



Ionic liquid forms of clopyralid with increased efficacy against weeds and reduced leaching from soils



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HIGHLIGHTS

- New HILs based on clopyralid with multifunction were synthesized and characterized.
- The physicochemical property of clopyralid can be regulated using different cations.
- HILs with great adsorption capacity and low leaching characteristic were achieved.
- New HILs reduced the risk to aquatic environment.
- Clopyralid ionic liquids showed a higher herbicidal activity.

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ABSTRACT

The excessive application of water-soluble pesticides poses enormous potential risks to groundwater by leaching or in runoff. Ionic liquids can regulate the physicochemical properties of pesticides and surmount their disadvantages. In this study, five herbicidal ionic liquids (HILs) based on clopyralid have been synthesized and characterized to reduce the risks to the aquatic environment and improve the herbicidal activity. The new HILs are prepared by pairing isopropylamine, 1-dodecylamine, 2-benzothiazolamine, 1-methylimidazole, benzyltriethylammonium chloride respectively. The results of the solubility, soil adsorption, surface activity, leaching characteristic and herbicidal activity of HILs show that the physicochemical properties can be optimized by selecting different counter cations. Compared with clopyralid potassium, HILs have better herbicidal activity, greater adsorption capacity and lower leaching characteristic. The HILs of clopyralid can reduce its hazardous impacts on the aquatic environment, suggesting a desirable candidate in clopyralid application in the future.

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1. Introduction

With the widespread use of pesticides, their side effects have emerged in recent years. Water is the primary access of pesticide dissemination from their applied areas to other parts of the environment, and water pollution caused by pesticides has become a worldwide problem [1,2]. The major pathway of pesticide transportation to groundwater is through leaching from soils or surface runoff following pesticide application [3,4]. The presence of pesticides, especially those polar and highly soluble types, has been reported in the groundwater or river [5]. According to the

literatures, the most frequently detected pesticides, including atrazine, simazine, alachlor, metolachlor, dicamba and clopyralid, are all classified as the type of chemical pollutants with high potential risks to leaching [6,7].

As an auxin-mimic type of herbicide, clopyralid (3,6-dichloropyridine-2-carboxylic acid) has been widely used for years due to its high selectivity. Clopyralid is a systemic herbicide registered by EPA and recommended for selective, postemergence control of many annual and perennial broadleaf weeds [8]. Nevertheless, clopyralid is a very mobile herbicide with weak absorption property to soils and its organic carbon adsorption coefficient is 5.0 mL g^{-1} [9,10]. Once being exposed to the soils through direct or indirect ways, clopyralid will disassociate to the anion form rapidly, becoming extremely soluble in water, and could not bind strongly with soil particles anymore [11]. Therefore clopyralid

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could easily leak to the depth as great as 180 cm within 20 days after application [12]. Due to these properties, clopyralid is one of the herbicides that are most frequently reported to exist in drinking water and the level as high as $0.23 \mu\text{g L}^{-1}$ in drinking water has been detected in the UK, vastly exceeding the Permitted Concentration Value for an individual pesticide of $0.1 \mu\text{g L}^{-1}$ (EU directive 98/83/EC) [13]. Also, the concentration of clopyralid as high as $1.05 \mu\text{g L}^{-1}$ was detected in surface water following snowmelt or rainfall runoff in North America [7]. Clopyralid is mainly degraded by microorganisms in soil, and is not susceptible to hydrolysis, photodegradation and chemical degradation [14,15]. The half-life of clopyralid in water ranges from 143 to 182 days, and it is not registered for usage in aquatic systems, which greatly restricts its range of application to areas where surface water is present, or intertidal areas below the mean high water mark [16,17]. Thus the chemical stability of clopyralid along with its mobility enables this herbicide to penetrate through the soil easily, causing a long-term contamination of the surface water and ground water [13,18].

Ionic liquids (ILs) are composed entirely of ions and generally defined as salts with melting points below 100°C [19,20]. Herbicidal ionic liquids (HILs) represent a group of ionic liquids with targeted herbicidal properties combined with specific physical and chemical properties [21]. Generating HILs via choosing appropriate counter ion pair is an excellent method to reduce the environmental hazards caused by herbicides [22]. The physicochemical properties of herbicides can be optimized by selecting the appropriate counter ion [23]. On the basis of recent researches, synthesized HILs based on 2,4-D, dicamba, fomesafen and MCPA could surmount their intrinsic disadvantages by altering their physicochemical properties. The new HILs possess desirable characteristics, like lower volatility and water solubility, increased herbicidal activity, reduced mobility in soil and groundwater [22–25].

The objective of this work is to prepare HILs of clopyralid via acid-base reaction or metathesis reaction to optimize its physicochemical properties and produce an eco-friendly herbicide with low mobility in the soils. The selected typical counter cations are isopropylamine, 1-dodecylamine, 2-benzothiazolamine, 1-methylimidazole, benzyltriethylammonium chloride, which represent amines with short-chain hydrocarbons, long-chain hydrocarbons, fused heterocycles, single heterocycles, and aromatic hydrocarbons respectively. The water solubility, surface activity, soil adsorption, leaching and herbicidal activity of the synthesized HILs are tested.

2. Methods

2.1. Chemicals and devices

All the chemicals were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Methanol and acetonitrile were high-performance liquid chromatography (HPLC)-grade from J.T. Baker (Phillipsburg, NJ, USA). Ultrapure water was obtained in the laboratory using a Milli-Q water purification system (Millipore, Billerica, MA, USA). Clopyralid was purchased from Beijing Yangguang Furuide Chemical Co., Ltd. Lontrel® was purchased from Dow AgroSciences LLC. ^1H NMR spectra was recorded on a Bruker Avance DPX 300 MHz NMR spectrometer (Bruker, Germany). Surface tension measurements were carried out by a JK 99B analyzer (Powereach, China, resolution $<0.05 \text{ mN m}^{-1}$). An HPLC system, which consisted of two LC-20ATvp pumps and a SPD-20Avp ultraviolet detector (Shimadzu), was used for analysis and separation. A reversed phase kromasil ODS C_{18} column (250 mm \times 4.6 mm, 5 μm) was used for separation at ambient

temperature, and a Chromato Solution Light Chemstation for LC system was employed to acquire and process chromatographic data. The mobile phase were acetonitrile (eluent A) and water with 0.1% acetic acid (eluent B) (75/25, v/v). Injection volume was 20 mL, and the detection wavelength was 280 nm. The flow rate was constant at 1.0 mL min^{-1} , and the column was kept at room temperature.

2.2. Preparation of HILs

Five new HILs of clopyralid were synthesized through acid-base reaction and metathesis reaction. In acid-base reaction, 0.01 mol of amine, 20 mL of distilled water, and 0.01 mol of clopyralid were mixed in a round-bottom flask equipped with a magnetic stir bar, a reflux condenser, and a thermometer. The mixture was stirred for 0.5 h at 70°C until the reaction system was absolutely clear. Then, the desirable HILs were obtained via the removal of distilled water. In metathesis reaction, 0.01 mol of quaternary ammonium halide, 20 mL of methanol, and 0.01 mol of clopyralid potassium (CP) were mixed in the same equipment described above, the mixture was stirred for 0.5 h at 25°C until the quantity of precipitation of potassium halide didn't add up any more. After the filtration of the precipitation of potassium halide, the methanol was evaporated from the liquid mixture at 45°C for 0.5 h. The obtained HILs were washed with chloroform for three times.

2.3. Water solubility

The solubilities of HILs at different pH values (ranging from 5.0 to 9.0) at 25°C were measured in phosphate buffer solutions (PBS) with the flask method of OECD Guideline for the testing of chemicals [26]. The drugs were added to the desired volume of PBS (10 mL) in the glass vessels until saturation occurred, indicated by observation of surplus undissolved drugs or turbidity. Then the vessels fitted with glass stoppers tightly were kept shaking on a shaker at 25°C . Preliminary experiments demonstrated that a contact time of 48 h was sufficient to attain the solubility equilibrium. After shaking for 48 h, the suspensions of the vessels were centrifuged at 8000 rpm for 5 min at 25°C and the filtered supernatants were analyzed by HPLC. There were three replicates for each treatment.

2.4. Soil adsorption

Soil adsorption experiments of HILs were carried out using batch equilibrium method [27]. The test soils sampled from the surface horizon (0–20 cm) of cultivated fields in Beijing China at $40^\circ03'34''\text{N}$ $116^\circ13'37''\text{E}$ were air-dried at 25°C and ground to pass through a 2-mm sieve. Aiming at avoiding the influence of the microorganisms in the soils on clopyralid degradation, the soils were disposed by hot air sterilization at 180°C for 4 h to prepare sterilized soils. The 2 mg L^{-1} HILs solutions (50 mL) prepared in 0.01 M CaCl_2 were added to the soils (2 g) in 100 mL teflon centrifuge tubes. The soil suspensions were agitated on a shaker at 25°C for 24 h until adsorption reached equilibrium (the equilibrium time was confirmed according to the preliminary experiment). Then, the mixtures in the tubes were centrifuged at 8000 rpm for 3 min and the supernatants were filtered through 0.22 mm filter membranes and analyzed by HPLC. The control experiments containing only clopyralid (no soil) and only sterilized soil (no clopyralid) in 0.01 M CaCl_2 solution respectively were performed according to the above mentioned procedure. Each treatment was conducted in triplicate. In this study, the adsorption percentage (A_{eq}) was calculated by the following formula:

$$A_{\text{eq}} = (C_0 - C_{\text{aq}}^{\text{ads}}(\text{eq.}))100\%/C_0$$

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