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Herbicidal Ionic Liquids with 2,4-D

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Three herbicidal ionic liquids (HILs)—alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate, and alkyltrimethylammonium (2,4-dichlorophenoxy)acetate—were synthesized and their activity against broad-leaved weeds was investigated under field conditions. HILs as [cation][2,4-D] used in winter wheat were much more active compared to 2,4-D-dimethylammonium salt and demonstrated efficacy similar to 2,4-D 2-ethylhexyl ester. HILs exhibited desirable surface properties such as low contact angle of droplets and low surface tension. Moreover, the HILs may be safer to operators and neighboring plants due to their nonvolatile nature. HILs at 450 g ha^{-1} of 2,4-D did not injure wheat.

Nomenclature: Alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.

Key words: 2,4-D, ionic liquids, weed control, selectivity, winter wheat.

2,4-D as a plant growth regulator was first described by Zimmerman and Hitchcock (1942). Nowadays 2,4-D is one of the most widely used herbicides in the world. This synthetic auxin is recommended for POST control of annual and perennial broad-leaved weeds in cereals, maize (*Zea mays* L.), grain sorghum [*Sorghum bicolor* (L.) Moench ssp. bicolor], grassland, orchards, surgar cane (*Saccarum officinarum* L.), and rice (*Oryza sativa* L.) as well as on noncrop land. It has been extensively reviewed by a variety of government regulatory organizations globally. This herbicide plays a significant role in management of herbicide-resistant weeds (Steckel et al. 2010). Although synthetic auxins have been widely used for over 60 yr, only 29 species of weeds have selected biotypes resistant to these herbicides. In contrast there are 112 weeds species with biotypes resistant to acetolactate synthase inhibitors, even though these substances have been used for only 28 yr (Heap et al. 2011). Low risk of weed resistance to auxin herbicides may be connected with multiple sites of action of these compounds, but additional studies focused on this phenomenon are needed (Mithila et al. 2011).

In recent years the manufacturers have developed the production of 2,4-D in the form of esters because of their greater efficacy compared to the salts, which allows the reduction of active ingredient doses. However, the disadvantage of esters is their high volatility (Strachan et al. 2010). Drift potential of 2,4-D as butyl ester is even 10-fold greater compared to a dimethylamine formulation (Matthews 2006). The herbicidal ionic liquids (HILs) have a similar effect as the ester form but they are nonvolatile compounds, thus they are safer to the operators and to the nontarget plants. The use of herbicides in the form of ionic liquids (ILs) opens up new possibilities for safer use of pesticides.

ILs are salts of bulky organic cations and organic or inorganic anions having melting points below 100 C and many are liquids at ambient temperature (Chowdhury et al. 2007; Olivier-Bourbigou et al. 2010; Rogers and Seddon 2003; Stark and Seddon 2007; Wasserscheid and Welton 2008).

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They are so-called "green solvents" and have recently become very attractive for biocatalysis and reaction media in chemical syntheses (Van Rantwijk and Sheldon 2007). ILs have attractive physical properties, such as negligible vapor pressure, miscibility with organic solvents, excellent thermal and chemical stability, high conductivities, and wide electrochemical windows. Therefore, they are nonvolatile and nonflammable. ILs can be recycled and reused without leading to solvent emissions into the atmosphere. They make a unique architectural platform on which, at least potentially, the properties of both anions and cations can be independently modified, enabling tenability in the design of new functional materials (Hough et al. 2007; Hough and Rogers 2007; Katritzky et al. 2006). Certain ILs are able to dissolve natural biopolymers such as cellulose (Li et al. 2011; Sun et al. 2011; Swatloski et al. 2002).

We demonstrate activity of three HILs—alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate, and alkyltrimethylammonium (2,4-dichlorophenoxy)acetate—against broad-leaved weeds under field conditions.

Materials and Methods

Herbicides. Three HILs with 2,4-D in anion form were investigated: alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate (HIL 1), dialkyldimethylammonium (2,4-dichlorophenoxy)acetate (HIL 2), and alkyltrimethylammonium (2,4-dichlorophenoxy)acetate (HIL 3). The characteristics of all tested herbicides are presented in Figure 1 and Table 1.

Surface Activity. Surface tension and contact angle were determined using the drop-shape method. The measurements were performed using a Drop Shape Analysis System DSA100E (KRÜSS GmbH, Hamburg, Germany, accuracy $\pm$ 0.01 mN m^{-1}) at 25 C. The image of the drop (6 µl) was taken from a Charge Coupled Device (CCD) camera and digitized. The surface tension (γ in mN m^{-1}) was calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Schwerte, Germany, accuracy $\pm$ 0.1 C). The values of the surface tension at the Critical Micelle Concentration (γ_{cmc}) were determined from the intersection of the two straight lines drawn in low- and

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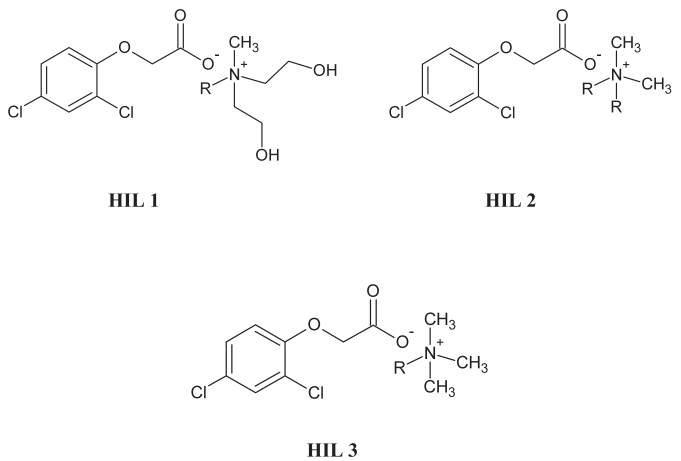

Figure 1. Structure of studied herbicidal ionic liquids (R chain distribution: C_8H_{17}, 5%; $C_{10}H_{21}$, 6%; $C_{12}H_{25}$, 50%; $C_{14}H_{29}$, 19%; $C_{16}H_{33}$, 10%; $C_{18}H_{37}$, 10%).

high-concentration regions in surface tension curves (γ-log C curves) using a linear regression analysis method. All measurements were performed for spray solutions containing herbicides at rate corresponding to 450 g ha^{-1} of 2,4-D and spray volume of 200 L ha^{-1}.

Efficacy and Selectivity Evaluation. The field trials were carried out in winter wheat (*Triticum aestivum* L.) cultivars 'Kris' (2010) and 'Figura' (2011) at an experimental station in Winna Gora, in the western part of Poland (N: 52°12′N, 17°26′E) in 2010 and 2011. Winter wheat was cultivated according to the local agricultural practice. Plot size was 16.5 m^2. The experimental design was a randomized block with four replications. All herbicides were applied at rate corresponding to 450 g 2,4-D with 1 ha^{-1} at the end of tillering (BBCH 30) using small plot spraying equipment with XR 11003 flat-fan nozzle (Teejet Technologies, Wheaton, IL) with a water volume of 200 L ha^{-1} and an operating pressure of 0.3 MPa. The standard products were herbicides containing 2,4-D as dimethylammonium salt (Aminopielik Standard 600 SL, Rokita Agro, Brzeg Dolny, Poland; 600 g L^{-1} 2,4-D) and as 2-ethylhexyl ester (Esteron 564 EC, Dow AgroSciences Polska, Warsaw, Poland; 460 g L^{-1} 2,4-D).

Weed control was evaluated visually 4 wk after herbicide applications using a scale of 0 (no control) to 100% (complete weed destruction).

The special selectivity studies were carried out in 2010 and 2011 in winter wheat using all herbicides at the rate corresponding to 1,200 g ha^{-1} of 2,4-D. The susceptibility of winter wheat to herbicides was evaluated visually, comparing plants treated with herbicide with the plants on the check plots (no herbicide application). The occurrence and intensity of damage symptoms of plants were determined using scale of 0 (no injury symptoms) to100% (total crop destruction).

Table 1. Characteristics of tested herbicidal ionic liquids.

Ionic liquids	Mole weight	Cation (%)	Anion (%)	Solubility
HIL 1[a]	552.15	60.2	39.8	Water, DMSO, chloroform, methanol, ethanol
HIL 2	664.10	66.9	33.1	DMSO, chloroform, methanol, ethanol
HIL 3	466.37	52.8	47.2	Water, DMSO, chloroform, methanol, ethanol

[a] HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate; DMSO, dimethyl sulfoxide.

Winter wheat was harvested using a Wintersteiger Classic plot combine harvester (Wintersteiger AG, Armstadt, Germany). Grains from each plot were weighed and their moisture was determined. The yield values were converted to tons per hectare in relation to standard moisture of 14%.

2,4-D Residue in Wheat Grains. Samples of winter wheat grain were taken from plots treated with herbicides at rate 1,200 g ha^{-1} of 2,4-D. A double system of detection and identification of herbicide was applied using a gas chromatograph Varian CP-3800 (Agilent Technologies, Santa Clara, CA) with electron capture detector and mass spectrometer Varian Saturn 2200 GC/MS. Analytical standards were purchased from LGC Standards. The detection limit of 2,4-D was 0.005 mg kg^{-1}.

Statistical Analyses. The data concerning efficacy of herbicides and yield of winter wheat were analyzed by ANOVA. Results of Fisher's test were evaluated on the 1 and 5% levels of significance. When significant differences were stated, detailed comparison of averages was performed with the usage of Tukey's test determining the LSD on the level of 5%. All calculations were performed using Agriculture Research Manager software (Gyllings Data Management, Inc., Brookings, SD).

Results and Discussion

Structure of Tested ILs. Preparation of HILs with 2,4-D followed the published method (Pernak et al. 2011). They were characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. (δ = chemical shift, J = the coupling interaction, s = singlet, d = dublet, dd = dublet of dublets, t = triplet, q = quintet, m = multiplet.)

Alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)-acetate (HIL 1). ^1H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.6 Hz, 3H), 1.21 (m, 20H), 1.59 (q, J = 7.3 Hz, 2H), 3.12 (s, 3H), 3.31 (t, J = 8.1 Hz, 2H), 3.49 (t, J = 4.0 Hz, 4H), 3.95

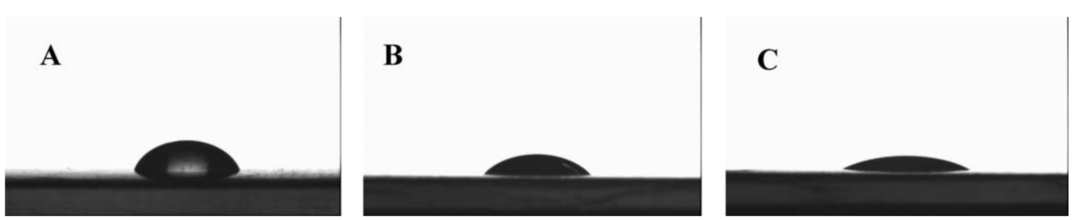

Figure 2. Contact angle of droplets. (A) 2,4-D-dimethylammonium salt, (B) 2,4-D 2-ethylhexyl ester, (C) HIL 3.

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Table 2. Contact angle and surface tension of spray solutions with different forms of 2,4-D.

Forms of 2,4-D	Contact angle (°)	Surface tension (mN m^{-1})
HIL 1[a]	54.32	30.4
HIL 2	40.99	27.7
HIL 3	49.74	28.9
2,4-D-dimethylammonium salt	99.16	72.6
2,4-D 2-ethylhexyl ester	53.50	31.6

[a] HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.

(t, J = 4.0 Hz, 4H), 4.43 (s, 2H), 4.82 (s, 2H), 6.84 (d, J = 9.1 Hz, 1H), 7.14 (dd, $J^{1,2}$ = 2.7 Hz, $J^{1,3}$ = 8.8 Hz, 1H), 7.29 (d, J = 2.7 Hz, 1H); ^{13}C NMR δ ppm = 14.1, 22.4, 22.6, 26.4, 27.2, 29.26, 29.30, 29.31, 29.54, 29.60, 29.62, 29.66, 31.9, 49.9, 55.5, 63.5, 64.0, 68.5, 114.6, 122.8, 125.3, 127.6, 129.6, 153.2, 173.4.

Dialkyldimethylammonium (2,4-dichlorophenoxy)acetate (HIL 2). ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 6H), 1.25 (m, 40H), 1.59 (q, J = 7.3 Hz, 4H), 3.17 (s, 6H), 3.24 (t, J = 8.4 Hz, 4H), 4.45 (s, 2H), 6.89 (d, J = 8.9 Hz, 1H), 7.11 (dd, $J^{1,2}$ = 2.6 Hz, $J^{1,3}$ = 8.9 Hz, 1H), 7.30 (d, J = 2.6 Hz, 1H); ^{13}C NMR δ ppm = 14.0, 22.5, 22.5, 26.1, 29.05, 29.18, 29.20, 29.26, 29.35, 29.45, 29.50, 29.54, 31.7, 51.1, 63.2, 68.9, 114.6, 122.4, 124.6, 127.4, 129.2, 153.6, 172.0.

Alkyltrimethylammonium (2,4-dichlorophenoxy)acetate (HIL 3). ^{1}H NMR ($CDCl_3$) δ ppm = 0.88 (t, J = 6.7 Hz, 3H), 1.25 (m, 20H), 1.52 (q, J = 7.3 Hz, 2H), 3.03 (s, 9H), 3.10 (t, J = 8.5 Hz, 2H), 4.36 (s, 2H), 6.84 (d, J = 8.8 Hz, 1H), 7.12 (dd, $J^{1,2}$ = 2.5 Hz, $J^{1,3}$ = 8.7 Hz, 1H), 7.26 (d, J = 2.5 Hz, 1H); ^{13}C NMR δ ppm = 14.1, 22.7, 22.9, 26.3, 29.4, 29.7, 29.8, 31.9, 52.9, 66.5, 68.3, 114.6, 122.6, 125.2, 127.8, 129.5, 153.1, 173.2.

Surface Activity. Herbicidal ionic liquids have high surface activity (Table 2). The values of surface tension between 27.7 and 30.4 mN m^{-1} are comparable to those obtained using the most effective spray adjuvants. The spray solution with HIL 2 had the most desirable properties, which determined very good absorption of herbicide by tested plants. In general, surface tension of HILs was over twofold lower than that of a 2,4-D-dimethylammonium salt formulation (Figure 2). Low values of contact angle and surface tension should result in good wetting of plants, enhancing spray retention, absorption, cuticle penetration, and translocation of the active ingredient. The important roles of the physical and chemical properties of a spray solution for efficacy of foliar-applied herbicides has been confirmed in many studies (Malec et al. 2010; Zollinger and Nalewaja 2010).

Table 4. Yield of winter wheat as influenced by different forms of 2,4-D used at a rate of 450 g ha^{-1}.

	Yield (t ha^{-1})	
Treatments	2010	2011
Untreated check	9.32 c[a]	4.84 d
HIL 1[b]	10.26 b	5.78 a
HIL 2	10.50 ab	4.98 cd
HIL 3	10.62 a	5.12 bc
2,4-D-dimethylammonium salt	10.45 ab	5.34 b
2,4-D 2-ethylhexyl ester	10.67 a	5.06 cd

[a] Values followed by the same letter means no significant difference between treatments.
[b] HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.

Efficacy Trials. Weed control by tested herbicides in both years of the study was at similar levels. HILs containing 2,4-D showed significantly greater efficacy compared to the 2,4-D-dimethylammonium salt. Their activity was similar to that of the 2-ethylhexyl ester. The type of cation in an IL had little effect on the activity of 2,4-D (Table 3). Differences have been found with regard to some weed species control, e.g., HIL 2, containing a dialkyldimethylammonium cation, was more effective against cornflower (*Centaurea cyanus* L.) than HIL 1, with the alkyldi(2-hydroxyethyl)methylammonium cation (Table 3). In general, the biological activity of HILs and 2,4-D 2-ethylhexyl ester was comparable and it was significantly higher than that of 2,4-D-dimethylammonium salt. A higher efficacy of esters of 2,4-D compared to the dimethylammonium salt formulation was found also in other studies (Zimdahl 1999).

All the tested herbicides had a beneficial effect on the yield of winter wheat (Table 4). However, in individual years of research the level of yield was strongly dependent on weather conditions. In 2011 there was very low rainfall in the months of April and May, which resulted in reduced yield (32.2 mm rainfall in 2011 compared to 136.4 mm in 2010).

The treatments with HILs provided an increase of yield of 0.94 to 1.3 t ha^{-1} (2010) and 0.14 to 0.94 t ha^{-1} (2011) compared to untreated check. The differences were statistically significant (excluding HIL 2 in 2011).

Table 3. Weed control in winter wheat by different forms of 2,4-D. Means from 2010 and 2011 (4 wk after treatment).

Treatments[a]	*Centaurea cyanus*	*Matricaria inodora*	*Papaver rhoeas*	*Brassica napus*	*Thlaspi arvense*	*Capsella bursa pastoris*
	%					
HIL 1[b]	71 b[c]	52 b	75 ab	82 a	77 ab	79 a
HIL 2	79 a	57 b	79 a	82 a	74 b	82 a
HIL 3	75 ab	56 b	73 b	80 a	78 ab	79 a
2,4-D-dimethylammonium salt	20 c	12 c	11 c	19 b	18 c	18 b
2,4-D 2-ethylhexyl ester	78 a	63 a	78 ab	78 a	82 a	79 a

[a] All treatments at a rate of 450 g ha^{-1} 2,4-D.
[b] HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.
[c] Values followed by the same letter in a column means no significant difference between treatments.

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Table 5. Crop injury by different forms of 2,4-D.

Treatments	1 WAT[a]		2 WAT		3 WAT	
	A[b]	B[c]	A	B	A	B
HIL 1	0	21	0	13	0	0
HIL 2	0	38	0	20	0	0
HIL 3	0	31	0	16	0	0
2,4-D-dimethylammonium salt	0	9	0	4	0	0
2,4-D 2-ethylhexyl ester	0	9	0	3	0	0

[a] WAT, week after treatment; HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.
[b] A: 2,4-D at a rate of 450 g ha^{-1}.
[c] B : 2,4-D at a rate of 1,200 g ha^{-1}.

Crop Safety. Special field trials were performed in 2010 and 2011 to estimate the selectivity of tested HILs to winter wheat. ILs with 2,4-D in anion form, as well as the standard form of the herbicide applied at a rate of 450 g ha^{-1} did not cause any symptoms of damage to winter wheat plants. Increasing doses of 2,4-D to 1,200 g ha^{-1} resulted in differences in response of winter wheat to the herbicide. In this case, ILs were more phytotoxic than the currently known forms of 2,4-D (Table 5). After 1 wk of treatment, the plots treated with ILs had some injury symptoms (chlorosis and necrosis of leaf apex). These symptoms were short-lived, because after the next 2 wk no differences between plants and no injuries were observed. The nature of the observed damage indicates that they were caused by a too-high concentration of the cation in the spray solution. It should be noted that to effectively control weeds, a dose of 450 to 600 g ha^{-1} of 2,4-D was required in the IL. Temporary crop injury observed in our trials with high rate of 2,4-D (1,200 g ha^{-1}) did not influence the yield of winter wheat using HILs and standard herbicide treatments (Table 6).

Residue of 2,4-D in Grains. No residue of 2,4-D was found in winter wheat grains when applied at a rate of 1,200 g ha^{-1} in both IL and standard forms of herbicide.

Acknowledgments

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Table 6. Yield of winter wheat from the selectivity trials.

Treatments[a]	Yield (t ha^{-1}) 2010	2011
Untreated check	6.83 d[c]	3.67 a
HIL 1	7.86 ab	3.41 b
HIL 2	7.63 b	3.46 b
HIL 3	7.35 c	3.45 b
2,4-D-dimethylammonium salt	7,98 a	3.44 b
2,4-D 2-ethylhexyl ester	7.83 ab	3.58 ab

[a] 2,4-D at a rate of 1,200 g ha^{-1}.
[b] HIL 1, alkyldi(2-hydroxyethyl)methylammonium (2,4-dichlorophenoxy)acetate; HIL 2, dialkyldimethylammonium (2,4-dichlorophenoxy)acetate; HIL 3, alkyltrimethylammonium (2,4-dichlorophenoxy)acetate.
[c] Values followed by the same letter in a column means no significant difference between treatments.

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