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Ionic liquids as herbicides and plant growth regulators

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ABSTRACT

New ILs containing the (2,4-dichlorophenoxy)acetate anion have been synthesized and characterized (properties, chemical and thermal stability, surface activity). Next, the possibility to use them as herbicides and plant growth regulators has been studied. The obtained ILs exhibited higher biological activity than the currently used herbicide (2,4-D salt) and plant growth regulator (CCC).

1. Introduction

Ionic liquids (ILs), due to their properties and enormous potential application still enjoy a great interest in both academia and industry. They are substances composed exclusively of ions, which form phases that are liquids below 100 °C.[1–6] ILs, from dependence on the cation, are divided into: imidazolium, ammonium, pyridinium, phosphonium, piperidinium, morpholinium, sulfonium, and lately pyrylium.[7] They have negligible vapor pressure under ambient conditions and are usually non-flammable. By modification of the cation and/or anion an enormous range of potential ILs is possible. The evaluation of these compounds proceeds very quickly from the first generation (ILs with unique tunable physical properties) to the second generation (ILs with targeted chemical properties combined with selected physical properties), to the third generation (ILs with targeted biological properties combined with physical and chemical properties).[8,9]

ILs might be easily adapted toward ‘designer drugs’, since the physical, chemical, and biological properties of a drug can be tuned by choice of the counterion.[10] Recently the third generation phytopharmaceuticals—herbicidal ionic liquids were published.[11–13] The novel hydrophobic fungicide with thiabendazole and imidazole as ILs, with increased rain persistence and activity against potato tuber diseases are also proposed in the agrochemistry field.[14] Enhanced stabilization of the tobacco mosaic virus using protic ILs has recently been described.[15]

Chlormequat chloride—2-chloroethyltrimethylammonium chloride (CCC), was prepared in 1910[16] and described as a plant growth regulator by Tolbert in 1960.[17,18] It is used to prevent lodging and to increase yields in wheat, rye, oats, and triticale. Moreover, CCC is also applied to increase lateral branching and flowering in some ornamental plants and to increase fruit setting in pears, olives, vines, and tomatoes.[19]

(2,4-Dichlorophenoxy)acetic acid (2,4-D) was first described by Zimmerman and Hitchcock.[20] This phenoxy acid is a systemic herbicide used in the control of broadleaf weeds and is also a synthetic auxin often used in laboratories for plant research.

Due to the toxicity and side effects of 2,4-D and CCC, their use is heavily criticized. However, these are cheap and widely used, especially 2,4-D. Additionally, both have an ionic structure. For this reason we have decided to use them as substrates in the synthesis of the third generation ILs.

The aim of our work was the synthesis of new salts and the study of the possibility to use them as herbicides and plant growth regulators. In our study we have looked for answers to two basic questions. First, whether these compounds are ionic liquids? Second, whether the activities of the cation and anion are maintained? To answer these questions the chemical and thermal stability, surface and biological activity of 2-chloroethyltrimethylammonium and trimethylvinylammonium (2,4-dichlorophenoxy)acetates have been tested.

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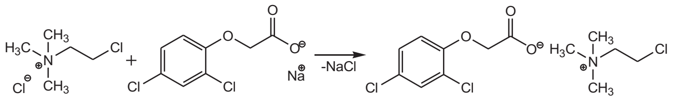
2. Results and discussion

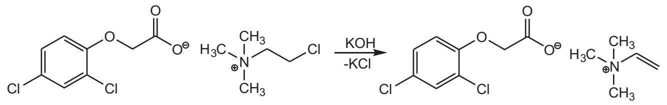
The reaction of sodium (2,4-dichlorophenoxy)acetate with 2-chloroethyltrimethylammonium chloride in water gave 2-chloroethyltrimethylammonium (2,4-dichlorophenoxy)acetate—[CC][2,4-D] in 95% yield (Scheme 1).



Scheme 1. Synthesis of 2-chloroethyltrimethylammonium (2,4-dichlorophenoxy) acetate—[CC][2,4-D], 95% yield.

Exchange of the chloride anion in the quaternary ammonium chlorides was effective. Many quaternary ammonium salts are highly hygroscopic, so water should be avoided as a solvent. Very good results were obtained by using anhydrous methanol as a solvent and a stoichiometric amount of a base (e.g., KOH). In this case, KCl came out of reaction mixture and anhydrous product was obtained after evaporation of the solvent under mild conditions.

For [CC][2,4-D] the exchange reaction could not be carried out in methanol with a base because elimination occurred. [CC][2,4-D] has proved to be unstable in an alkaline medium. In contact with base trimethylvinylammonium (2,4-dichlorophenoxy)acetate was formed—[TMVA][2,4-D] as shown in Scheme 2. The yield was 97%.

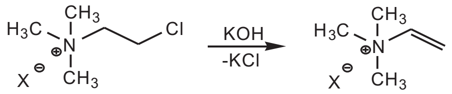


Scheme 2. Synthesis of trimethylvinylammonium (2,4-dichlorophenoxy)acetate—[TMVA][2,4-D], 97% yield.

[CC][2,4-D] and [TMVA][2,4-D] can be made anhydrous by heating at 70 °C in vacuo and storing over P_4O_{10}. The water content in the prepared salts was determined to be less than 500 ppm by coulometric Karl Fischer titration. These salts are stable in air and in contact with water and common organic solvents. They are soluble in DMSO, alcohols (methanol, ethanol, and propanol), chloroform and are insoluble in hexane and diethyl ether. The two new salts were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Generally, we observed specific signals from the anion and cation. The ^{1}H NMR spectra of the [CC][2,4-D] and [TMVA][2,4-D] indicate significantly different chemical shifts for the $N^+(CH_3)_3$ protons (move over 0.20 ppm). Moreover, signals from protons of 2-chloroethyl group—$N^+CH_2CH_2Cl$ (3.80 and 4.09 ppm) for [CC][2,4-D] are absent on the [TMVA][2,4-D] spectra, which possess three characteristic signals for the vinyl substituent (5.50, 5.80, and 6.77 ppm). The ^{13}C NMR spectra present similar differences in chemical shifts of the methyl groups in the cation—$N^+(CH_3)_3$, in the range 0.69 ppm. Signals of the carbons from the 2-chloroethyl group (36.42 and 64.83 ppm) in [CC][2,4-D] spectra are replaced by two peaks characteristic for the vinyl group (111.24 and 143.20 ppm).

The values of $T_{onset5\%}$ and T_{onset}, determined using TGA, for [CC][2,4-D] were equal to 180 and 255 °C, respectively, and for [TMVA][2,4-D]: 170 and 240 °C. Additional physicochemical data were provided by DSC analysis. For [CC][2,4-D] there was only the glass transition temperature at 8 °C. For [TMVA][2,4-D] the glass transition was observed at −16 °C, the temperature of crystallization at 10 °C and the melting point at 16 °C. At room temperature [CC][2,4-D] is a solid and melts at 92–94 °C, and [TMVA][2,4-D] is a liquid of high viscosity. The synthesized [CC][2,4-D] and [TMVA][2,4-D] salts can be classified as ionic liquids. This is the answer to the first question posed at the beginning of our work.

The product of dehydrochlorination of CCC or [CC][2,4-D] via elimination was a vinyl group attached to the nitrogen atom (Scheme 3). The reactions order (n) was calculated by the Ostwald–Zawicki method. It has been found that it is an E2 elimination reaction.



Scheme 3. Elimination reaction in 2-chloroethyltrimethylammonium cation, when X=Cl or 2,4-D anion.

The change in concentration as time function during the reaction between CCC or [CC][2,4-D] and potassium hydroxide in water at 30 °C, with 0.100 mol L^{-1} initial concentration of both reactants, is shown in Fig. 1.

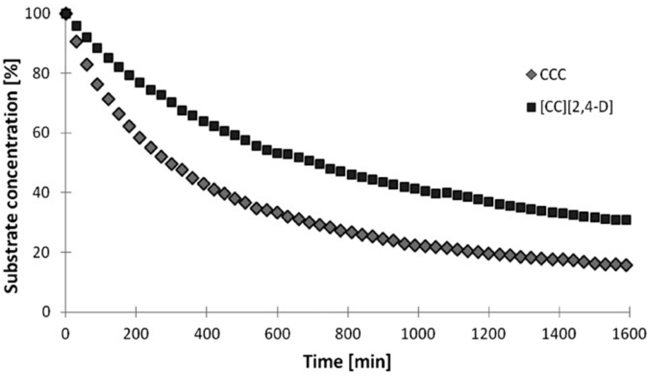


Fig. 1. Concentration versus time for the decomposition of CCC and [CC][2,4-D] in water at 30.0 °C (303.2 K).

At low temperatures (20–40 °C) there is a considerable impact on elimination reaction kinetics as is shown in Fig. 1. It is noticeable that the reaction rate of degradation (k) for CCC is approximately 2.5 times greater than for [CC][2,4-D] at 30.0 °C (303.2 K). At this temperature [CC][2,4-D] is decomposed much slower than CCC. The linear relationship in the Arrhenius plots demonstrates the correct assumption of the kinetic equation and reaction order (Fig. 2). It means that the reaction with the participation of [CC][2,4-D] is less dependent on the temperature.

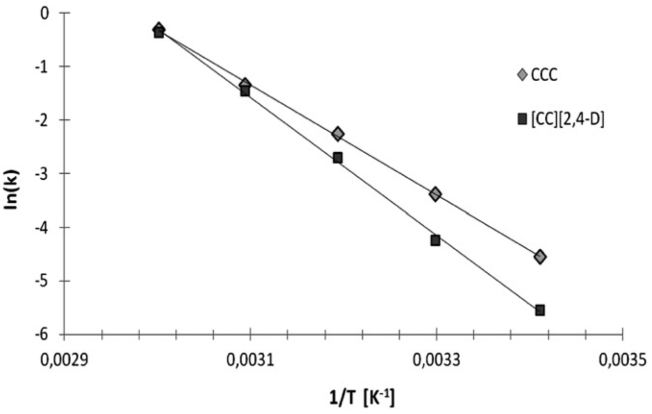


Fig. 2. Arrhenius plot of CCC and [CC][2,4-D] E2 elimination reaction in water.

Table 1 summarizes a series of calculated kinetic parameters: reaction half-life ($\tau_{1/2}$), activation energy (E_a), enthalpy of activation