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2,4-D based herbicidal ionic liquids

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ABSTRACT

Herbicidal ionic liquids (HILs) with a 2,4-D anion were synthesized and characterized. These salts have chemical and thermal stability. HILs exhibited higher biological activity than currently used salts of 2,4-D. HILs are nonvolatile and showed substantially lower water solubility than starting herbicides. © 2012 Elsevier Ltd. All rights reserved.

1. Introduction

(2,4-Dichlorophenoxy)acetic acid (2,4-D) was first described by Zimmerman and Hitchcock.¹ 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. It has been researched in various capacities by scientists and government regulatory agencies for more than six decades. Owing to the longevity and extent of use, 2,4-D is among the most thoroughly studied herbicides with respect to its environmental properties. Despite its short half-life in soil and in aquatic environments, the compound has been detected in groundwater supplies. It has also been detected in surface waters throughout the United States at very low concentrations. Concern over 2,4-D is such that it is currently not approved for use on lawns and gardens in Sweden,² Denmark, Norway, Kuwait, and the Canadian provinces of Québec³ and Ontario.⁴ Generally, 2,4-D does not present risk to human health or the environment when used according to the label.

The available, on-the-market herbicides utilizing 2,4-D contain this active phenoxy acid in several forms, including acid, salts, and esters.⁵ Esters are more active in comparison with acids and salts. However, they have the disadvantage of being very volatile.

lonic liquids (ILs) represent a new class of non-molecular liquids with unique and fascinating properties offering a phenomenal opportunity for science and technology.^{6–10} The evaluation of these compounds progresses 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), and to the third generation (ILs with targeted biological properties combined with chosen physical and chemical properties).^{11–17} Recently the third generation has been extended by phytopharmaceuticals—herbicidal ionic liquids.¹⁸

The structures of commercial 2,4-D-ammonium salts are shown in Fig. 1, with the abbreviations and melting points. The two ammonium salts can be classified as the protic ionic liquids (diolamine and triisopropanolammonium). These two examples contain secondary and tertiary 2,4-D-ammonium salts. Lately Dow Agrosciences LLC patent¹⁹ describes seven quaternary 2,4-D-ammonium salts (inter alia 2,4-D-teraalkylammonium, 2,4-D-benzyltrimethylammonium, and 2,4-D-hexadecyltrimethylammonium).

2. Results and discussion

Freshly crystallized (2,4-dichlorophenoxy)acetic acid, characterized by melting point T_m =139–140 °C, was used in the synthesis. The sources of cations were quaternary ammonium, pyridinium, imidazolium, piperidinium, morpholinium, and pyrrolidinium halides. Structure of cations and abbreviation used in this paper are presented in Fig. 2. The prepared quaternary ammonium (N) salts (Scheme 1) and synthesized pyridinium (**Pyr**), imidazolium (**Im**),



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



Fig. 2. Structure of cations of prepared 2,4-D-salts.

piperidinium (**Pip**), morpholinium (**Mor**), and pyrrolidinium (**Pyrr**) salts are summarized in Tables 1 and 2, respectively. Using 2,4-D in comparison with MCPA (4-chloro-2-methylphenoxy)acetic acid (MCPA—herbicidal activity reported by Slade^{20}) meant that we had to change the method of synthesis described before.¹⁸ The metathesis reaction run easier for MCPA in comparison with 2,4-D. These phenoxy acids have similar pK_a values (3.73 and 2.73 for MCPA and 2,4-D, respectively⁵), however react in a different way.



where X = H or Na, Y = Cl, Br, I, OH **Scheme 1.** Synthesis of quaternary 2,4-D-ammonium salts.

All synthesized salts are liquid or grease, except **N-8** (T_m =86–87.5 °C) and **Pyr-2** (T_m =132–134 °C). These new salts, except **Pyr-2**, may be considered as ILs. **Pyr-2** is a salt, PP vitamin derivative. This kind of salt is usually characterized by a high melting point.²¹

Synthesized ILs are stable in air and in contact with water and common organic solvents. They can be made anhydrous by heating at 70 °C in vacuo and storing them over P_4O_{10} . The water content was determined to be less than 500 ppm by coulometric Karl–Fischer titration.

The obtained ILs were soluble in DMSO, alcohols (methanol, ethanol, and propanol), and chloroform. All synthesized ILs are insoluble in hexane and diethyl ether. Selection of the cation determined the hydrophilicity of the synthesized ILs. Limited solubility in water was observed when using large ammonium cations with long alkyl substituents (Table 1).

The synthesized new ILs were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. In the ¹H NMR spectra the proton chemical shifts were observed for the protons located around the quaternary nitrogen atom coming up to 0.5 ppm. These chemical shift values are lower than the corresponding signals from the precursor, indicating that the 2,4-D anion causes greater shielding of the protons. The ¹³C NMR spectra of the studied ILs indicated no significant variation in the carbon signal shifts, which is consistent with our earlier observations.²²

Data presented in Table 3 show that the prepared quaternary 2,4-D-ammonium ILs were thermally stable. They have glass transition temperatures in the area from -35 to -54 °C. **N-4**, **N-7**, and **N-8** do not have the glass transition temperature. Some ammonium ILs like **N-2**, **N-7**, **N-4**, and **N-8** have a melting point. In the case of **N-8** two different melting points depending on the measuring technique are observed. A higher value indicated differential scanning calorimetry of at 108 °C in comparison with the measure for the resulting crystalline form 86–87.5 °C.

The prepared new forms of 2,4-D have been investigated under field conditions. The results of trials established on a field heavily infested by dicot weed species showed that 2,4-D as ILs (**N-1** and **N-2**) gave excellent control of common lambsquarters (*Chenopodium album*), field pennycress (*Thlaspi arvense*), and shepherd's-purse (*Capsella bursa pastoris*). Standard herbicide containing 2,4-D as the sodium salt was much less effective (Table 4). Moreover, it is interesting that the studied ILs have shown much faster effects on weeds than standard herbicide. This aspect is very profitable for growers because the weed competition can be eliminated in a few days after ILs application.

In another experiment conducted on spring barley we found excellent weed control using this form of 2,4-D. The efficacy of **N-6** was similar to that of 2,4-D-ethylhexyl ester and it was much better compared to the 2,4-D-dimethylammonium salt (Table 5). It is also important that a quaternary 2,4-D-ammonium salt applied at tillering growth stage at a rate of 450 g a.i. ha⁻¹ did not cause any symptoms of injury on spring barley plants. The obtained results allow us to qualify the tested salts as herbicidal ionic liquids (HILs). Because HILs are nonvolatile compounds they are more safe to the operators and to the nontarget plants compared to esters, moreover they are relatively safe to transport and store.

The surface activity of the cation affects the herbicidal efficiency of the studied salt. Fig. 3 shows surface tension as a function of concentration for the three synthesized quaternary 2,4-D-ammonium salts. Critical micelle concentration (CMC), surface tension, and contact angle values are shown in Table 6. In addition, surface activity for didecyldimethylammonium (4-chloro-2-methylphenoxy) acetate is given. Comparing the designated values for obtained HILs: **N-2** and **N-2-MCPA** (the second HIL has the same cation and only the differ anion), it is observed no significant differences. Anion in this case is not weakened the surface activity of the cation.

| Table 1 | |
|--|--|
| The prepared quaternary 2,4-D-ammonium salts | |

| Salt | R ¹ | R ² | R ³ | Yield (%) | Purity (%) | State at 25 °C | Solubility in water |
|------|---------------------------------|---|---|-----------|------------|--------------------|---------------------|
| N-1 | CH ₃ | CH ₂ C ₆ H ₅ | Alkyl ^a | 81 | 99.0 | Liquid | Limited |
| N-2 | CH ₃ | C ₁₀ H ₂₁ | C ₁₀ H ₂₁ | 91 | 99.5 | Liquid | Limited |
| N-3 | CH ₃ | C ₁₂ H ₂₅ | C ₆ H ₅ OCH ₂ CH ₂ | 88 | 99.0 | Liquid | Limited |
| N-4 | CH ₃ | CH ₃ | C ₁₆ H ₃₃ | 99 | 99.5 | Grease | Limited |
| N-5 | C ₁₂ H ₂₅ | (CH ₂ CH ₂ O) _x H ^b | (CH ₂ CH ₂ O) _v H ^b | 77 | 99.0 | Liquid | Total |
| N-6 | Alkyl ^c | (CH ₂ CH ₂ O) _x H ^d | (CH ₂ CH ₂ O) _v H ^d | 95 | 99.0 | Grease | Total |
| N-7 | CH ₃ | Alkyl ^e | Alkyl ^e | 97 | 99.0 | Liquid | Limited |
| N-8 | CH ₃ | cyclo-C ₁₂ H ₂₃ OCH ₂ | CH ₂ CH ₂ OH | 96 | 99.0 | Solid ^f | Limited |
| N-9 | CH ₃ | C ₁₀ H ₂₁ SCH ₂ | CH ₂ CH ₂ OH | 92 | 99.0 | Grease | Total |
| N-10 | CH ₃ | CH ₂ =CHCH ₂ | CH ₂ =CHCH ₂ | 90 | — | Grease | Total |

^a Alkyl chain distribution $C_{12}H_{25}$ —60, $C_{14}H_{29}$ —40%.

^b x+y=15.

^c Oleyl chain distribution C₁₂H₂₅-1, C₁₄H₂₉-4, C₁₆H₃₃-12, C₁₈H₃₅-82%.

^d x+y=2.

^e Alkyl (*hydrogenated tallow* chain distribution C₁₂H₂₅-1, C₁₄H₂₉-4, C₁₆H₃₃-31, C₁₈H₃₇-64%). ^f Mp 86–87.5 °C.

Table 2

The prepared 2,4-D-imidazolium (Im), 2,4-D-pyridinium (Pyr), 2,4-D-piperidinium (Pip), 2,4-D-morpholinium (Mor), and 2,4-D-pyrrolidinium (Pyrr) salts

| Salt | R ¹ | R ² | Yield (%) | State at 25 $^\circ\text{C}$ | Solubility in water |
|--------|---|----------------|-----------|------------------------------|---------------------|
| Im-1 | C ₈ H ₁₇ OCH ₂ | _ | 96 | Grease | Total |
| Im-2 | C ₈ H ₁₇ SCH ₂ | _ | 91 | Liquid | Total |
| Im-3 | C_4H_9 | _ | 90 | Grease | Total |
| Pyr-1 | C ₁₆ H ₃₃ | Н | 99 | Grease | Total |
| Pyr-2 | CH ₃ | $CONH_2$ | 91 | Solid ^a | Total |
| Pip-1 | CH ₃ | _ | 82 | Grease | Total |
| Pip-2 | C ₃ H ₇ OCH ₂ | _ | 98 | Liquid | Total |
| Pip-3 | $C_5H_{11}OCH_2$ | _ | 97 | Liquid | Total |
| Mor-1 | C_4H_9 | _ | 98 | Grease | Total |
| Pyrr-1 | C_4H_9 | _ | 99 | Liquid | Total |

^a Mp=132-134 °C with decomposition.

Table 3

| The physicochemica | l properties o | f 2,4-D-quaternary | ammonium ILs |
|--------------------|----------------|--------------------|--------------|
|--------------------|----------------|--------------------|--------------|

| IL | $T_{g}^{a}(^{\circ}C)$ | $T_{\text{cryst}}^{\mathbf{b}}(^{\circ}\text{C})$ | $T_{\mathbf{m}}^{\mathbf{c}}(^{\circ}\mathbf{C})$ | $T_{\text{onset5\%}}^{d}$ (°C) | T_{onset}^{e} (°C) |
|------|------------------------|---|---|--------------------------------|-----------------------------|
| N-1 | -51 | _ | _ | 204 | 252 |
| N-2 | -50 | -39 ^f | -3 | 208 | 260 |
| N-3 | -42 | _ | _ | 214 | 273 |
| N-4 | _ | _ | -20 | 218 | 253, 335 |
| N-5 | -54 | _ | _ | 219 | 285, 372 |
| N-6 | -55 | _ | _ | 222 | 244 |
| N-7 | _ | _ | 16 | 219 | 256, 330 |
| N-8 | _ | _ | 108 | 242 | 280 |
| N-9 | -35 | _ | _ | 205 | 219, 272 |
| N-10 | -42 | _ | _ | 187 | 196, 237 |

 $T_{\rm g}$ —glass transition temperature.

b $T_{\rm cryst}$ —temperature of crystallization.

с *T*_m—melting point.

 $T_{\text{onset5\%}}$ —decomposition temperature of 5% sample. d

Tonset—decomposition temperature.

^f $T_{\text{cold crystallization}} = -20 \,^{\circ}\text{C}.$

Table 4

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Weed control on fallow by different forms of 2,4-D
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| Treatments | Concent. | Chenopodium album | | Thlaspi arvense | | Capsella bursa pastoris | |
|----------------------|----------|----------------------|---------|-----------------|--------|----------------------------|--------|
| | (M) | 6 DAT ^a | 30 DAT | 6 DAT | 30 DAT | 6 DAT | 30 DAT |
| | | % Weed | control | | | | |
| N-1 | 0.01 | 85 | 100 | 81 | 100 | 81 | 100 |
| N-1 | 0.02 | 97 | 100 | 90 | 100 | 96 | 100 |
| N-2 | 0.01 | 89 | 100 | 82 | 100 | 81 | 100 |
| N-2 | 0.02 | 98 | 100 | 96 | 100 | 99 | 100 |
| 2,4-D-sodium salt | 0.01 | 55 | 25 | 31 | 100 | 28 | 100 |
| 2,4-D-sodium salt | 0.02 | 60 | 75 | 48 | 100 | 55 | 100 |

^a DAT=days after treatment.

| Table 5 | |
|---------|-----------|
| T1 | - 6 -1:66 |

The influence of different forms of 2,4-D on weed control in spring barley (4 WAT^a)

| Treatments | Rate of 2,4-D | Chenopodium | Centaurea |
|--|-----------------------|---------------------------------------|-----------------|
| | (g ha ⁻¹) | album | cyanus |
| N-6 2,4-D-Dimethylammonium 2,4-D-Ethylhexyl | 450 450 450 | % Weed control 100 60 100 | 100 20 80 |

^a WAT=weeks after treatment.



Fig. 3. Surface tension as a function of concentration (log *C*) of HILs at 25 °C in water.

| Table 6 |
|--|
| The CMC, surface tension (γ_{CMC}), and contact angle CA (paraffin) of aqueous solution |
| of HILs, at 25 °C |

| HIL | $CMC (mmol L^{-1})$ | $\gamma_{CMC} (mNm^{-1})$ | CA (°) |
|-----------------------|-------------------------|---------------------------|----------------------|
| N-1 N-2 N-6 | 0.501 0.316 0.158 | 31.2 26.6 32.5 | 49.4 33.0 51.8 |
| N-2-MCPA ^ª | 0.251 | 26.2 | 33.2 |

^a Didecyldimethylammonium (4-chloro-2-methylphenoxy)acetate.¹⁸

3. Conclusion

New forms of 2,4-D as ionic liquids were synthesized. The synthesized salts are thermally stable. Their solubility in water can be regulated by selection of the cation. In synthesized ILs with the 2,4-D anion, the herbicidal activity of the anion was increased. According to the law in force, with a view to the environmental protection, the proposed HILs with 2,4-D anion pose a real possibility of extending the applications one of the most important herbicide (2,4-D). HILs are nonvolatile. Additionally, lower water solubility than starting herbicides, is likely to reduce soil and groundwater mobility.

4. Experimental section

4.1. General

¹H NMR spectra were recorded on a Mercury Gemini 300 spectrometer operating at 300 MHz with tetramethylsilane as the internal standard. ¹³C NMR spectra were obtained with the same instrument at 75 MHz. CHN elemental analyses were performed at Adam 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 solvent.

4.2. Preparation

Quaternary 2,4-D-ammoniums (**N-1**)–(**N-9**), 2,4-D-imidazolium (**Im-1**), (**Im-2**), and 2,4-D-pyrrolidinium (**Pyr-1**) salts: (2,4-Dichlorophenoxy)acetic acid (0.01 mol), distilled water (20 mL), and a 10% aqueous solution of NaOH (0.011 mol) were mixed in a roundbottomed flask, equipped with a magnetic stirring bar, a reflux condenser, and an addition funnel. The mixture was heated at 50 °C until it became a clear solution. After that the quaternary ammonium or imidazolium or pyrrolidinium chloride or bromide (0.01 mol) dissolved in water (30 mL) was added and stirred for 30 min at room temperature. Then product was extracted from the aqueous phase with chloroform (50 mL) and washed with distilled water until chloride or bromide ions were no longer detected using AgNO₃. After removal of chloroform the product was dried under reduced pressure at 70 °C for 24 h.

Quaternary 2,4-D-ammonium (**N-1**), 2,4-D-imidazolium (**Im-3**), 2,4-D-pyridinium (**Pyr-2**), 2,4-D-piperidinium (**Pip-2**), (**Pip-3**), 2,4-D-morpholinium (**Mor-1**) and 2,4-D-pyrrolidinium (**Pyrr-1**) salts: Quaternary ammonium or imidazolium or pyridinium or piperidinium or morpholinium or pyrrolidinium chloride, bromide or iodide (0.01 mol) was exchanged into OH ion using anion exchange resin Dowex-Monosphere 550A (OH). After that was added (2,4-dichlorophenoxy)acetic acid (0.011 mol). The mixture was stirred for 10 min. Then excess of (2,4-dichlorophenoxy)acetic acid was filtered out, and water was evaporated. Finally product was dried under reduced pressure at 70 °C for 24 h.

4.2.1. Benzalkonium (2,4-dichlorophenoxy)acetate (**N-1**). ν_{max} (liquid film) 3600–3100 (br), 2925, 2854, 1615, 1483, 1391, 1347, 1284, 1265, 1237, 1065, 725, 704 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.44 (5H, m, Ph), 7.22 (1H, d, *J* 2.5 Hz, CICCH=CCl), 7.03 (1H, dd, *J*^{1,2} 2.5 Hz, *J*^{1,3} 8.8 Hz, CIC=CHCCl), 6.87 (1H, d, *J* 9.1 Hz, HCCH=CO), 4.50 (2H, s, OCH₂COO⁻), 4.70 (2H, s, CH₂Ph), 3.24 (2H, t, *J* 8.4 Hz, N⁺CH₂CH₂), 3.09 (6H, s, MeN⁺Me), 1.68 (2H, q, *J* 7.3 Hz, N⁺CH₂CH₂), 1.26 (20H, m, CH₂(CH₂)₁₀CH₃), 0.88 (3H, t, *J* 6.7 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 171.8, 153.5, 132.8, 130.3, 129.2, 128.9, 127.4, 127.3, 124.4, 122.4, 114.5, 70.0, 67.4, 63.2, 49.5, 31.86, 31.84, 29.63, 29.59, 29.54, 29.43, 29.37, 29.3, 29.2, 26.3, 22.7, 22.6, 14.1.

4.2.2. Didecyldimethylammonium (2,4-dichlorophenoxy)acetate (**N**-**2**). Found: C, 65.7; H, 9.85; N, 2.68. C₃₀H₅₃O₃NCl₂ requires C, 65.90; H, 9.79; N, 2.56%. ν_{max} (liquid film) 3600–3100 (br), 2925, 2855, 1614, 1483, 1390, 1347, 1283, 1265, 1242, 1105, 1065, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.29 (1H, d, *J* 2.6 Hz, ClCC<u>H</u>=CCl), 7.09 (1H, dd, *J*^{1,2})

2.5 Hz, $J^{1.3}$ 8.8 Hz, CIC=CHCCI), 6.91 (1H, d, J 8.9 Hz, HCCH=CO), 4.47 (2H, s, OCH₂COO⁻), 3.29 (4H, t, J 8.4 Hz, CH₂N⁺CH₂), 3.20 (6H, s, MeN⁺Me), 1.60 (4H, q, J 7.3 Hz, CH₂CH₂N⁺CH₂CH₂), 1.26 (28H, m, CH₂(CH₂)₇Me), 0.88 (6H, t, J 6.7 Hz, (CH₂Me)₂); δ_{C} (75 MHz, CDCl₃) 171.3, 153.6, 129.1, 127.2, 124.3, 122.3, 114.5, 69.1, 63.2, 50.7, 31.7, 29.31, 29.27, 29.12, 29.10, 28.9, 26.2, 22.5, 14.0.

4.2.3. Dodecyldimethylphenoxyethylammonium (2,4-dichloropheno-xy)acetate (**N-3**). Found: C, 64.59; H, 8.19; N, 2.62. C₃₀H₄₅O₄NCl₂ requires C, 64.96; H, 8.19; N, 2.53%. ν_{max} (liquid film) 3600–3100 (br), 2924, 2854, 1613, 1483, 1430, 1391, 1347, 1283, 1265, 1241, 1064, 801, 755, 691 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.29 (2H, t, *J* 4.5 Hz, meta-Ph), 7.25 (1H, d, *J* 2.5 Hz, ClCCH=CCl), 7.06 (1H, dd, *J*^{1,2} 2.7 Hz, *J*^{1,3} 9.0 Hz, ClC=CHCCl), 7.00 (1H, t, *J* 8.4 Hz, para-Ph), 6.87 (1H, d, *J* 9.1 Hz, HCCH=CO), 6.84 (2H, d, *J* 3.2 Hz, ortho-Ph), 4.45 (2H, s, OCH₂COO⁻), 4.37 (2H, t, *J* 3.8 Hz, OCH₂CH₂N⁺), 3.99 (2H, t, *J* 4.3 Hz, OCH₂CH₂N⁺), 3.38 (2H, t, *J* 8.5 Hz, N⁺CH₂CH₂), 3.27 (6H, s, MeN⁺Me), 1.70 (2H, q, *J* 7.3 Hz, N⁺CH₂CH₂), 1.25 (18H, m, CH₂(CH₂)₉Me), 0.88 (3H, t, *J* 6.7 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.0, 156.8, 153.4, 129.6, 129.3, 127.4, 124.6, 122.4, 121.8, 114.5, 114.1, 69.0, 65.6, 62.2, 61.9, 51.7, 31.9, 29.6, 29.5, 29.3, 29.2, 26.3, 22.8, 22.7, 14.1.

4.2.4. Hexadecyltrimethylammonium (2,4-dichlorophenoxy)acetate (*N*-4). Found: C, 63.98; H, 9.47; N, 2.71. $C_{28}H_{43}O_3NCl_2$ requires C, 64.26; H, 9.41; N, 2.78%. ν_{max} (thin film) 3600–3100 (br), 3017, 2918, 2850, 1644, 1609, 1484, 1430, 1346, 1282, 1242, 1107, 1064, 1044, 961, 868, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.28 (1H, d, *J* 2.5 Hz, ClCC<u>H</u>=CCl), 7.13 (1H, dd, *J*^{1,2} 2.5 Hz, *J*^{1,3} 8.7 Hz, ClC=C<u>H</u>CCl), 6.86 (1H, d, *J* 8.8 Hz, ClC=C<u>H</u>CCl), 4.43 (2H, s, OC<u>H₂COO⁻), 3.20 (2H, t, *J* 8.5 Hz, N⁺C<u>H₂CH₂</u>), 3.13 (9H, s, (<u>Me)₃N⁺</u>), 1.59 (2H, q, *J* 7.3 Hz, N⁺CH₂C<u>H₂</u>), 1.26 (26H, m, CH₂(C<u>H₂)13</u>CH₃), 0.88 (3H, t, *J* 6.7 Hz, CH₂<u>Me</u>); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.2, 153.1, 129.3, 127.5, 124.9, 122.5, 114.6, 68.4, 66.6, 53.0, 31.9, 29.70, 29.65, 29.59, 29.52, 29.34, 29.31, 26.3, 23.0, 22.7, 14.1.</u>

4.2.5. Dodecyldi(polyoxyethylene)methylammonium (2,4dichlorophenoxy)acetate (**N-5**). ν_{max} (liquid film) 3600–3100 (br), 2923, 2854, 1616, 1483, 1348, 1283, 1245, 1106, 1042, 948, 868, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.30 (1H, d, J 2.5 Hz, ClCCH=CCl), 7.09 (1H, dd, J^{1.2} 2.5 Hz, J^{1.3} 8.8 Hz, ClC=CHCCl), 6.90 (1H, d, J 9.1 Hz, HCCH=CO), 4.49 (2H, s, OCH₂COO⁻), 3.86 (4H, m, (CH₂CH₂OH)₂), 3.70 (4H, m, N⁺(CH₂CH₂O)₂), 3.65 (52H, m, (CH₂CH₂O)₁₃), 3.43 (2H, t, J 6.6 Hz, N⁺CH₂CH₂), 3.21 (3H, s, MeN⁺), 1.68 (2H, m, N⁺CH₂CH₂), 1.26 (18H, m, CH₂(CH₂)₉Me), 0.88 (3H, t, J 7.0 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 171.8, 153.7, 129.1, 127.2, 124.3, 122.6, 114.6, 72.67, 72.61, 72.58, 72.55, 72.45, 70.36, 70.3, 70.2, 70.0, 69.98, 69.80, 68.9, 64.7, 63.8, 61.5, 61.23, 61.18, 61.13, 61.06, 60.9, 49.0, 31.7, 29.5, 29.39, 29.31, 29.28, 29.1, 29.0, 26.1, 22.5, 22.3, 13.9.

4.2.6. Oleyldi(2-hydroxyethyl)methylammonium (2,4dichlorophenoxy)acetate (**N-6**). ν_{max} (thin film) 3500–3100 (br), 2924, 2854, 1615, 1482, 1430, 1346, 1282, 1266, 1243, 1106, 1065, 1043, 868, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.31 (1H, d, *J* 2.8 Hz, CICC<u>H</u>=CCl), 7.13 (1H, dd, J^{1,2} 2.6 Hz, J^{1,3} 8.9 Hz, CIC=CHCCl), 6.83 (1H, d, *J* 9.1 Hz, HCC<u>H</u>=CO), 5.35 (2H, m, C<u>H</u>=C<u>H</u>), 4.45 (2H, s, OC<u>H</u>₂COO⁻), 3.96 (4H, t, *J* 4.0 Hz, N⁺(CH₂C<u>H</u>₂OH)₂), 3.54 (4H, t, *J* 4.3 Hz, N⁺(C<u>H</u>₂CH₂OH)₂), 3.34 (2H, t, *J* 8.4 Hz, N⁺C<u>H</u>₂CH₂), 3.14 (3H, s, <u>MeN⁺</u>), 2.00 (4H, m, C<u>H</u>₂CH=CHC<u>H</u>₂), 1.26 (26H, m, CH₂(C<u>H</u>₂)₁₃Me), 0.88 (3H, t, *J* 6.9 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 173.1, 153.3, 129.9, 129.51, 129.48, 127.5, 125.1, 122.8, 114.5, 68.6, 64.1, 63.6, 55.5, 50.0, 32.5, 31.81, 31.80, 31.7, 29.64, 29.62, 29.61, 29.56, 29.50, 29.46, 29.42, 29.38, 29.33, 29.26, 29.22, 29.17, 29.13, 29.09, 29.04, 27.12, 27.10, 27.07, 26.3, 22.6, 22.4, 14.0.

4.2.7. Di(hydrogenatedtallowalkyl)dimethylammonium (2,4dichlorophenoxy)acetate (**N-7**). ν_{max} (liquid film) 2923, 2853, 1620, 1482, 1468, 1389, 1284, 1264, 1065, 722 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.29 (1H, d, *J* 2.6 Hz, ClCC<u>H</u>=CCl), 7.11 (1H, dd, *J*^{1,2} 2.7 Hz, *J*^{1,3} 8.8 Hz, ClCC<u>H</u>=CCl), 6.89 (1H, d, *J* 8.8 Hz, HCC<u>H</u>=CO), 4.46 (2H, s, OC<u>H</u>₂COO⁻), 3.25 (4H, t, *J* 8.4 Hz, C<u>H</u>₂N⁺C<u>H</u>₂), 3.18 (6H, s, <u>MeN⁺Me</u>), 1.59 (4H, q, *J* 6.9 Hz, C<u>H</u>₂CH₂N⁺CH₂C<u>H</u>₂), 1.26 (50H, m, CH₂(C<u>H</u>₂)₂₅Me), 0.88 (6H, t, *J* 6.9 Hz, (CH₂<u>Me</u>)₂); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.0, 153.6, 129.3, 127.4, 124.6, 122.5, 114.6, 68.9, 63.2, 51.1, 31.8, 29.6, 29.54, 29.50, 29.4, 29.3, 29.2, 29.1, 26.1, 22.6, 22.5, 14.0.

4.2.8. Cyclododecyloxymethyl(2-hydroxyethyl)dimethylammonium (2,4-dichlorophenoxy)acetate (**N-8**). Found: C, 59.00; H, 8.07; N, 2.65. C₂₅H₄₁O₅NCl₂ requires C, 59.27; H, 8.17; N, 2.77%. v_{max} (pellet with KBr) 3219, 2929, 2903, 2862, 2845, 1611, 1473, 1399, 1346, 1267, 1138, 1065, 812, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.31 (1H, d, *J* 2.7 Hz, ClCCH=CCl), 7.11 (1H, dd, *J*¹² 2.5 Hz, *J*^{1,3} 8.8 Hz, ClC=CHCCl), 6.85 (1H, d, *J* 9.1 Hz, HCCH=CO), 6.06 (1H, s, CH₂OH), 4.72 (2H, s, N⁺CH₂O), 4.44 (2H, s, OCH₂COO⁻), 3.99 (2H, t, *J* 4.5 Hz, N⁺CH₂CH₂OH), 3.78 (1H, q, *J* 3.7 Hz, CH₂OCH), 3.51 (2H, t, *J* 4.7 Hz, N⁺CH₂CH₂OH), 3.12 (6H, s, MeN⁺Me), 1.65 (2H, m, HaHbCOCHaHb—cyclic), 1.49 (2H, m, CHaHbCHaHbCO-CHaHb—cyclic) and CHaHbCOaHbbCHaHbCO-CHaHbCHaHb—cyclic); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.2, 153.4, 129.3, 127.3, 124.8, 122.6, 114.4, 89.7, 81.4, 68.7, 63.0, 55.4, 48.0, 28.4, 24.8, 24.5, 22.6, 22.4, 19.8.

4.2.9. Decylthiomethyl(2-hydroxyethyl)dimethylammonium (2,4-dichlorophenoxy)acetate (**N-9**). Found: C, 55.26; H, 8.01; N, 2.93. C₂₃H₃₉O₄NSCl₂ requires C, 55.62; H, 7.93; N, 2.82%. ν_{max} (thin film) 2925, 2854, 1612, 1480, 1392, 1339, 1287, 1104, 1065, 868, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.32 (1H, d, *J* 2.5 Hz, ClCCH=CCl), 7.13 (1H, dd, *J*^{1,2} 2.6 Hz, *J*^{1,3} 8.8 Hz, ClC=CHCCl), 6.84 (1H, d, *J* 8.8 Hz, HCCH=CO), 4.73 (2H, s, N⁺CH₂S), 4.45 (2H, s, OCH₂COO⁻), 3.99 (2H, t, *J* 4.5 Hz, N⁺CH₂CH₂OH), 3.58 (2H, t, *J* 4.5 Hz, N⁺CH₂CH₂OH), 3.14 (6H, s, MeN⁺Me), 2.75 (2H, t, *J* 7.3 Hz, SCH₂CH₂), 1.56 (2H, q, *J* 7.3 Hz, SCH₂CH₂), 1.25 (14H, m, CH₂(CH₂)₇Me), 0.88 (3H, t, *J* 6.7 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.6, 153.4, 129.5, 127.5, 125.0, 122.7, 114.4, 70.7, 68.7, 65.0, 55.8, 49.6, 35.9, 31.8, 29.51, 29.45, 29.39, 29.2, 29.1, 28.5, 22.6, 14.0.

4.2.10. Diallyldimethylammonium (2,4-dichlorophenoxy)acetate (**N-10**). Found: C, 55.32; H, 6.03; N, 4.16. $C_{16}H_{21}O_3NCl_2$ requires C, 55.49; H, 6.13; N, 4.05%. ν_{max} (thin film) 3600–3100 (br), 1613, 1482, 1424, 1390, 1346, 1283, 1265, 1241, 1106, 1065, 954, 869, 801, 764, 721 cm⁻¹; δ_{H} (300 MHz, D₂O) 7.37 (1H, d, J 2.6 Hz, CICCH=CCI), 7.21 (1H, dd, J^{1,2} 2.6 Hz, J^{1,3} 8.9 Hz, CIC=CHCCI), 6.83 (1H, d, J 8.8 Hz, HCCH=CO), 6.00 (2H, m, (H_aH_bC=CHCH₂)₂N⁺), 5.70 (2H, m, (H_aH_bC=CHCH₂)₂N⁺), 5.63 (2H, m, (H_aH_bC=CHCH₂)₂N⁺), 4.50 (2H, s, OCH₂COO⁻), 3.84 (4H, d, J 7.1 Hz, H_aH_bC=CHCH₂)₂N⁺), 2.98 (6H, s, <u>MeN⁺Me</u>); δ_{C} (75 MHz, D₂O) 178.0, 155.0, 132.3, 131.9, 130.6, 128.1, 126.9, 125.1, 116.9, 70.2, 68.7 (t, J 3.1 Hz), 52.1 (t, J 4.3 Hz).

4.2.11. 1-Methyl-3-octyloxymethylimidazolium (2,4-dichlorophenoxy) acetate (**Im-1**). Found: C, 56.71; H, 6.73; N, 6.26. C₂₁H₃₀O₄N₂Cl₂ requires C, 56.62; H, 6.80; N, 6.29%. ν_{max} (liquid film) 3600–3100 (br), 3149, 2925, 2855, 1609, 1481, 1425, 1392, 1346, 1283, 1265, 1241, 1159, 1106, 1064, 868, 801 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 10.05 (1H, t, *J* 1.1 Hz, NCH=N⁺), 7.44 (1H, t, *J* 1.9 Hz, MeNCH=CHN⁺), 7.39 (1H, t, *J* 1.9 Hz, CH₃NCH=CHN⁺), 7.26 (1H, d, *J* 2.5 Hz, CICCH=CCl), 7.10 (1H, d, *J*^{1.2} 2.5 Hz, *J*^{1.3} 8.8 Hz, CIC=CHCCl), 6.87 (1H, d, *J* 8.8 Hz, HCCH=CO), 5.54 (2H, s, N⁺CH₂O), 4.46 (2H, s, OCH₂COO⁻), 4.19 (3H, s, MeN), 3.40 (2H, t, *J* 6.5 Hz, OCH₂CH₂), 1.48 (2H, q, *J* 6.3 Hz, OCH₂CH₂), 1.22 (10H, m, CH₂(CH₂)₅CH₃), 0.87 (3H, t, *J* 6.9 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.3, 153.1, 138.1, 129.2, 127.3, 124.7, 123.6, 122.4, 120.6, 114.3, 78.8, 70.2, 68.6, 36.2, 31.7, 29.3, 29.2, 29.1, 25.8, 22.5, 14.0.

4.2.12. 1-Methyl-3-octyltiomethylimidazolium (2,4-dichlorophenoxy) acetate (**Im-2**). Found: C, 64.81; H, 10.26; N, 11.49. C₂₁H₃₀O₃N₂SCl₂

requires C, 64.65; H, 10.46; N, 11.60%. ν_{max} (liquid film) 3600–3100 (br), 3143, 3095, 2955, 2926, 2854, 1643, 1611, 1482, 1430, 1346, 1282, 1266, 1242, 1106, 1065, 868, 801, 764 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃) 10.19 (1H, t, *J* 1.1 Hz, NCH=N⁺), 7.50 (1H, t, *J* 1.8 Hz, MeNCH=CHN⁺), 7.38 (1H, t, *J* 1.8 Hz, MeNCH=CHN⁺), 7.28 (1H, d, *J* 2.5 Hz, ClCCH=CCl), 7.11 (1H, dd, *J*^{1,2} 2.6 Hz, *J*^{1,3} 8.9 Hz, ClC=CHCCl), 6.89 (1H, d, *J* 8.9 Hz, HCCH=CO), 5.33 (2H, s, N⁺CH₂S), 4.48 (2H, s, OCH₂COO⁻), 3.90 (3H, s, MeN), 2.52 (2H, t, *J* 7.3 Hz, SCH₂CH₂), 1.49 (2H, q, *J* 7.3 Hz, SCH₂CH₂), 1.23 (10H, m, CH₂(CH₂₎₅Me), 0.87 (3H, t, *J* 6.8 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, CDCl₃) 172.5, 153.3, 138.4, 129.4, 127.4, 124.8, 123.4, 122.5, 121.1, 114.5, 68.7, 51.3, 36.2, 31.7, 31.6, 29.0, 28.6, 28.5, 22.5, 13.9.

4.2.13. 1-Butyl-3-methylimidazolium (2,4-dichlorophenoxy)acetate (**Im-3**). Found: C, 53.20; H, 5.53; N, 8.11. $C_{16}H_{20}O_3N_2Cl_2$ requires C, 53.48; H, 5.62; N, 8.00%. ν_{max} (liquid film) 3600–3100 (br), 3148, 3093, 2961, 2935, 1613, 1573, 1482, 1424, 1397, 1346, 1283, 1266, 1241, 1170, 1106, 1066, 801, 770 cm⁻¹; δ_H (300 MHz, DMSO-*d*₆) 10.05 (1H, t, *J* 1.1 Hz, NCH=N), 7.90 (1H, t, *J* 1.9 Hz, MeNCH=CHN⁺), 7.84 (1H, t, *J* 1.9 Hz, MeNCH=CHN⁺), 7.54 (1H, d, *J* 2.5 Hz, CICCH=CCI), 7.35 (1H, dd, *J*^{1.2} 2.5 Hz, *J*^{1.3} 8.8 Hz, CIC=CHCCI), 6.97 (1H, d, *J* 8.9 Hz, HCCH=CO), 4.38 (2H, s, OCH₂COO⁻), 4.28 (2H, t, *J* 7.1 Hz, N⁺CH₂CH₂), 3.95 (3H, s, MeN), 1.87 (2H, q, *J* 7.4 Hz, N⁺CH₂CH₂CH₂), 1.38 (2H, sex, *J* 7.4 Hz, CH₂CH₂Me), 0.98 (3H, t, *J* 7.3 Hz, CH₂Me); δ_C (75 MHz, DMSO-*d*₆) 179.4, 153.7, 136.8, 128.8, 127.6, 123.6, 123.3, 122.3, 121.9, 115.1, 68.5, 48.57, 35.7, 31.4, 18.8, 13.3.

4.2.14. 1-Hexadecylpyridinium (2,4-dichlorophenoxy)acetate (**Pyr-1**). Found: C, 65.99; H, 8.52; N, 2.62. $C_{29}H_{43}O_3NCl_2$ requires C, 66.39; H, 8.28; N, 2.67%. ν_{max} (thin film) 3052, 2923, 2852, 1611, 1485, 1429, 1391, 1283, 1239, 1065, 867, 800 cm⁻¹; δ_H (300 MHz, CDCl₃) 9.01 (2H, d, *J* 5.5 Hz, CH=N⁺CH), 8.42 (1H, t, *J* 7.8 Hz, CH=CHCH=N⁺), 8.02 (2H, t, *J* 7.1 Hz, CHCH=N⁺CH=CH), 7.25 (1H, d, *J* 2.5 Hz, CICCH=CCl), 7.09 (1H, dd, *J*^{1,2} 2.6 Hz, *J*^{1,3} 8.7 Hz, CIC=CHCCl), 6.86 (1H, d, *J* 9.1 Hz, HCCH=CO), 4.65 (2H, t, *J* 7.4 Hz, N⁺CH₂CH₂), 4.49 (2H, s, OCH₂COO⁻), 1.86 (2H, q, *J* 7.2 Hz, N⁺CH₂CH₂), 1.25 (26H, m, CH₂(CH₂)₁₃Me), 0.87 (3H, t, *J* 6.7 Hz, CH₂Me); δ_C (75 MHz, CDCl₃) 172.2, 153.9, 145.1, 144.4, 129.4, 128.2, 127.5, 125.1, 122.6, 114.5, 68.1, 61.9, 31.9, 31.6, 29.69, 29.64, 29.59, 29.4, 29.3, 29.1, 26.1, 22.7, 14.1.

4.2.15. 1-Methyl-3-carbamoylpyridinium (2,4-dichlorophenoxy)acetate (**Pyr-2**). Found: C, 50.78; H, 3.78; N, 7.96. C₁₅H₁₄O₄N₂Cl₂ requires C, 50.43; H, 3.96; N, 7.84%. ν_{max} (pellet with KBr) 3298, 3131, 1691, 1617, 1482, 1424, 1384, 1346, 1281, 1265, 1244, 1210, 1107, 1064, 1043, 801, 764, 635 cm⁻¹; $\delta_{\rm H}$ (300 MHz, D₂O) 9.24 (1H, s, N⁺= CHCC(O)NH₂), 8.96 (1H, d, *J* 6.0 Hz, N⁺CH=CH), 8.82 (1H, d, *J* 8.2 Hz, N⁺CH=CHCH), 8.14 (1H, t, *J* 7.3 Hz, N⁺CH=CHCH), 7.22 (1H, d, *J* 2.6 Hz, ClCCH=CCl), 7.10 (1H, dd, *J*^{1,2} 2.6 Hz, *J*^{1,3} 8.9 Hz, ClC= CHCCl), 6.77 (1H, d, *J* 8.8 Hz, HCCH=CO), 4.86 (2H, s, OCH₂COO⁻), 4.49 (3H, s, N⁺Me); $\delta_{\rm C}$ (75 MHz, D₂O) 178.1, 168.0, 154.9, 150.0, 147.8, 146.2, 136.0, 132.2, 130.9, 130.6, 128.0, 125.0, 116.8, 70.2, 51.4.

4.2.16. 1,1-Dimethylpiperidinium (2,4-dichlorophenoxy)acetate (**Pip-1**). Found: C, 53.76; H, 6.59; N, 4.01. $C_{15}H_{21}O_3NCl_2$ requires C, 53.89; H, 6.35; N, 4.19%. ν_{max} (thin film) 2999, 2940, 1644, 1608, 1483, 1430, 1347, 1282, 1266, 1243, 1107, 1064, 1043, 868, 801, 766 cm⁻¹; δ_{H} (300 MHz, DMSO- d_{6}) 7.46 (1H, d, *J* 2.6 Hz, CICC<u>H</u>=CCl), 7.26 (1H, dd, J^{1.2} 2.6 Hz, J^{1.3} 8.8 Hz, CIC=C<u>H</u>CCl), 6.83 (1H, d, *J* 8.9 Hz, HCC<u>H</u>=CO), 4.22 (2H, s, OC<u>H</u>₂COO⁻), 3.33 (4H, t, *J* 5.8 Hz, CH₂C<u>H</u>₂N⁺C<u>H</u>₂CH₂), 3.07 (6H, s, <u>MeN⁺Me</u>), 1.73 (4H, q, *J* 5.2 Hz, C<u>H</u>₂CH₂N⁺CH₂CH₂), 1.48 (2H, q, *J* 5.9 Hz, N⁺CH₂CH₂CH₂); δ_{C} (75 MHz, DMSO- d_{6}) 168.7, 153.8, 128.7, 127.5, 122.9, 121.6, 115.0, 68.7, 61.4, 50.7, 20.5, 19.6.

4.2.17. 1-Propoxymethyl-1-methylpiperidinium (2,4-dichlorophenoxy) acetate (**Pip-2**). Found: C, 57.51; H, 7.82; N, 3.58. C₁₈H₂₉O₃NCl₂ requires C, 57.13; H, 7.74; N, 3.70%. *v*_{max} (liquid film) 3600–3100 (br),

2965, 1612, 1482, 1391, 1346, 1283, 1266, 1240, 1185, 1123, 1106, 1065, 1040, 869, 838, 801, 764 cm⁻¹; $\delta_{\rm H}$ (300 MHz, D₂O) 7.36 (1H, d, *J* 2.6 Hz, ClCC<u>H</u>=CCl), 7.21 (1H, dd, *J*^{1,2} 2.6 Hz, *J*^{1,3} 8.9 Hz, ClC=CHCCl), 6.85 (1H, d, *J* 9.0 Hz, HCCH=CO), 4.62 (2H, s, OCH₂COO⁻), 4.50 (2H, s, N⁺CH₂O), 3.76 (2H, t, *J* 6.5 Hz, OCH₂CH₂), 3.25 (4H, t, *J* 7.0 Hz, CH₂CH₂N⁺CH₂CH₂), 2.97 (3H, s, N⁺Me), 1.84 (2H, m, N⁺CH₂CH₂CH₂), 1.83 (2H, m, OCH₂CH₂), 1.61 (4H, q, *J* 7.0 Hz, CH₂CH₂N⁺CH₂CH₂), 0.91 (3H, t, *J* 7.4 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, D₂O) 177.7, 155.2, 132.2, 130.6, 128.1, 125.2, 117.1, 93.6, 78.6, 70.3, 60.1, 47.4, 25.1, 23.4, 21.8, 12.3.

4.2.18. 1-Pentyloxymethyl-1-methylpiperidinium (2,4-dichlorophenoxy) acetate (**Pip-3**). Found: C, 59.68; H, 8.31; N, 3.60. C₂₀H₃₃O₃NCl₂ requires C, 60.00; H, 8.20; N, 3.45%. ν_{max} (liquid film) 3600–3100 (br), 2955, 2871, 1611, 1482, 1391, 1346, 1283, 1266, 1241, 1106, 1065, 1043, 869, 801, 764, 722 cm⁻¹; $\delta_{\rm H}$ (300 MHz, D₂O) 7.25 (1H, d, *J* 2.5 Hz, CICCH=CCI), 7.17 (1H, dd, *J*^{1,2} 2.5 Hz, *J*^{1,3} 8.9 Hz, CIC=CHCCI), 6.86 (1H, d, *J* 8.9 Hz, HCCH=CO), 4.54 (2H, s, OCH₂COO⁻), 4.45 (2H, s, N⁺CH₂O), 3.66 (2H, t, *J* 6.7 Hz, OCH₂CH₂), 3.19 (4H, t, *J* 7.0 Hz, CH₂CH₂D, ¹.76 (4H, m, CH₂CH₂N⁺CH₂CH₂), 1.50 (2H, q, *J* 7.0 Hz, OCH₂CH₂), 1.23 (4H, m, CH₂CH₂CH₃), 0.85 (3H, t, *J* 6.8 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, D₂O) 176.9, 155.2, 131.8, 130.2, 127.6, 16.0.

4.2.19. 4-Butyl-4-methylmorpholinium (2,4-dichlorophenoxy)acetate (**Mor-1**). Found: C, 53.57; H, 6.82; N, 3.89. $C_{17}H_{25}O_4N_2Cl_2$ requires C, 53.87; H, 6.67; N, 3.70%. ν_{max} (thin film) 3600–3100 (br), 2964, 2875, 1644, 1608, 1483, 1430, 1347, 1282, 1267, 1243, 1107, 1064, 1044, 898, 868, 801, 764 cm⁻¹; $\delta_{\rm H}$ (300 MHz, DMSO- d_6) 7.47 (1H, d, *J* 2.7 Hz, CICC<u>H</u>=CCl), 7.26 (1H, dd, *J*^{1,2} 2.7 Hz, *J*^{1,3} 9.0 Hz, CIC=C<u>H</u>CCl), 6.84 (1H, d, *J* 9.0 Hz, HCC<u>H</u>=CO), 4.25 (2H, s, OC<u>H</u>₂COO⁻), 3.89 (4H, t, *J* 5.8 Hz, CH₂C<u>H₂OCH₂CH₂), 3.71 (2H, t, *J* 4.4 Hz, N⁺CH₂CH₂), 3.43 (4H, t, *J* 4.7 Hz, CH₂CH₂OCH₂CH₂), 3.14 (3H, s, MeN⁺), 1.65 (2H, q, *J* 4.0 Hz, N⁺CH₂CH₂), 1.30 (2H, sex, *J* 7.3 Hz, CH₂C<u>H₂Me</u>), 0.92 (3H, t, *J* 7.2 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, DMSO- d_6) 168.7, 153.8, 128.7, 127.5, 123.0, 121.7, 115.0, 68.5, 63.6, 59.9, 58.9, 45.9, 22.7, 19.2, 13.5.</u>

4.2.20. 1-Butyl-1-methylpyrrolidinium (2,4-dichlorophenoxy)-acetate (**Pyrr-1**). Found: C, 56.55; H, 6.82; N, 3.77. C₁₇H₂₅O₃NCl₂ requires C, 56.35; H, 6.97; N, 3.87%. ν_{max} (liquid film) 3600–3100 (br), 2963, 1613, 1483, 1424, 1346, 1282, 1266, 1244, 1107, 1064, 1043, 801, 763 cm⁻¹; $\delta_{\rm H}$ (300 MHz, DMSO- d_6) 7.47 (1H, d, *J* 2.5 Hz, CICCH=CCI), 7.26 (1H, dd, *J*^{1,2} 2.5 Hz, *J*^{1,3} 8.8 Hz, CIC=CHCCI), 6.83 (1H, d, *J* 9.0 Hz, HCCH=CO), 4.21 (2H, s, OCH₂COO⁻), 3.47 (4H, m, CH₂CH₂CH₂CH₂CH₂), 3.30 (2H, t, *J* 8.4 Hz, N⁺CH₂CH₂CH₂CH₂Me), 2.98 (3H, s, CH₃N⁺), 2.07 (4H, m, CH₂CH₂CH₂CH₂), 1.66 (2H, q, *J* 4.1 Hz, N⁺CH₂CH₂CH₂Me), 1.30 (2H, sex, *J* 7.4 Hz, CH₂CH₂CH₃), 0.92 (3H, t, *J* 7.3 Hz, CH₂Me); $\delta_{\rm C}$ (75 MHz, DMSO- d_6) 168.9, 153.9, 128.8, 127.6, 123.0, 121.7, 115.1, 68.7, 63.4, 62.9, 47.4, 25.0, 21.1, 19.4, 13.6.

4.3. 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 min⁻¹ and cooled at a cooling rate of 10 °C min⁻¹ to -100 °C.

Thermogravimetrical analysis was performed on a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples between 2 and 10 mg were placed in alumina pans and were heated from 30 to 500 °C with a heating rate of 10 °C min⁻¹.

4.4. Herbicidal activity

Prepared ILs were tested in field experiments performed in 2009–2010 at Experimental Station in Winna Gora (Poland) on fallow land and in spring barley. Plot size was 16 m². The experimental design was a randomized block with four replications. All treatments were applied using a small plot spraying equipment with XR 11003 flat-fan nozzle 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 sodium salt (Pielik 85 SP—85% 2,4-D), dimethy-lammonium salt (Aminopielik Standard 600 SL—600 g 2,4-D per 1 L) and as 2-ethylhexyl ester (Esteron 460 EC—460 g 2,4-D per 1 L).

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

4.5. Surface activity

Surface tension measurements were carried out by the use of a DSA 100 analyzer (Krüss, Germany, accuracy $\pm 0.01 \text{ mN m}^{-1}$), at 25 °C. The surface tension was determined using the shape drop method. Basically, 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 (3 µL) is taken from a CCD camera and digitized. The surface tension (γ in mN m⁻¹) is calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy ± 0.1 °C). The values of the critical micelle concentration (CMC) and the surface tension at the CMC (γ_{CMC}) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves (γ -log *C* curves) using a linear regression analysis method.

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Supplementary data

This material include the physicochemical data of 2,4-D-imidazolium (**Im**), 2,4-D-pyridinium (**Pyr**), 2,4-D-piperidinium (**Pip**), 2,4-D-morpholinium (**Mor**), and 2,4-D-pyrrolidinium (**Pyrr**) salts, as well as description of HILs as solvents in Diels—Alder reaction. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.03.065.

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