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Phenoxy herbicidal ammonium ionic liquids

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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.

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-2-methoxybenzoate,[9,10] mecoprop—2-(4-chloro-2-methylphenoxy) propionate,[10] and glyphosate[10]) or two herbicidal ions (2-chloroethyltrimethylammonium cation with MCPA[11] or 2,4-D anion[12]) 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 patent[13] describes seven quaternary 2,4-D-ammonium salts (inter alia 2,4-D-tetraalkylammonium, 2,4-D-benzyltrimethylammonium, and 2,4-D-hexadecyltrimethylammonium).

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 HIL[6]), 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

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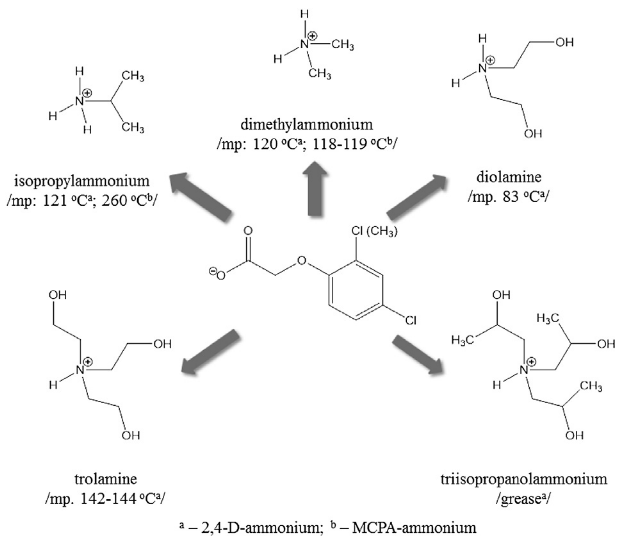


Fig. 1. Structures of cations of commercial primary, secondary, and tertiary 2,4-D-ammonium and MCPA-ammonium salts.

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.

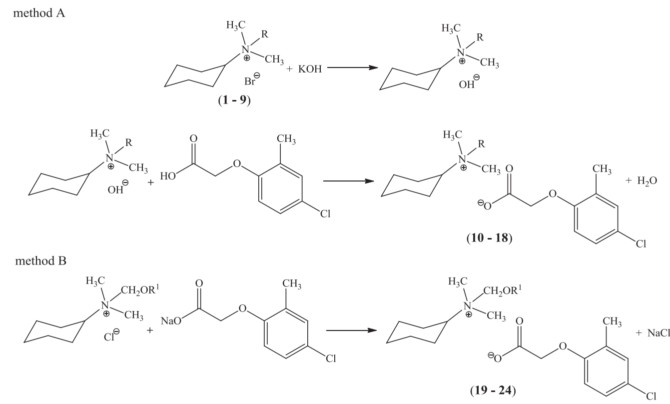
The addition of functional groups (e.g., ether oxygens) to the ions may change the properties of salts. Zhou and co-workers demonstrated that the replacement of a methylene group in various cations by an oxygen atom significantly decreases the melting point and viscosity for ILs.[14] The effects of an alkoxy group on the properties of ILs have been studied from the aspects of crystallographical,[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 HILs. 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-methylphenoxyacetate (**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 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 alkoxymethyl-based 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.



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

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_6H_{13}	98	—
13	C_8H_{17}	97	98
14	$C_{10}H_{21}$	98	99
15	$C_{12}H_{25}$	99	98
16	$C_{14}H_{29}$	97	98
17	$C_{16}H_{33}$	98	99
18	$C_{18}H_{37}$	98	98
19	$CH_2OC_4H_9$	94	—
20	$CH_2OC_6H_{13}$	93	—
21	$CH_2OC_8H_{17}$	90	92
22	$CH_2OC_{10}H_{21}$	98	89
23	$CH_2OC_{12}H_{25}$	94	90
24	$CH_2OC_{14}H_{29}$	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 °C. In case of acetates **23** and **24**, the crystallization and melting temperatures were observed and valued: −15.6 and −9.6 °C for crystallization, and −26.0 and −3.2 °C for melting temperature, respectively. Decomposition temperatures T_{onset5} for all tested alkyl-based ILs (**10**–**18**) were at least around 190 °C, up to 214 °C for **18**. For the ILs with an alkoxymethyl substituent (**19**–**24**) decomposition temperatures T_{onset5} were lower to about 160 °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