Walkiewicz, F. Bis(ammonium) ionic liquids with herbicidal anions. *RSC Adv.* **2015**, 5, 15487-15493.

(20) Pernak, J.; Czerniak, K.; Niemczak, M.; Chrzanowski, Ł.; Ławniczak, Ł.; Fochtman, P.; Marcinkowska K.; Praczyk, T. Herbicidal ionic liquids based on esterquats. *New J. Chem.* **2015**, 39, 5715-5724.

(21) Pernak, J.; Niemczak, M.; Materna, K.; Żelechowski, K.; Marcinkowska K.; Praczyk, T. Synthesis, properties and evaluation of biological activity of herbicidal ionic liquids with 4-(4-chloro-2-methylphenoxy)butanoate anion. *RSC Adv*. **2016**, 6, 7330-7338.

(22) Cojocaru, O. A.; Shamshina, J. L.; Gurau, G.; Syguda, A.; Praczyk, T.; Pernak, J.; Rogers, R. D. Ionic liquid forms of the herbicide dicamba with increased efficacy and reduced volatility. *Green Chem.* **2013**, 15, 2110-2120.

(23) Ding, G.; Liu, Y.; Wang, B.; Punyapitak, D.; Guo, M.; Duan, Y.; Li J.; Cao, Y. Preparation and characterization of fomesafen ionic liquids for reducing the risk to the aquatic environment *New J. Chem.* **2014**, 38, 5590-5596.

(24) Pernak, J.; Niemczak, M.; Giszter, R.; Shamshina, J. L.; Gurau, G.; Cojocaru, O. A.; Praczyk, T.; Marcinkowska K.; Rogers, R. D. Glyphosate-Based Herbicidal Ionic Liquids with Increased Efficacy. *ACS Sustainable Chem. Eng*. **2014**, 2, 2845-2851.

(25) Zhu, J.; Ding, G.; Liu, Y.; Wang, B.; Zhang, W.; Guo, M.; Geng, Q.; Cao, Y. Ionic liquid forms of clopyralid with increased efficacy against weeds and reduced leaching from soils. *Chem. Eng. J.* **2015**, 279, 472-477.

(26) Pernak, J.; Niemczak, M.; Shamshina, J. L.; Gurau, G.; Głowacki, G.; Praczyk, T.; Marcinkowska K.; Rogers, R. D. Metsulfuron-Methyl-Based Herbicidal Ionic Liquids. *J. Agric. Food Chem.* **2015**, 13, 3357-3366.

(27) Wang, B.; Ding, G.; Zhu, J.; Zhang, W.; Guo, M.; Geng, Q.; Gou D.; Cao, Y. Development of novel ionic liquids based on bentazone. *Tetrahedron* **2015**, 71, 7860-7864.

(28) Pernak, J.; Niemczak, M.; Zakrocka K.; Praczyk, T. Herbicidal ionic liquid with dual-function. *Tetrahedron* **2013**, 69, 8132-8136.

(29) Pernak, J.; Markiewicz, B.; Zgoła-Grześkowiak, A.; Chrzanowski, Ł.; Gwiazdowski, R.; Marcinkowska K.; Praczyk, T. Ionic liquids with dual pesticidal function. *RSC Adv.* **2014**, 4, 39751-39754.

(30) Minguet, M.; Subirats, N.; Castán P.; Sakai, T. Behenamidopropyl Dimethylamine: unique behaviour in solution and in hair care formulations. *Int. J. Cosmetic Sci.* **2010**, 32, 246-257.

(31) Liu, X.; Tao, S.; Yu, X.; Liu, G.; Zhang, N.; Xu, W.; Wang, W.; Xie, Y.; Zhu, Y.; Xie, J.; Wu, W. Effects of cetyltrimethylammonium chloride on uptake of pyrene by fish gills. *J. Environ. Sci. Heal A* **2009**, 44, 791-798.

(32) Tanamachi, H.; Inoue, S.; Tanji, N.; Tsujimura, H.; Oguri, M.; Ishita, M.; Tokunaga S.; Sazanami, F. Deposition of 18-MEA onto alkaline-color-treated weathered hair to form a persistent hydrophobicity. *J. Cosmet. Sci.* **2009**, 60, 31-44.

(33) Mozrzymas, A.; Różycka-Roszak, B. Prediction of critical micelle concentration of cationic surfactants using connectivity indices. *J. Math. Chem.* **2011**, 49, 276-289.

(34) Itoh, Y.; Akasaka, R. Comparison Of Surface-Active Properties of (Alkyloxycarbonylmethyl)trimethylammonium Chlorides and Alkyltrimethylammonium Chlorides. *J. Surfact. Deterg*. **2009**, 12, 101-107.

(35) Okada, T.; Venkateswaran, A.; Yang, J. Z. Hair conditioning composition containing behenyl trimethyl ammonium chloride, and having higher yield point. WO Patent. 2009158439 A2, , Dec 30, 2009.

(36) Cepeda, M.; Daviña, R.; García-Río, L.; Parajó, M.; Rodríguez-Dafonte P.; Pessêgo, M. Competition between surfactant micellization and complexation by cyclodextrin. *Org. Biomol. Chem.* **2013**, 11, 1093-1102.

(37) Opinion on alkyl (C16, C18, C22) trimethylammonium chloride for other uses than as a preservative, European Commission (2010):

http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_012.pdf last accessed Mar 15, 2016.

(38) Annex VI List of preservatives allowed for use in cosmetic products (2015): http://www.fda.gov.ph/attachments/article/15926/Annex%20VI%20revised%20as%20per%20August%202015.pdf last accessed Mar 15, 2016.

(39) Nakamura. T.; Ogawa, M. Attachment of the Sulfonic Acid Group in the Interlayer Space of a Layered Alkali Silicate, Octosilicate. *Langmuir*, **2012**, 28, 7505-7511.

(40) Ogawa, M.; Iwata, D. Arrangements of Interlayer Quaternary Ammonium Ions in a Layered Silicate, Octosilicate. *Cryst. Growth Des*., **2010**, 10, 2068-2072.

(41) Ikeda, T.; Nagase, T.; Hiyoshi, N.; Matsuura, S.; Abe C.; Chiba, M. Solvothermal synthesis and characterization of a layered silicate including a large quantity of Al atom and its mesoporous derivatives. *Microporous Mesoporous Mater*., **2014**, 191, 38-47.

(42) Richardson, M. C.; Kim, J.; Ho, D.; Snyder, C.R.; D'souza N. A.; Holmes, G. A. Organofunctionalized montmorillonite/epoxy nanocomposites: The effect of interlayer cation distribution on mechanical properties. *Polym. Compos*., **2011**, 32, 67-78.

(43) Mohsenipour, A. A.; Pal R.; Prajapati, K. Effect of cationic surfactant addition on the drag reduction behaviour of anionic polymer solutions. *Can. J. Chem. Eng*. **2013**, 91, 181-189.

(44) Uyama, M.; Ikuta, K.; Teshigawara, T.; Watanabe K.; Miyahara, R. The viscosity stability of O/W emulsion containing α-gel through an ionic-complex system. *J. Oleo Sci.* **2013**, 62, 9-16.

(45) Fernández, I.; Pérez-Juste J.; Hervés, P. Cationic Mixed Micelles as Reaction Medium for Hydrolysis Reactions. *J. Solution Chem.* **2015**, 44, 1866-1874.

(46) Vogel A. I., Textbook of Practical Organic Chemistry, 5th ed. (Eds.: B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell), Wiley, New York, 1989.

(47) Sokal, R. R.; Rohlf, F. J. Biometry 4th ed. WH Feeman and Company, New York, 2012.

(48) Zuur, A. F.; Ieno, E. N.; Walker, N. J.; Saveliev A. A.; Smith, G. M. Mixed effects models and extensions in ecology with R. Gail, M.; Krickeberg, K.; Samet, J. M.; Tsiatis, A.; Wong, W. editors. New York, NY: Spring Science and Business Media, New York, 2009.

(49) R Core Team 2016. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria: https://www.R-project.org/ last accessed Dec 2, 2016.

(50) Russell, V. L. Least-Squares Means: The R Package lsmeans. *J. Stat. Softw.* **2016**, 69, 1-33.

(51) Wu, T. Y.; Su, S. G.; Gung, S. T.; Lin, M. W.; Lin, Y. C.; Ou-Yang, W. C.; Sun I. W.; Lai, C. A. Synthesis and characterization of protic ionic liquids containing cyclic amine cations and tetrafluoroborate anion. *J. Iran. Chem. Soc.* **2011**, 8, 149-165.

(52) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical Properties and Structures of Room Temperature Ionic Liquids. 2. Variation of Alkyl Chain Length in Imidazolium Cation. *J. Phys. Chem. B.* **2005**, 109, 6103-6110.

(49) Cepeda, M.; Daviña, R.; García-Río, L.; Parajó, M.; Rodríguez-Dafonte P.; Pessêgo, M. Competition between surfactant micellization and complexation by cyclodextrin. *Org. Biomol. Chem.* **2013**, 11, 1093-1102.

FIGURE CAPTIONS.

Figure 1. Structures of used herbicidal acids.

Figure 2. Viscosity and density values for **1d** and **2d**.

Figure 3. Surface tension of obtained salts.

Figure 4. Efficacy of HILs and reference products against two weed species in spring barley (Winna Gora – western part of Poland).

Scheme 1. General synthesis of alkyltrimethylammonium salts derived from different herbicides, where A is herbicidally active anion.

TABLES

Table 1. Prepared salts.

Salt	R	Anion (A)	Yield (%)	Purity[a] (%)	State at 25 °C
1a	$C_{16}H_{33}$	MCPA	98	99	Solid
2a	$C_{18}H_{37}$		99	99	Solid
3a	$C_{22}H_{45}$		98	99	Solid
1b	$C_{16}H_{33}$	2,4-D	97	99	Solid
2b	$C_{18}H_{37}$		98	98	Solid
3b	$C_{22}H_{45}$		97	99	Solid
1c	$C_{16}H_{33}$	dicamba	98	99	Solid
2c	$C_{18}H_{37}$		98	99	Solid
3c	$C_{22}H_{45}$		98	98	Solid
1d	$C_{16}H_{33}$	MCPP	96	99	Liquid
2d	$C_{18}H_{37}$		96	99	Liquid
3d	$C_{22}H_{45}$		97	98	Grease

[a] the direct two-phase titration technique

Table 2. Thermal analysis (DSC and TGA) of synthesized salts.

Salt	T_m[c] (°C)	T_{cryst}[b] (°C)	$T_{onset5\%}$[d] (°C)	T_{onset}[e] (°C)
1a	57	---	190	214
2a	68	---	196	222
3a	63	---	195	232
1b	74	---	197	222
2b	55	---	197	221
3b	61	---	199	230
1c	101	117	181	215
2c	76	---	186	226
3c	72	---	185	229
1d	---	---	190	221
2d	---	---	186	213
3d	---	---	194	227

[a]T_m – melting point; [b]T_{cryst} – temperature of crystallization; [d]$T_{onset5\%}$ – decomposition temperature of 5% sample; [e]T_{onset}– decomposition temperature of 50% sample

Table 3. Solubility of prepared salts at 25 °C.

Salt	**Water**	**Methanol**	**DMSO**	**Acetonitrile**	**Acetone**	**Isopropanol**	**Ethyl acetate**	**Cloroform**	**Toluene**	**Hexane**
	9.0[a]	6.6	6.5	6.2	5.1	4.3	4.3	4.1	2.3	0.0
1a	±	+	±	–	±	–	–	+	±	–
2a	–	+	±	–	+	±	–	+	±	–
3a	–	+	–	–	±	±	–	±	±	–
1b	±	+	±	–	–	±	–	±	–	–
2b	–	+	–	–	–	±	–	+	–	–
3b	–	+	–	–	–	±	–	±	–	–
1c	–	+	–	–	–	–	–	±	–	–
2c	–	+	–	–	–	±	–	+	–	–
3c	–	+	–	–	–	+	–	+	–	–
1d	+	+	+	+	+	+	–	+	+	–
2d	±	+	–	–	±	±	–	+	±	–
3d	–	+	–	–	–	±	–	+	+	–

[a] Snyder polarity index + complete solubility; ± limited solubility; – insoluble

Table 4. The CMC and surface tension (γ_{CMC}) of prepared salts.

Salt	**CMC ($mmol \cdot L^{-1}$)**	**γCMC ($mN \cdot m^{-1}$)**	**pC_{20}**	**Γ_{max} ($\mu mol \cdot m^{-2}$)**	**A_{min} (10^{-19} m^2)**	**CA (°)**
1a	0.459	32.75	3.92	2.98	5.56	61.6
2a	0.074	34.27	4.43	5.36	3.09	55.7
3a	0.043	37.56	4.53	8.15	2.03	77.5
1b	0.123	33.98	4.31	4.06	4.08	57.7
2b	0.037	36.81	4.62	7.60	2.28	61.0
3b	0.043	34.12	4.54	9.33	1.78	96.7
1c	0.347	34.15	4.02	2.94	5.65	60.6
2c	0.087	36.31	4.34	5.01	3.31	66.1
3c	0.085	37.10	4.22	9.19	1.81	84.4
1d	0.174	33.62	4.20	3.75	4.43	57.9
2d	0.048	31.02	4.57	7.66	2.16	59.7
3d	0.041	38.72	4.50	1.10	1.51	81.2

Table 5. Efficacy of HILs and reference products against two weed species under greenhouse conditions.

Treatment	Common lambsquarters		Flixweed	
	Fresh weight (g)	Fresh weight reduction (%)	Fresh weight (g)	Fresh weight reduction (%)
Control 1[a]	5.23	-	5.22	-
Control 2[b]	6.14	-	4.96	-
1a	1.08	82	1.32	73
2a	2.99	51	1.55	69
3a	0.92	68	0.97	80
1d	3.81	38	1.31	74
2d	1.97	68	0.69	86
3d	3.28	47	0.91	82
MCPA[c]	2.95	44	2.98	43
1b	3.97	35	1.53	69
2b	3.54	42	1.39	72
3b	4.13	33	2.89	42
2,4-D[c]	3.72	29	1.84	65
1c	0.92	85	2.83	43
2c	1.52	75	1.23	75
3c	0.95	85	2.27	54
Dicamba[c]	3.01	42	2.39	54

[a] water treatment, [b] water:etanol treatment; [c] the commercial herbicide

Table. 6. Estimates of basic contrasts with significant differences ($p < 0.05$) for common lambsquarters (standard error SE=0.9703426; df=34).

Contrast	Estimate	T ratio	p. value
Control 2[a] – 1a	5.057	5.211	0.0009
Control 2 – 3a	4.187	4.315	0.0113
Control 2 – 1c	5.220	5.380	0.0006
Control 2 – 2c	4.620	4.761	0.0034
Control 2 – 3c	5.193	5.352	0.0006
Control 2 – 2d	4.170	4.297	0.0119

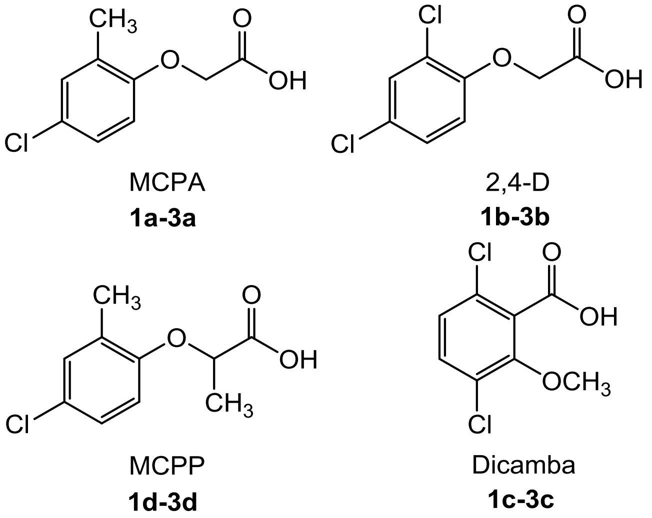
[a] water treatment

Table. 7. Estimates of basic contrasts with significant differences ($p < 0.05$) for flixweed (standard error SE=0.6478017; df=34).

Contrast	Estimate	T ratio	p value
Control 1[a] – 2.4-D[c]	3.373	5.207	0.001
Control 1 – dicamba[c]	2.827	4.363	0.01
Control 2[b] – 1a	3.637	5.614	0.000
Control 2 – 2a	3.407	5.259	0.001
Control 2 – 3a	3.983	6.149	0.000
Control 2 – 1b	3.430	5.295	0.001
Control 2 – 2b	3.567	5.506	0.000
Control 2 – 2c	3.727	5.753	0.000
Control 2 – 3c	2.683	4.142	0.018
Control 2 – 1d	3.650	5.634	0.000
Control 2 – 2d	4.267	6.586	<0.0001
Control 2 – 3d	4.047	6.247	<0.0001

[a] water treatment, [b] water:etanol treatment; [c] the commercial herbicide

FIGURES



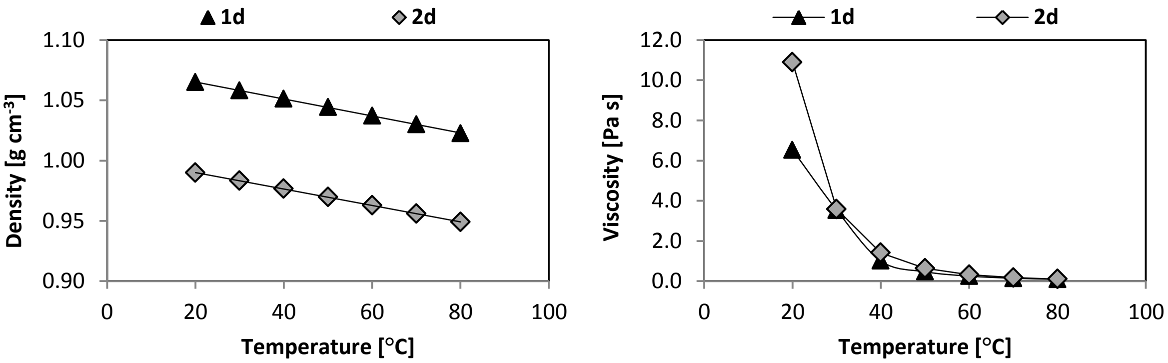
MCPA
1a-3a

2,4-D
1b-3b

MCPP
1d-3d

Dicamba
1c-3c

Figure 1.



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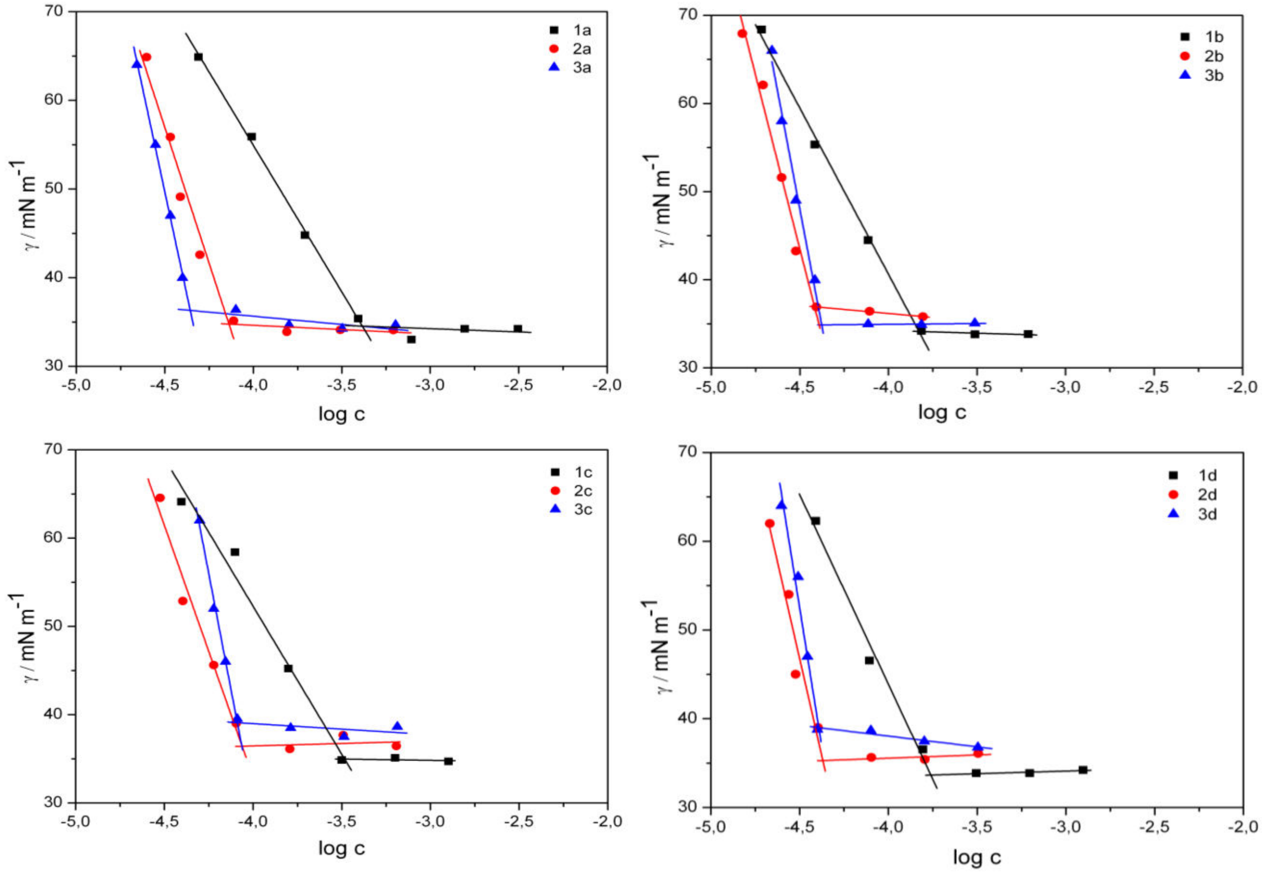


Figure 3.

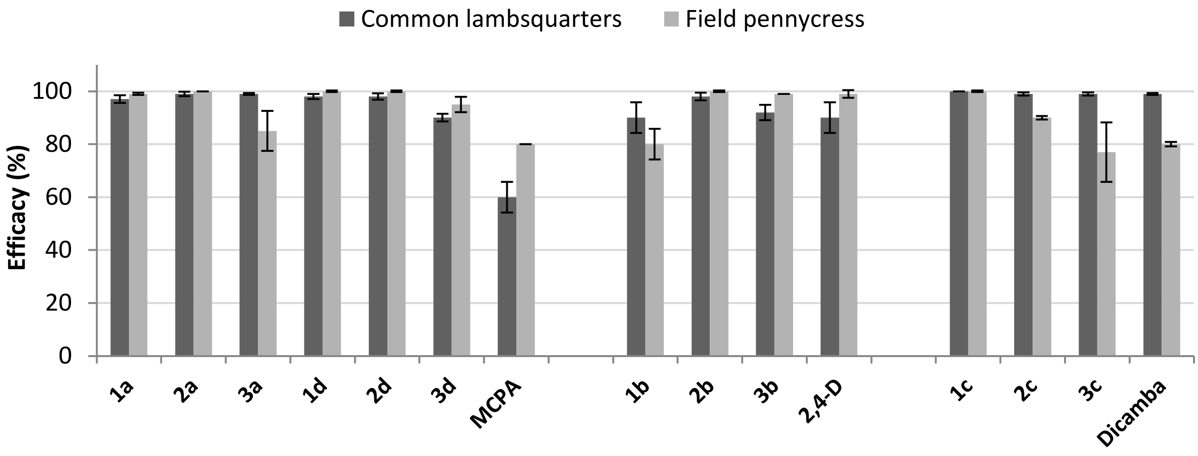
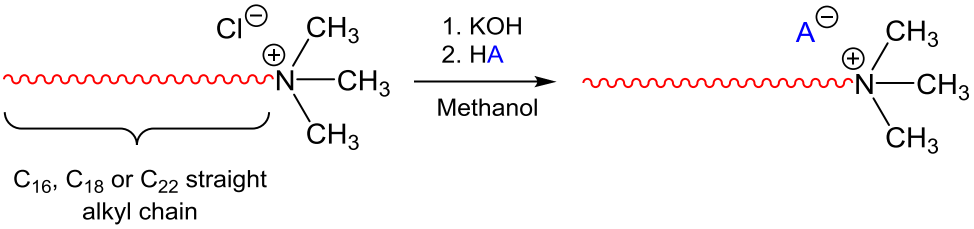


Figure 4.



Cl
CH3
N
CH3
CH3
C16, C18 or C22 straight alkyl chain
1. KOH
2. HA
Methanol
A
CH3
N
CH3
CH3

Scheme 1.

Graphic for Table of Content