



Synthetic auxin-based double salt ionic liquids as herbicides with improved physicochemical properties and biological activity



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ABSTRACT

Over the past decade, numerous advantages of double salt ionic liquids have been discovered, including beneficial physicochemical properties and a synergistic increase in biological activity resulting from competitive interaction among three or more ions based on their chemical structures. Therefore, we applied the approach mentioned above in our study by designing new ionic liquids consisting of amphiphilic choline-like cations and two or three anions derived from synthetic auxins. The influence of combining three anions with herbicidal activity in one compound on its physical, chemical and biological properties is discussed here for the first time. Double salts were obtained according to a fast, reliable and sustainable synthesis method, which made it possible to obtain pure ionic liquids, reaching 99–100% efficiency. Comparison of NMR spectra of products containing one or more anions has revealed that the introduction of additional ions has a clear impact on the chemical environment of atoms, which may explain the observed changes in double salt properties. The effects of the addition of the 2nd and 3rd anions on basic physicochemical parameters (including density, refractive index, viscosity, phase transitions, solubility and surface activity) were studied. Biological experiments have confirmed that the herbicidal activity of the obtained ionic liquids with three herbicide anions is higher than that of commercial preparations and most tested ionic liquids with only one biologically active anion, which confirms numerous advantages of the “double salt ionic liquid” approach.

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1. Introduction

Adverse phenomena associated with the presence of undesirable vegetation in the fields constitute one of the main reasons for the qualitative and quantitative deterioration of crop yields. Intense weed infestation may reduce yields by 34% on average [1]. This issue can be effectively addressed by the use of selective herbicides – plant protection products that enable the destruction of undesirable plants with no impact on crops. The key active ingredients used for this purpose are synthetic compounds belonging to the class of growth regulators termed auxins, including 4-chloro-2-methylphenoxyacetic acid (MCPA), (R)-2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop-P) and 3,6-dichloro-2-methoxybenzoic acid (dicamba) (Fig. 1). These compounds affect dicotyledonous plants in a manner similar to the action of natural plant growth hormones, although they are characterized by signif-

icantly greater biological activity. Therefore, their application results in uncontrolled growth and drying of the target organisms [2,3]. Ready biodegradability of synthetic auxins [4] and their limited toxicity at low concentrations [5,6] are the main reasons for their widespread use in agricultural production worldwide [3].

Nevertheless, it is estimated that a very small portion of applied active substance interacts directly with target organisms, and for this reason approximately 95% of plant protection products directly burden the environment [7]. Therefore, the use of synthetic auxins, as well as other herbicides, is associated with numerous problems; *i.e.*, permeation into urban rivers and groundwater [8,9], toxicity of intermediate decomposition products [10], and nonnegligible volatility [11,12]. Moreover, the increasing resistance of various weed species to herbicides remains one of the most serious problems in plant protection and requires the use of special preventive strategies. However, it should be noted that a relatively small number of weed species have developed resistance toward auxin-like herbicides compared with other classes of plant protection products (*e.g.*, sulfonylureas) [2,3].

With regard to the abovementioned concerns, actions aimed at limiting the adverse effects of synthetic auxin use constitute one of

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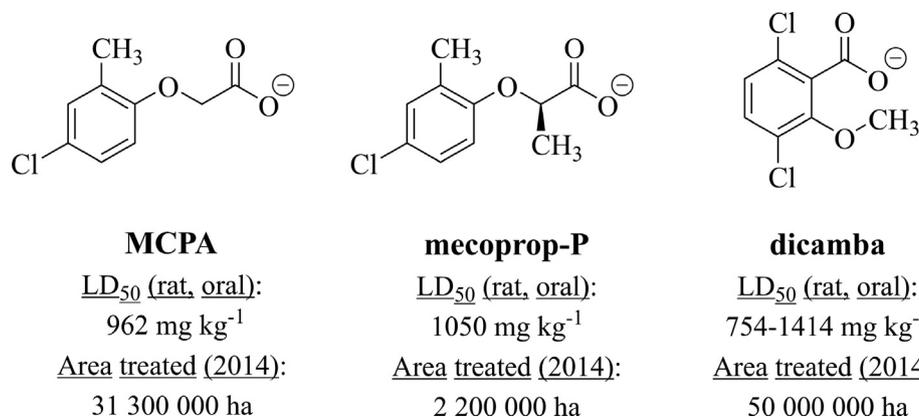


Fig. 1. Commonly used synthetic auxins.

the key challenges for present-day weed management. Therefore, more effective techniques for application of synthetic auxins have been intensively researched. It has been repeatedly reported that the approach of transforming known herbicides into ionic liquids (ILs) provides a number of beneficial solutions to the problems mentioned above [13,14]. The use of herbicidal ionic liquids (HILs) instead of conventional forms of synthetic auxins directly addresses the problems associated with herbicide volatility [12,15] and significantly reduces the adverse effects associated with solid-form application, *i.e.*, spontaneous crystallization from spray solutions [16]. A higher level of biological activity compared to commercial forms of HILs results mostly from the presence of an amphiphilic counterion, which reduces the surface tension of the spray solution and improves the bioavailability of the active ingredient [17]. This approach successfully eliminates the need to include synthetic adjuvants (usually of unspecified toxicity and with registration rules less restrictive than herbicides) in pesticidal formulations [16–19]. In addition, the selection of an appropriate counterion at the stage of HIL synthesis allows for significant reductions in toxicity [20], levels of leaching to groundwater [21] and accumulation in soil [19,22] and ensures sufficient biodegradability of active substances while maintaining favorable biological activity [23].

The advantages associated with the transformation of active ingredients into their IL forms may be considerably enhanced by merging several ILs into new systems—double-salt ionic liquids (DSILs). A DSIL can be defined as a system with a melting point not exceeding 100 °C and containing 3 or more types of ions. The increasing popularity of this kind of system is associated with the presence of unique interactions between different ions at the nanometric level. These substances show properties differing from those of their single-anion equivalents [24], resulting in high application potential; *e.g.*, as media for CO₂ capture [25] or solvents for biopolymers [26]. In 2016, the combination of ILs exhibiting herbicidal activity to obtain a double salt herbicidal ionic liquid (DSHIL) containing two different herbicidal anions with distinctive mechanisms of action was first described [27]. Further explorations in this area have resulted in the discovery of DSHILs with selective activity based exclusively on synthetic auxins—MCPA and dicamba [28]. A careful analysis of the impact of the combined action of these herbicides in DSHIL form indicated the occurrence of a synergistic effect unobserved with conventional MCPA-dicamba tank mixes. This leads to the conclusion that certain DSHILs can be used effectively at lower doses than with two-ion HILs, which may turn out to be crucial in the development of innovative pesticidal formulations. Moreover, since the acquisition of herbicide resistance by weeds can be significantly reduced by combining different active ingredients [29–32], and the use of more than one herbicide

allows broadening of the spectrum of action of the formulation [33], these challenges can also be overcome through the DSHIL strategy.

In the framework of this study, we are continuing the development of the described concept in two dimensions: by analyzing the properties of previously undescribed HILs and DSHILs containing the mecoprop-P anion and by combining 3 herbicides with the same mechanism of action (MCPA, mecoprop-P and dicamba) in a single compound. According to our research, this is the first report on ILs containing 3 different anions designed for agrochemical applications. As a source of a common counterion we adopted one of two alkyl[2-(2-hydroxyethoxy)ethyl]dimethylammonium cations with a choline-like structure and an alkyl substituent including 8 or 16 carbon atoms. The cations are based on the hydrophilic amine diglycolamine, which is added to herbicide formulations to reduce the volatility of active substances (*e.g.*, Xtendi-Max, Monsanto). In our previous work, the transformation of diglycolamine into a quaternary form with an alkyl substituent including 8 carbon atoms or more was found to result in strong amphiphilic properties that promote the biological activity of the resulting systems, and the presence of the hexadecyl chain resulted in a synergistic activity of both herbicides in the tested DSHILs [28]. Therefore, the use of two cations with octyl and hexadecyl substituents allowed us to test whether an occurrence of synergy between active ingredients in other DSHILs is also dependent on the length of the alkyl substituent in their common cation.

During our studies we found that the physicochemical properties and surface activity of DSHILs deviate from the mean values predicted from the corresponding single-anion HILs, thus confirming the unique character of interactions in multi-ion systems. We also confirmed that interactions between many herbicide anions noticeably improve their biological activity, even if the dose of the most efficient ingredient (MCPA) is halved. The ability to tune the properties of the new substances, as well as the advantages associated with synergistic effects, underscore the utility of the DSIL approach, both in agrochemistry and in other industries.

2. Experimental

2.1. Materials

2-[2-(Dimethylamino)ethoxy]ethanol (purity 98%) was purchased from Sigma-Aldrich and subjected to additional purification by vacuum rectification. The fraction boiling at 79–80 °C at a pressure of 1–2 mbar was collected and used for further syntheses. 1-Bromooctane (purity 98%), 1-bromohexadecane (purity 97%), all solvents (methanol, ethanol, dimethyl sulfoxide, acetonitrile, acetone, 2-propanol, ethyl acetate, chloroform, toluene, xylene, hex-

ane and octane) and the anionic resin Dowex Monosphere 550A were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA) and used without further purification. The herbicidal acids used in this study were supplied by PESTINOVA S.A., Poland (MCPA and dicamba) and Organika-Sarzyna S.A. Poland (mecoprop-P) and additionally purified by recrystallization from xylene (MCPA, dicamba) or mixture of xylene and octane (mecoprop-P). Water for solubility and surface activity measurements was deionized, with a conductivity less than $0.1 \mu\text{S cm}^{-1}$, from demineralizer HLP Smart 1000 (Hydrolab, Straszyn, Poland).

2.2. Methods

2.2.1. General

^1H NMR spectra were obtained using Mercury Gemini 300 and Varian VNMR-S 400 MHz spectrometers operating at 400 MHz. ^{13}C NMR spectra were obtained using the same instruments at 100 MHz. In both cases TMS was used as the internal standard. The IR spectra were collected by using semi-automated system EasyMax™ 102 (Mettler Toledo) connected with ReactIR™ 15 (Mettler Toledo) probe equipped with an MCT detector and a 9.5-mm AgX probe with a diamond tip. The data were sampled from 3000 to 650 cm^{-1} with 8-cm^{-1} resolution and processed by iCIR 4.3 software. Thermal transition temperatures of the obtained ILs were determined by differential scanning calorimetry (DSC) using a Mettler Toledo Star^e DSC1 (Leicester, UK) unit under nitrogen. Samples between 5 and 15 mg were placed in aluminum pans and heated from 25 to $105 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and cooled with an intracooler at a cooling rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $-100 \text{ }^\circ\text{C}$ and then heated again to $105 \text{ }^\circ\text{C}$. Thermal gravimetric analyses (TG) were performed by using a Mettler Toledo Stare TGA/DSC1 unit (Leicester, UK) under nitrogen as an inert gas. Samples (2–10 mg) were placed in aluminum pans and heated from 30 to $450 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Density was determined by using an Automatic Density Meter DDM2911 (Rudolph Research Analytical, Hackettstown, NJ) with the mechanical oscillator method. The density of the samples (about 1.0 cm^3) was measured at $20 \text{ }^\circ\text{C}$, and the temperature was controlled with a Peltier module. Before the series of measurements, the apparatus was subjected to a two-point calibration using deionized water and air as the references. After each series of measurements, the densimeter was washed with water and organic solvents (methanol and acetone) and dried with airflow. In addition, density measurements in the range from 20 to $80 \text{ }^\circ\text{C}$ were performed for all DSILs. The uncertainty of the density measurement was estimated to be less than $5 \cdot 10^{-4} \text{ g cm}^{-3}$. Refractive index was determined by using an Automatic Refractometer J357 (Rudolph Research Analytical, Hackettstown, NJ) with electronic temperature control at $20 \text{ }^\circ\text{C}$ for single-ion HILs and in range from 20 to $80 \text{ }^\circ\text{C}$ for DSHILs. The apparatus was calibrated using deionized water before use, and the accuracy of refractive index measurements was $\pm 2 \cdot 10^{-4}$ according to the manufacturer's specifications. Viscosity was determined by using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosity of the samples (about 1.5 cm^3) was measured at $20 \text{ }^\circ\text{C}$ for single-ion HILs and in range from 20 to $80 \text{ }^\circ\text{C}$ for DSHILs. Before each series of measurements, the apparatus was calibrated using a calibration standard with the viscosity of 15.664 Pa s at $20 \text{ }^\circ\text{C}$, manufactured and certified by Central Office of Measures in Poland. The accuracy of the viscosity measurement was estimated to be less than 1% of the determined value by the by the apparatus manufacturer.

2.2.2. Preparation of HILs

Alkyl[2-(2-hydroxyethoxy)ethyl]dimethylammonium bromides were obtained *via* quaternization of 2-[2-(dimethylamino)ethoxy]

ethanol with both 1-bromoalkanes according to the procedure previously described.²⁸ Then, a respective quaternary bromide (0.06 mol) was dissolved in ethanol (30 cm^3) and placed in a 100 cm^3 EasyMax™ reactor equipped with a stir bar and a temperature sensor. Then, 60 cm^3 of the anionic resin Dowex Monosphere 550A in the form of an ethanolic suspension were added, and the mixture was stirred for 1 h at $25 \text{ }^\circ\text{C}$. In the next step, the resin was filtered and washed three times with small volumes (10 cm^3) of ethanol. The solutions of obtained alkyl[2-(2-hydroxyethoxy)ethyl]dimethylammonium hydroxides were subsequently neutralized using stoichiometric amounts of the respective herbicidal acid (MCPA, mecoprop-P or dicamba) in the form of ethanolic solution. Next, the solvent was removed using rotary evaporator, and the obtained products were thoroughly dried under reduced pressure (5 mbar) at $60 \text{ }^\circ\text{C}$ for 10 h. All synthesized HILs were stored under reduced pressure over P_4O_{10} .

2.2.3. Preparation of DSHILs

Double salts comprising two herbicidal anions (**4a**, **4b**) were prepared by mixing single-anion ILs comprising the same cation and MCPA (**1a**, **1b**) and mecoprop-P (**2a**, **2b**) at a mass ratio of active substances equal to 1:0.75 MCPA-mecoprop-P (which corresponds to molar ratio 1.38:1). The salts were dissolved in ethanol and the obtained solutions were stirred for 2 h. In the next step, the solvent was evaporated, and the remaining DSIL was dried at the same conditions as HILs containing single anion. DSHILs with three herbicidal anions (**5a**, **5b**) were prepared analogously at a mass ratio of anions equal to 1:0.75:0.2 MCPA-mecoprop-P-dicamba (molar ratio: 5.30:3.70:1).

2.2.4. Solubility

Water and nine popular organic solvents were selected for the solubility test and arranged in order of decreasing Snyder polarity index: water, 9.0; methanol, 6.6; DMSO, 6.5; acetonitrile, 6.2; acetone, 5.1; isopropanol, 4.3; ethyl acetate, 4.3; chloroform, 4.1; toluene, 2.3 and hexane, 0.0. The solubility of the obtained ILs in organic solvents was determined according to the previously described methodology [34]. The sample of IL ($0.1 \pm 0.0001 \text{ g}$) was introduced into a specific volume of solvent. The measurements were conducted at $25 \text{ }^\circ\text{C}$ and each measurement was replicated three times. Depending on the volume of solvent used, three outcomes have been recorded: "ready solubility" applies to ILs that dissolved in 1 cm^3 of the solvent, "limited solubility" applies to compounds that dissolved in 3 cm^3 of the solvent, and "low solubility" applies to ILs that did not dissolve in 3 cm^3 of the solvent.

2.2.5. Surface properties

The surface tension and contact angle values of the analyzed ionic liquids were carried out by the use of a drop shape analyzed (DSA 100), (KRUSS GmbH, accuracy $\pm 0.001 \text{ mN m}^{-1}$) at $25 \text{ }^\circ\text{C}$. The temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy $\pm 0.1 \text{ }^\circ\text{C}$). The surface tension was carried out using the drop shape method. Generally, the principle of this method is to form an axisymmetric drop at a tip of a needle of a syringe. An image of the drop (3 cm^3) from a CCD camera was taken and digitized. The surface tension (γ in mN m^{-1}) is calculated by analyzing the profile of the drop according to the Laplace equation. The recorded sets of surface tension records were characterized by standard deviations in the range from 0.05 to 0.52% of the mean value. The values of the critical micelle concentration (CMC) and the surface tension (γ_{CMC}) at the CMC were determined based on intersection of the two straight lines drawn in low and high-concentration regions in surface tension ($\gamma - \log C$ curves) using a linear regression analysis method. The pC_{20} is defined as the molality of the compounds that leads to a reduction of the surface tension of the solvent by 20 mN m^{-1} . This parame-

ter represents the efficiency of surface adsorption on an air–water interface.

The contact angle (CA) was determined using the sessile drop method, *i.e.*, a drop of spray solution is deposited on an analyzed surface. After determination of actual drop shape and the contact line, the drop shape is adapted to fit a mathematical model used to calculate the contact angle. The most precise method to calculate this value is Young-Laplace fitting, where complete drop contour is evaluated. After successful fitting of the Young-Laplace equation, the CA was determined as the slope of the contour line at the 3-phase contact point (solid–liquid, liquid–air and air–solid). The accuracy of the CA determination in this method is estimated to be less than 0.1° by the manufacturer. The solid phase was paraffin. This surface is common wrap material used as a standard model for waxy leaf surface. In addition, we determined the CA values on the adaxial surface of cornflower (*Centaurea cyanus* L.) and winter rapeseed (*Brassica napus* L.) leaves.

2.2.6. Herbicidal activity

Cornflower (*Centaurea cyanus* L.) and winter rapeseed (*Brassica napus* L.) were used in greenhouse experiments as test plants during the evaluation of herbicidal efficacy of the obtained salts. All plants were grown in 0.5 dm³ plastic pots containing commercial peat-based potting material. Stable conditions (temperature of 20 ± 2 °C, humidity of 60% and a photoperiod of 16/8 day/night hours) were maintained in the greenhouse during the entire growth period. Within 10 days after emergence, the plants were thinned to five per pot and watered when necessary. The tests were performed in 12 independent experiments in a completely randomized setup. Each test was carried out in 4 replications.

The plants were treated by herbicides at the 4–5 leaves growth stage. Commercially available herbicide: Chwastox Extra 300 SL (300 g dm⁻³ of sodium and potassium salts of MCPA, CIECH Sarzyna, Poland, which correspond to molar concentration of 10.02 mmol dm⁻³) was used as a reference product for MCPA and mecoprop-P-based single-anion HILs. For HILs involving dicamba, Dicash (480 g dm⁻³ dicamba as dimethylamine salt, Sharda Europe, Dilbeek, Belgium, equivalent to 4.54 mmol dm⁻³) was used instead. The product that has been used as a reference for DSHILs, Chwastox Trio 390 SL, CIECH Sarzyna, Poland, involved potassium salts of the following active ingredients: 200 g dm⁻³ of MCPA + 150 g dm⁻³ of mecoprop-P + 40 g dm⁻³ of dicamba. The obtained single-anion HILs were applied in doses corresponding to 400 g of the active ingredient (a.i.) per 1 ha for compounds with MCPA and mecoprop-P anions and 200 g of the active ingredient (a.i.) per 1 ha for compounds with dicamba anion. The DSHILs were evaluated in doses corresponding to 200 g of the active ingredient (a.i.) of MCPA, 150 g of the active ingredient (a.i.) of mecoprop-P and 40 g of the active ingredient of dicamba per 1 ha.

All HILs and DSHILs, as well as the respective reference herbicides, were dissolved in water and applied with a moving sprayer (APORO, Poznan, Poland) by using a TeeJet VP 110/02 (TeeJet Technologies, Wheaton, IL, USA) with a flat-fan nozzle capable of delivering 200 dm³ of spray solution per 1 ha at an operating pressure of 0.2 MPa. The sprayer was moved at a constant speed of 3.1 m s⁻¹ at the height of 40 cm above the plants. The treated plants were subsequently placed in a greenhouse under the environmental conditions defined previously. Two weeks after treatment, the plants were cut at the soil level and weighed at 0.01 g accuracy. The results of the experiment were expressed in form of percent of the fresh weight reduction in comparison to the weight of control objects (plants untreated with any herbicidal formulations). Each error margin range represents standard errors of the mean (SEM). The SEM values were calculated according to following equation:

$$SEM = \frac{s}{n^{0.5}}$$

Where:

SEM - standard error of the mean

s - sample standard deviation

n - number of samples.

3. Results and discussion

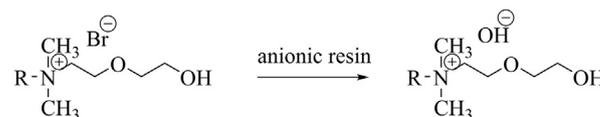
3.1. Synthesis

Alkyl[2-(2-hydroxyethoxy)ethyl]dimethylammonium bromides obtained according to a previously described methodology [28] were used as a cation source for the synthesis of all HILs. To obtain single-anion HILs, the quaternization products were subsequently subjected to an ion-exchange reaction, which was performed in 2 stages (Scheme 1). In the first stage, the quaternary bromides were dissolved in ethanol and alkalinized with ion exchange anionic resin. To avoid decomposition of the obtained quaternary ammonium hydroxides, they were neutralized with appropriate herbicide acids immediately after the resin was separated from the postreaction mixture.

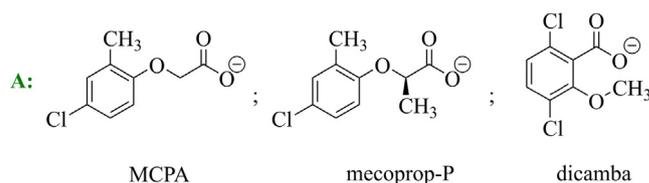
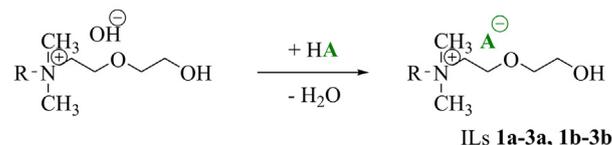
With the use of pure reagents, the proposed method has a number of advantages over the typical methodology used in IL synthesis. First, no inorganic halide is formed in the process; therefore, no purification of the resulting products by leaching or extraction is required. Moreover, instead of toxic organic solvents (chloroform, methanol) commonly used in metathesis reactions, we used ethanol. Both the resin and ethanol can be regenerated and reused. This method has been successfully applied for the synthesis of eco-friendly ILs with tetraalkylammonium cations in previous studies [35,36].

All 6 obtained HILs were in liquid state at 20 °C; therefore, the products obtained can be classified as room-temperature ionic liquids (RTILs). It should be noted that ILs with alkyl[2-(2-hydroxyethoxy)ethyl]dimethylammonium cations and (*R*)-2-(4-chloro-2-methylphenoxy)propanoate anions (**2a**, **2b**) have not been described previously and are reported here for the first time. The synthesis yield does not depend on the structure of the anion or on the

Step 1: Alkalinization



Step 2: Neutralization with herbicidal acid



Scheme 1. Synthesis of HILs (**1a-3a**, **1b-3b**).

length of the alkyl substituent in the cation and is very high in each case (99–100%). This further confirms that obtaining ILs in the anion-exchange reaction with an alkaline ion exchange resin is a highly efficient method that is also beneficial from an environmental point of view. Due to the avoidance of inorganic halide formation in the reaction system, the halide level determined by the AgNO₃ test was below 500 ppm (above this value, AgBr precipitation was observed) for each obtained IL. Moreover, no visible signs of chemical decomposition (color change or state change) were observed for any of the obtained HILs after 18 months from synthesis.

The ILs described in Table 1 were finally used as substrates for the synthesis of DSHILs that included either 2 (MCPA and mecoprop-P) or 3 anions derived from synthetic auxins. The equation is presented in Scheme 2. The products were obtained via homogenization of single-anion HILs (**1a–3a**, **1b–3b**) in an appropriate molar ratio. The proposed process is facile and time-efficient and can be conducted at room temperature. It should also be stressed that this stage of DSHIL synthesis is lossless, and after evaporation of the solvent, all products were obtained at 100% yield (Table 2).

The ratio of anions in the cases of ILs **5a** and **5b** was adopted according to the ratio of synthetic auxins in a commercially available preparation (Chwastox[®] Nowy Trio 390 SL, CIECH Sarzyna, Poland). The small molar share of dicamba in commercial mixtures is related to the higher price of this herbicide, as well as a much stronger effect compared to MCPA or mecoprop-P [37]. In previous studies, we noticed that the introduction of a dicamba anion into the structure of a DSHIL results in a significant change in the physicochemical and biological properties of the final product [28]. To assess this effect in ILs **5a** and **5b**, 2 dicamba-free DSHILs (**4a** and **4b**) were also synthesized, both involving MCPA and mecoprop-P in molar ratios similar to the ratios for **5a** and **5b**.

It should be stressed that all 4 obtained DSHILs are new ionic systems that have not been described previously. The presence of all designed DSHILs in liquid form at room temperature is particularly beneficial from the perspective of application, since these compounds can provide a solution to a number of technological problems (spontaneous crystallization, volatility, limited solubility, polymorphic changes of the solid active ingredient), which in many cases hinder the use of conventional forms of plant protection products [7,12,16].

The analysis of the obtained FT-IR and NMR spectra (Figures A.1–A.32, Supplementary Data) confirms that the designed single-anion HILs and DSHILs were successfully obtained. In addition, the integration of signals present in the ¹H NMR spectra of DSHILs **4a**, **5a**, **4b**, and **5b** confirms that the molar ratios of the individual herbicidal anions are correct [27,38]. On the basis of the analysis of the spectra, it can also be concluded that the introduction of a second herbicidal anion caused noticeable deshielding of the protons in the vicinity of carboxylate moieties. This effect resulted in signals originating from methylene (MCPA anion) and

methine (mecoprop-P anion) groups in compounds **4a** and **4b** occurring at chemical shifts higher than 0.08 ppm in the ¹H NMR spectra compared to the respective signals in the spectra of the parent ILs (Fig. 2).

Following the addition of the dicamba-based HILs, these differences increased by another 0.03–0.04 ppm for three-anion DSHILs (**5a**, **5b**). It should also be noted that no significant differences in chemical shifts were observed for the signals originating from the dicamba anion in **5a** and **5b** (due to the lack of hydrogen atoms in the vicinity of the dicamba carboxylate group) or from the alkyl [2-(2-hydroxyethoxy)ethyl]dimethylammonium cation in any DSHIL. Thus, the above-described phenomena indicate that the formation of competing ionic bonds in DSHILs has a specific effect on the chemical environment of a portion of the structure in the vicinity of a negatively charged moiety. This discovery is consistent with previously reported data regarding the spectral analysis of similar multi-ion compounds [38–40]. Moreover, additional NMR experiments were performed 18 months after the synthesis for compounds **2a**, **2b**, **5a**, and **5b** to verify the chemical stability of the products. No differences were observed compared to the spectra acquired immediately after the synthesis, which confirms that the chemical structures of both single-anion HILs and DSHILs do not undergo any noticeable decomposition under aerobic conditions. Comparisons of the spectra are included in the Supplementary Data (Figures A.33 and A.34).

3.2. Physicochemical properties

Since the ILs described here for the first time (**2a**, **4a**, **5a**, **2b**, **4b**, and **5b**) were liquid at 20 °C, we were able to examine their basic physicochemical properties; *i.e.*, density, refractive index and dynamic viscosity. In addition, we also discuss the influence of the mecoprop-P anion on the physicochemical properties of the ILs and compare the results with previously reported records for the single-anion HILs **1a**, **3a**, **1b** and **3b** [28].

3.2.1. Thermal analysis

The results of the thermal analysis (phase transitions and thermal stability) of the synthesized single-anion HILs and their double salts are presented in Table 3. As in the case of many previously analyzed ILs containing a herbicidal anion [17,20,23,41], for the majority of the obtained compounds, only glass transition temperatures were recorded. The temperatures at which transition occurred were in the relatively narrow range from –30 (**2a**) to –38 °C (**3a**). For HILs based on mecoprop-P, elongation of the alkyl substituent by 8 methylene groups did not have a very significant effect on glass transition temperature. The difference in this value between **2a** and **2b** amounted to 7 °C. For both DSHIL systems, a similar effect was observed: compounds with an octyl substituent (**4a**, **5a**) underwent glass transition at –32 °C, while for their counterparts bearing a hexadecyl substituent (**4b**, **5b**), transition occurred at temperatures lower than 3 °C. Therefore, it can be con-

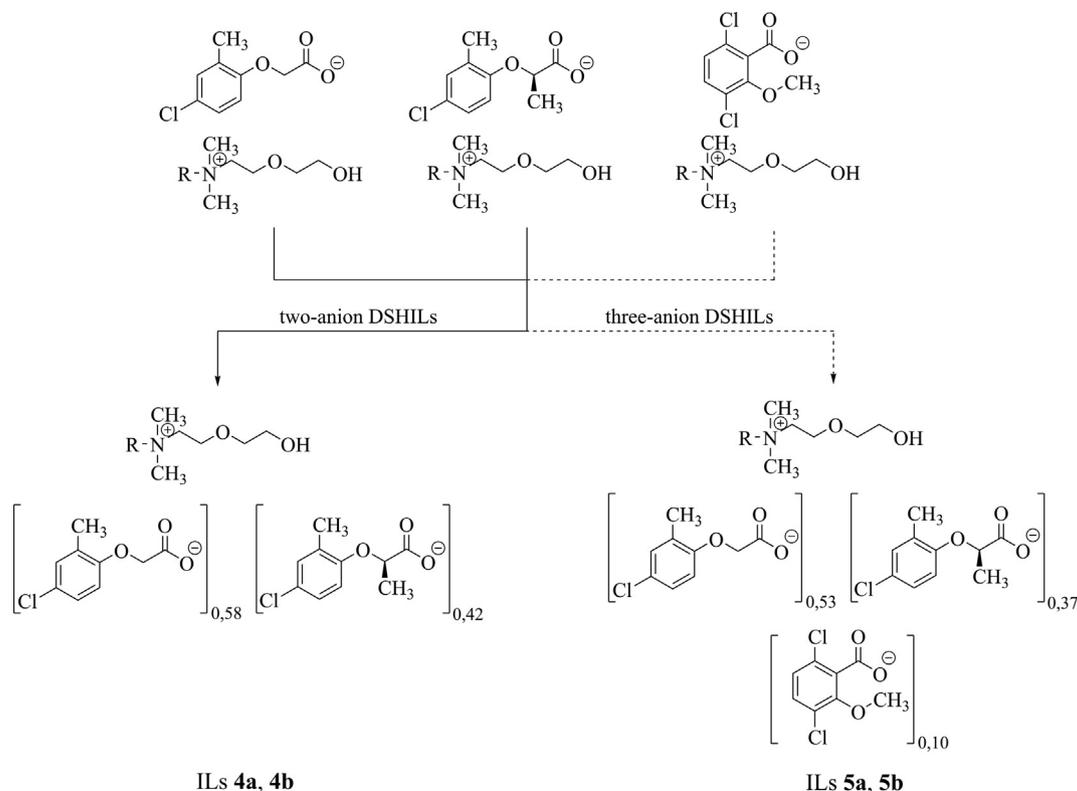
Table 1
Obtained single-anion HILs (**1a–3a**, **1b–3b**).

IL	R	Anion	Yield[%]	State at 25 °C
1a	C ₈ H ₁₇	MCPA ^[a]	100	liquid
2a	C ₈ H ₁₇	mecoprop-P ^[b]	99	liquid
3a	C ₈ H ₁₇	dicamba ^[c]	99	grease
1b	C ₁₆ H ₃₃	MCPA	100	liquid
2b	C ₁₆ H ₃₃	mecoprop-P	100	liquid
3b	C ₁₆ H ₃₃	dicamba	99	grease

^a 4-chloro-2-methylphenoxyacetate.

^b (*R*)-2-(4-chloro-2-methylphenoxy)propionate.

^c 3,6-dichloro-2-methoxybenzoate.

Scheme 2. Synthesis of DSHILs (**4a**, **5a**, **4b**, **5b**).Table 2
Synthesized DSHILs.

IL	R	Anions	Yield [%]	State at 25 °C
4a	C ₈ H ₁₇	[MCPA] _{0,58} [mecoprop-P] _{0,42}	100	liquid
5a	C ₈ H ₁₇	[MCPA] _{0,53} [mecoprop-P] _{0,37} [dicamba] _{0,1}	100	liquid
4b	C ₁₆ H ₃₃	[MCPA] _{0,58} [mecoprop-P] _{0,42}	100	liquid
5b	C ₁₆ H ₃₃	[MCPA] _{0,53} [mecoprop-P] _{0,37} [dicamba] _{0,1}	100	liquid

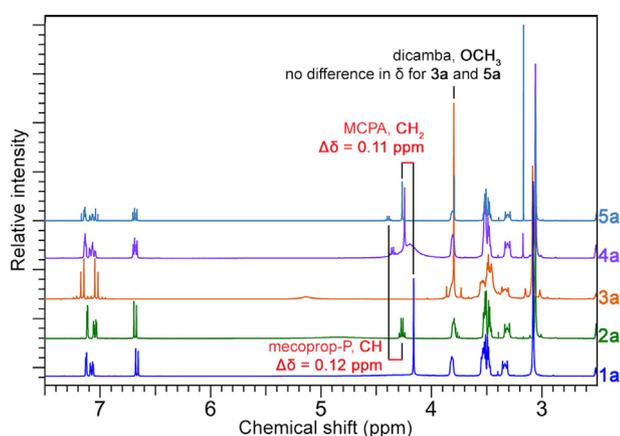


Fig. 2. Comparison of the spectra of HILs and DSHILs with [2-(2-hydroxyethoxy)ethyl]dimethyloctylammonium cation in the range of chemical shifts from 2.5 to 7.5 ppm.

cluded that neither the elongation of an alkyl chain nor the introduction of the second and third anions into the structures of HILs had any significant influence on T_g values.

Unlike **2b**, two other single-anion HILs with a hexadecyl substituent in the cation structure (**1b** and **3b**) did not undergo glass

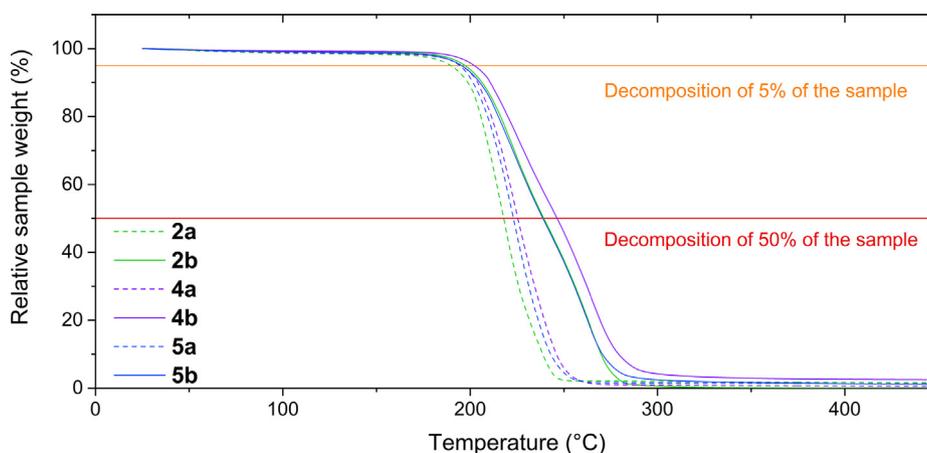
transition during the analysis. Instead, melting events were able to be observed at -34 and -29 °C, respectively, and analogous crystallization points were noted at -9 and 2 °C for these HILs during the same heating/cooling cycle. It should be emphasized that similar differences in the occurrence of phase transitions of HILs with MCPA and dicamba anions compared to their mecoprop-P-based counterparts have also been observed in previous studies [18,20].

Thermograms of all HILs listed here for the first time (**2a**, **4a**, **5a**, **2b**, **4b**, and **5b**) are presented in Fig. 3. According to the results of thermogravimetric analysis listed in Table 3, single-anion HILs based on mecoprop-P (**2a**, **2b**) exhibited better thermal stability than did their counterparts with dicamba ($T_{\text{onset}5\%}$ values higher by 12 °C) but were marginally less stable than compounds involving an anion derived from MCPA (**1a**, **1b** – $T_{\text{onset}5\%}$ values lower by 2 and 8 °C, respectively). These relationships were consistent with previously reported data [18]. Considering the findings described above, DSHILs involving two anions derived from phenoxy acids (**4a**, **4b**) were characterized by similar values of $T_{\text{onset}5\%}$ compared to their parent compounds, and the addition of a less stable dicamba anion (compounds **5a** and **5b**) did not result in any significant change in the parameter. In addition, no increase or decrease in thermal stability resulting from the presence of two or three anions in the same IL was observed.

Table 3

Thermal analysis of the obtained HILs and DSHILs.

DSIL	T_g^a [°C]	T_m^b [°C]	T_c^c [°C]	$T_{onset5\%}^d$ [°C]	T_{onset}^e [°C]
1a^f	-34	—	—	193	222
2a	-30	—	—	191	218
3a^f	-38	—	—	179	205
4a	-32	—	—	196	222
5a	-32	—	—	194	220
1b^f	—	-34	-9	205	255
2b	-37	—	—	197	237
3b^f	—	-23	2	185	214
4b	-35	—	—	203	246
5b	-35	—	—	198	238

^a glass transition temperature.^b melting point.^c crystallization temperature.^d decomposition temperature of 5% of the sample.^e decomposition temperature of 50% of the sample.^f according to Ref. [28].**Fig. 3.** TGA thermograms of the obtained single-anion HILs (**2a**, **2b**) and DSHILs (**4a**, **4b**, **5a**, **5b**).

The differences between the determined T_{onset} temperatures were correspondingly greater, and unlike $T_{onset5\%}$, they were mostly dependent on the length of an alkyl substituent in the cation. We observed that the compounds involving a cation with an octyl chain (**1a–5a**) were characterized by T_{onset} values in the range from 205 (**3a**) to 222 °C (**1a**, **4a**), while for the hexadecyl derivatives, the temperatures were significantly higher—from 214 (**3b**) to 255 (**1b**) °C. This observed increase in thermal stability is commonly observed for ILs involving long chains in their structures [16,23,42,43], and it results from the fact that longer alkyl substituents decompose to compounds of lower volatility [18].

3.2.2. Density

The results of the density measurements are shown in Fig. 4. The exact data, as well as calculated molar volumes at 20 °C, are listed in Table A.1 in the Supplementary Data. As in our previous studies [28], we were unable to determine the densities of single-anion ILs involving dicamba anion (**3a**, **3b**) due to their greasy state. The densities of the remaining compounds ranged from 1.0475 (**2b**) to 1.1200 (**5a**). According to these results, both single-anion HILs and DSHILs are characterized by densities higher than those of water (1.00 g cm⁻³) and many conventional organic solvents; e.g., acetone (0.78 g cm⁻³), ethanol (0.79 g cm⁻³) and toluene (0.87 g cm⁻³). However, the values determined for the synthesized compounds are comparable to the densities of other ILs containing synthetic auxins and various cations involving alkyl substituents, including tetraalkylammonium [44], 1-alkyl-1-

methylpiperidinium [16] and 1-alkyl-1-cyclohexyldimethylammonium [41]. It should be emphasized that the parameter on which the densities of the tested HILs were most dependent was the length of the alkyl substituent in the cation structure, which is consistent with other findings [16,45]. We observed that each IL with an octyl substituent (**1a**, **2a**, **4a**, and **5a**) exhibited a density higher by approximately 0.05–0.08 g cm⁻³ than values for analogs with a hexadecyl substituent (**1b**, **2b**, **4b**, and **5b**). Moreover, IL **2b** is characterized by density lower by 0.0175 g cm⁻³ compared to a previously described compound that consists of mecoprop anion and hexadecyltrimethylammonium cation (density of 1.0650 g cm⁻³ at 20 °C) [18]. These data may imply that the introduction of the 2-(2-hydroxyethoxy)ethyl substituent into the cation results in a decrease in density of mecoprop-based ILs. However, this change may be not as significant as the difference in an alkyl chain length. In contrast to the differences in cation structure, the type of synthetic auxin anion had relatively little effect on density of HILs. In the case of **2a**, the presence of an additional methyl group in the mecoprop-P anion caused a slight increase in this parameter (by 0.0024 g cm⁻³) compared to **1a**, while in the case of their hexadecyl counterparts, the density of **2b** was lower (by 0.0064 g cm⁻³) than that of **1b**. Both **1b** and **2b** contain long alkyl substituents in their cation and are characterized by strong van der Waals interactions. Therefore, an additional methyl group on the herbicidal anion may cause an increase in the average distance between ions, which directly translates into an increase in molar volume (Table A.1, Supplementary Data) as well as a decrease in

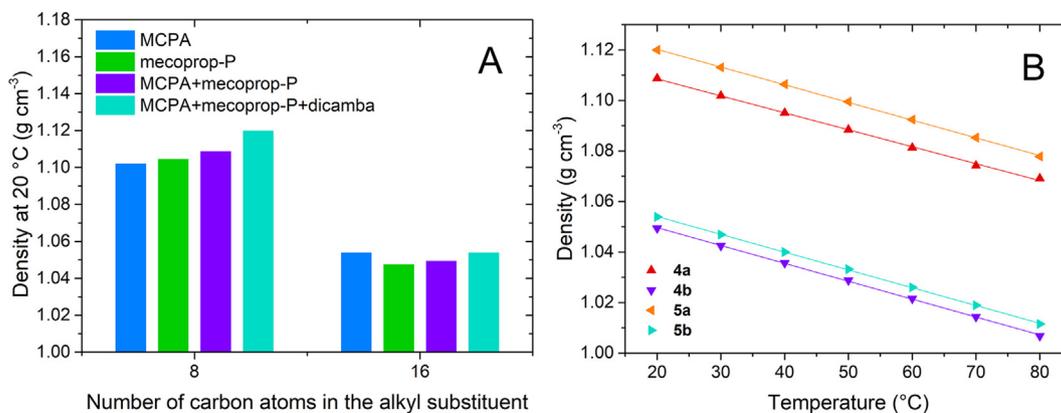


Fig. 4. Densities of the analyzed ILs at 20 °C (A) and the effect of temperature on the densities of DSHILs (**4a**, **5a**, **4b**, **5b**) (B).

density. For HILs with an octyl substituent (**1a** and **2a**), this effect does not occur.

The formation of a DSHIL containing MCPA and mecoprop-P anions (**4a**) resulted in an unexpected increase in density compared to both corresponding single-anion counterparts, **1a** (by 0.0066 g cm⁻³) and **2a** (by 0.0042 g cm⁻³). This phenomenon may indicate the existence of a new type of interaction between different anions in the DSHIL, resulting in a decrease in the average distance between the ions and a consequent increase in density. In the case of IL **5a**, the introduction of the third herbicidal anion causes an even greater increase in density. Despite the small molar fraction of the dicamba anion (0.1), the increase compared to **4a** is relatively significant (0.0113 g cm⁻³).

An analogous, although less clear, relationship can be observed for both DSHILs with a hexadecyl substituent in their structures (**4b**, **5b**). IL **5b** is characterized by a density of 1.0539 g cm⁻³, which is higher than the values determined for **4b** and **2b** by 0.0045 g cm⁻³ and 0.0064 g cm⁻³, respectively. However, it should be emphasized that the density value of **4b** (1.0494 g cm⁻³) is close to the theoretical mean of the values recorded for both single-anion parent ILs **1b** and **2b** (1.0512 g cm⁻³), taking into account their molar ratio in **4b**, which is consistent with other studies on density of DSILs [46,47]. Thus, the presence of a long alkyl substituent in **4b** most likely mitigates the phenomenon of reducing the mean distance between ions in DSHIL systems, which was observed for the DSHILs **4a** and **5a** that have octyl chains in their cations.

The influence of temperature on the densities of DSHILs **4a**, **4b**, **5a**, and **5b** was also investigated (Fig. 4B). The exact results are listed in Table A.2 (Supplementary Data). Our findings are consistent with those of the majority of previous studies concerning ILs, where the temperature-density relationship was linear and the slope coefficient was usually 0.0007 [16,45]. For all 4 DSHILs, this dependency can be approximated by linear functions with R² values exceeding 0.999 and slope coefficients equal to 0.0007. Thus, we can conclude that parameters such as the alkyl substituent length, the anion structure and even the number of anions with different chemical structures have marginal influence on the characteristics of the temperature-density relationships of ILs.

3.2.3. Refractive index

The refractive index (RI) is a characteristic feature of chemical compounds; therefore, its measurement allows us to determine the identity of the substance, its purity or, in the case of chiral substances, enantiomeric excess [48,49]. For the HILs and DSHILs tested, the RI values at 20 °C ranged from 1.4993 (**4b**) to 1.5201 (**3a**) (Fig. 5A). The exact values are listed in Table A.1 (Supplementary Data). As expected, ILs with a hexadecyl substituent (**1b-5b**)

were characterized by values of RI lower than their analogs bearing shorter chains (**1a-5a**). This well-known phenomenon is related to the increase in the average distance between molecules with increasing chain length [16,28,45].

It should be emphasized that the RI value of a given substance depends on its molar volume; hence, it is correlated with density [16,49]. Therefore, HILs with dicamba anions, which are usually denser than HILs with anions derived from phenoxy acids, are characterized by higher RI values than their counterparts with MCPA anions [17,23]. A similar effect was observed for compounds **1a** and **3a**. In contrast, we observed no difference of this kind between MCPA and dicamba-based ILs bearing a hexadecyl substituent (**1b** and **3b**). This particular discrepancy can be explained by the effect of cation size; a larger counterion may eliminate the impact of structural differences between MCPA and dicamba anions [28]. However, this effect of a hexadecyl chain cannot be observed for the synthesized single-anion HILs with mecoprop-P anions (**2a** and **2b**) that, regardless of the alkyl chain length, have lower refractive index values than their counterparts involving MCPA (**1a**, **1b**) or dicamba (**3a**, **3b**).

The RI value measured for DSHIL **4a** (1.509) was significantly lower than the result obtained for the MCPA-based HIL (**1a**) and comparable to the RI of its second single-anion component (**2a**). The results obtained are consistent with recent reports describing the nonadditivity of RI in DSILs [45,50]. The addition of dicamba to DSIL **5a** resulted in a slight increase in RI to 1.511. However, it should be noted that even greater deviation from the RI values expected based on the molar ratio of single-anion counterparts was observed for both DSHILs with hexadecyl chains (**4b**, **5b**). Both **4b** and **5b** were characterized by similar RI values (1.499 and 1.500, respectively) that were even 0.005 lower than all the values recorded for their single-anion counterparts (**1b**, **2b**, **3b**). Our results confirm that the refractive index of a multi-ion liquid system does not depend solely on the ratio of single-anion IL components and may deviate significantly from the linear mixing average of values recorded for the IL parents.

As with density, an increase in the temperature during measurement results in a decrease in the RI (Fig. 5B and Table A.2 in Supplementary Data). This relationship can be approximated as a linear function, since the RI decreases by approximately 0.003 as the temperature increases by 10 °C. Similar results have been recorded for other ILs [16,45,49]. Neither the change in alkyl chain length nor the formation of DSILs with 2 or 3 anions affects these characteristics.

3.2.4. Viscosity

The influence of alkyl chain length and anion type on the viscosity of the obtained ILs is shown in Fig. 6. The exact results are pre-

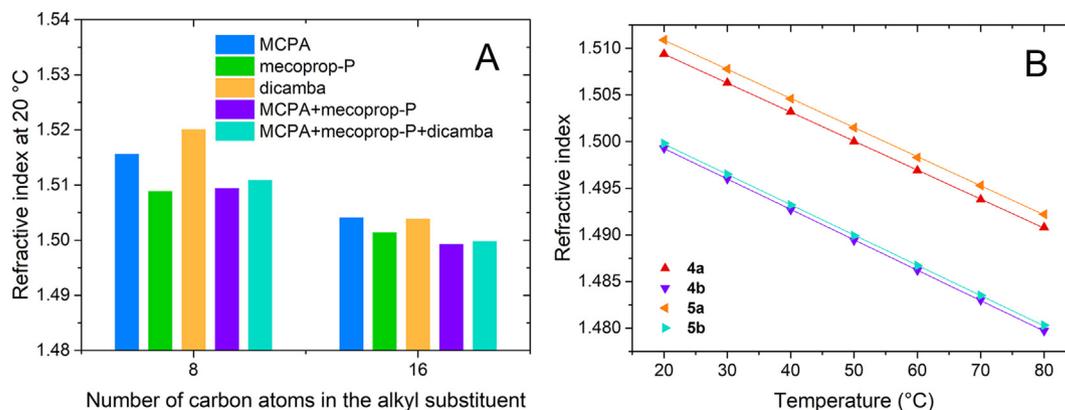


Fig. 5. Refractive indices of the synthesized ILs at 20 °C (A) and the dependence of refractive index on temperature for DSHILs (**4a**, **5a**, **4b**, **5b**) (B).

sented in Tables A.1 and A.3 (Supplementary Data). As with the density analysis, the viscosities of both single-anion HILs with dicamba (**3a**, **3b**) were impossible to determine with the adopted method. The remaining single-anion ILs involving phenoxy acid-derived anions were characterized by highly differentiated viscosity values in the range from 2.768 Pa s (**1a**) to 32.289 Pa s (**2a**). The presence of the methyl group in the mecoprop-P anion had the greatest influence on the values of this parameter; ILs **2a** and **2b** were characterized by viscosities many times higher than those of their MCPA-based counterparts (approximately 3.5 times greater for the hexadecyl derivative and almost 12 times greater for the octyl derivative). The acquired results are consistent with previous reports regarding HILs with mecoprop-P anions and natural cations that were also characterized by viscosity values exceeding 10 Pa [20,51]. Interestingly, despite a significant difference in the length of the alkyl substituent in the cation, the viscosity of compound **2b** differed by only 3 Pa s compared to **2a**. However, it should be stressed that this phenomenon most likely does not signify that the length of the alkyl substituent has no effect on the viscosities of ILs with mecoprop-P anion. In a previous study on a homologous series of mecoprop-P-based ILs, where the octyl and hexadecyl derivatives were also characterized by similar viscosities, significant differences were observed for the other elements of the series [52]. Meanwhile, a significant discrepancy between the viscosity values was observed for single-ion ILs with MCPA anions (**1a**, **1b**) where the elongation of the substituent by 8 methylene groups resulted in an increase in viscosity by approximately 200% of the value determined for **1a** (from 2.7682 to 8.4043 Pa s).

Depending on the length of the alkyl chain in the cation, the viscosities of the obtained DSIL systems exhibited different values with respect to the results obtained for the respective two-ion salts. In the case of DSHIL **4a**, the experimental value (12.651) deviates by approximately 16.5% from the predicted linear average viscosity, based on the values recorded for **1a** and **2a** (15.167 Pa s). Numerous studies on DSIL systems incorporating various cations and anions indicate that competing Coulombic interactions between multiple ions might cause the experimental data on the viscosity of such systems to be unequal to predictions resulting from mixing laws [24,53–55]. In the case of **5a**, the addition of a third herbicidal anion caused a slight (approximately 1.1 Pa s) increase in viscosity with respect to **4a**. However, due to the greasy state of the dicamba-based parent HIL (**3a**), it was not possible to estimate the deviation of **5a** viscosity from the ideal mixing average value.

A completely different behavior was observed for the synthesized DSHILs containing a common cation with a hexadecyl substituent (**4b**, **5b**). Surprisingly, at 20 °C, system **4b** possessed a viscosity of 4.543 Pa s, which was significantly lower than that of both its parent ILs **1b** and **2b**, characterized by viscosities of 8.404 Pa s and 29.216 Pa s, respectively. This result indicates that the actual viscosity of **4b** deviates markedly (by approximately 75%) from the predicted linear average, which was equal to 17.145 Pa s. A similar phenomenon has been observed in our previous studies on other DSHILs with cations derived from diglycolamine [28] as well as in the description of imidazolium ILs designed for electrochemical applications [56]. The exact causes of this effect have not yet been discovered; however, it is known

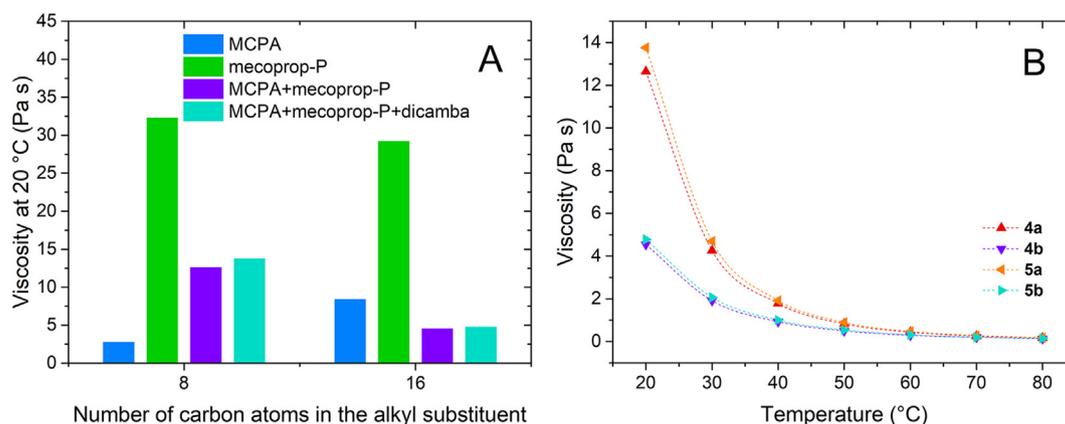


Fig. 6. Viscosities of the synthesized ILs at 20 °C (A) and the influence of temperature on the viscosities of DSHILs (**4a**, **5a**, **4b**, **5b**) (B).

that the viscosity of DSIL systems is significantly influenced by the abovementioned Coulombic interactions at the nanometric level [24]. The observed results are consistent with the hypothesis stated previously that the introduction of structurally different counterions causes disturbances in the parallel arrangement of ionic pairs, and the influence of van der Waals interactions responsible for the increase in viscosity of compounds containing long alkyl chains is limited [28]. Moreover, the introduction of a third anion with a different chemical structure to DSHIL **5b** did not result in a further decrease in viscosity compared to a system containing only MCPA and mecoprop-P (**4b**). This result indicates that the mere presence of more than two ions in a DSIL system is responsible for the structural disturbances that cause the unexpected phenomenon, while the exact increment in the number of ions in the system is irrelevant to the scale of this effect. It should also be stressed that the phenomenon of the viscosity of a DSIL being lower than values for all its components is highly beneficial from the perspective of application, since low-viscosity liquids can be handled and transferred on the production stage more easily. This greatly facilitates their synthesis compared to highly viscous systems. However, to utilize this advantage, it is necessary to obtain more data on viscosities of a wider spectrum of DSILs involving one or more long alkyl substituents and to define the “structure–property” relationship more precisely.

Similar to observations with known single-anion ILs [16,20,57] and DSILs involving a common 1-ethyl-3-methylimidazolium cation [58], an increase in the measurement temperature resulted in a rapid decrease in viscosity in the DSHIL systems tested. At 80 °C, the differences in viscosity among systems disappeared, and the parameter ranged from 0.1338 Pa s (**4b**) to 0.1811 Pa s (**5a**). Thus, technical problems related to the relatively high viscosity of the obtained systems can be mitigated by increasing temperature.

3.3. Solubility

The synthesized HILs **2a** and **2b**, as well as DSHILs, were tested for solubility in water and in protic and aprotic organic solvents of varying polarity. The findings from all three replicates of each sample were fully consistent. The results of the analysis are presented in Table 4, where they are compared with the affinities of ILs (**1a**, **3a**, **1b** and **3b**) previously obtained by us [28]. The presence of a highly hydrophilic 2-(2-hydroxyethoxy)ethyl substituent renders all the analyzed compounds very soluble in water. All tested compounds also exhibited ready solubility in the other two protic solvents – methanol and 2-propanol. It should be noted that most of the analyzed HILs and DSHILs were also characterized by high affinity toward aprotic organic solvents of both strong and weak

polarity, with the exception of dicamba-based single-anion ILs (**3a**, **3b**). A highly hydrophilic structure of dicamba anion limits affinity to aprotic solvents of polarity lower than DMSO. It is also worth noting that compound **2b**, which involved both a cation with a long alkyl chain and the mecoprop-P anion, showed limited solubility in the only nonpolar solvent tested – hexane. Generally, due to the presence of a highly polar ionic bond, ILs are characterized by very low affinity to nonpolar solvents, and the known exceptions involve multiple long alkyl chains and hydrophobic anions [59–61]. It is also known that certain HILs based on mecoprop-P and dichlorprop-P exhibit ready or limited solubility in hexane, while their analogs with MCPA and 2,4-D anions, which do not possess an additional methyl group, are not soluble in this solvent [17,44]. Therefore, this unusual result acquired for **2b** agrees with findings of previous studies.

The formation of DSHILs **4a**, **4b**, **5a** and **5b** results in an increased affinity for all organic solvents. Moreover, systems **4b** and **5b** involving a cation with a hexadecyl substituent show similar affinity to hexane as does HIL **2b**, despite the significant share of nonsoluble IL **1b** in the composition of both DSHILs. Similar effects of unique interactions in DSIL systems resulting in elevated or reduced affinity to a particular solvent have been described in previous studies [62,63]. In addition, despite the low solubility of dicamba-based HILs **3a** and **3b** in the majority of organic diluents, it was observed that the addition of dicamba-based IL anions in compounds **5a** and **5b** did not hinder solubility in any solvent. In a previous study on compounds **1a**, **1b**, **3a**, **3b** and their DSHILs, the opposite phenomenon was observed [28]. Thus, it can be concluded that the solubility of a DSIL system can be significantly influenced by a change in the proportion of specific constituent ions, although any predictions of the effects of a particular combination on solubility in a given solvent should be confirmed experimentally.

3.4. Surface activity

Through the possibility of ion selection during the synthesis of compounds, the surface properties of ionic liquids can be changed. Such behavior allows for a conscious use of ILs in industry, which is of key significance from an ecological point of view. Both the surface activity parameters (Table A.4, Supplementary Data) and the physicochemical properties described in the previous chapters are important factors that improve the characteristics of the ILs under investigation. The analyzed HILs are able to reduce the surface tension at the CMC (γ_{CMC}) to values in the range from 32.65 to 38.81 mN m⁻¹. Values in this range are typical for cationic surfactants [64]. Moreover, the synthesized DSHILs are characterized by γ_{CMC} parameter values in the same range as those for single-anion

Table 4
Solubility of synthesized ILs.

IL	A ^a	B	C	D	E	F	G	H	I	J
	9.0 ^b	6.6	6.5	6.2	5.1	4.3	4.3	4.1	2.3	0.0
1a^c	+	+	+	+	+	+	±	+	–	–
2a	+	+	+	+	+	±	+	+	+	–
3a^c	+	+	+	–	–	+	–	–	–	–
4a	+	+	+	+	+	+	+	+	+	–
5a	+	+	+	+	+	+	+	+	+	–
1b^c	+	+	+	+	+	+	+	+	+	–
2b	+	+	+	+	+	±	+	+	+	±
3b^c	+	+	+	–	–	+	–	–	–	–
4b	+	+	+	+	+	+	+	+	+	±
5b	+	+	+	+	+	+	+	+	+	±

^a A – water, B – methanol, C – DMSO, D – acetonitrile, E – acetone, F – 2-propanol, G – ethyl acetate, H – chloroform, I – toluene, J – hexane.

^b Snyder polarity index, “+” (green), ready solubility, “±” (yellow), limited solubility, “–” (red), low solubility.

^c solubility described in Ref. [28].

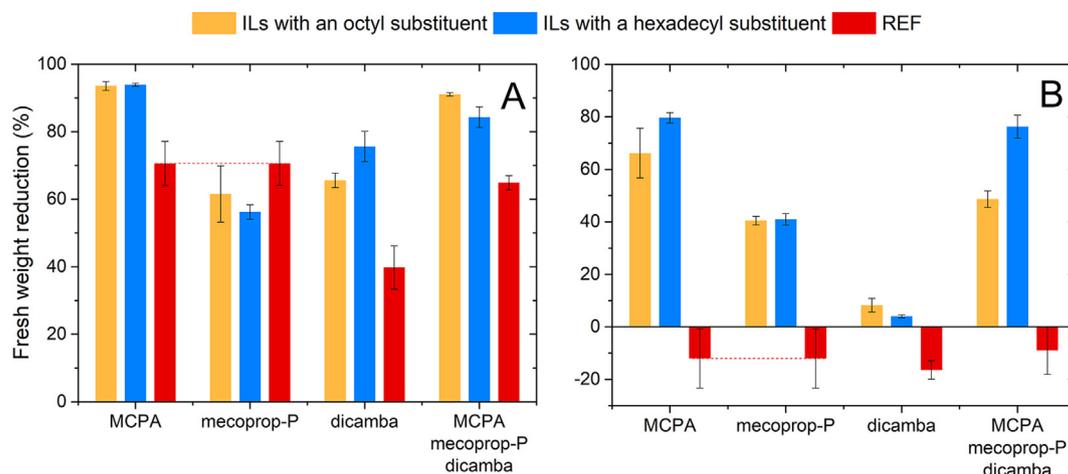


Fig. 7. Herbicidal activity of the ILs obtained against cornflower (A) and winter rapeseed (B), where REF is a reference commercial herbicide; for MCPA and mecoprop-P-based ILs: sodium and potassium salts of MCPA, for dicamba-based ILs: dimethylamine salt of dicamba, for DSHILs: mixture of potassium salts of MCPA, mecoprop-P and dicamba.

HILs. No significant differences in the values of the γ_{CMC} parameter were observed among ILs with one, two or three herbicidal anions [12,28,65].

The CMC values (Table A.4, [Supplementary Data](#)) obtained for the studied single-anion ILs were within the broad range from 0.20 to 31.26 mmol dm⁻³. As expected, the values recorded for compounds with the octyl chain (**1a–3a**) were approximately 60–150 times higher than those of the hexadecyl derivatives (**1b–3b**). The results confirmed that the micellization process of HILs depends mostly on the length of the alkyl chain in the cation [17,18,28]. Moreover, it was noted that the dicamba-based HILs **3a** and **3b** exhibited significantly lower adsorption efficiency than did the other studied compounds, mainly due to the increased hydrophilicity of the dicamba anion [18]. For DSHILs involving a cation with the octyl substituent (**4a, 5a**), the CMC values were equal to 9.13 and 5.58 mmol dm⁻³, respectively, whereas systems **4b** and **5b** were characterized by CMC values of 0.14 and 0.36 mmol dm⁻³. Based on these results, we can conclude that the addition of 2nd and 3rd anions to single-anion ILs significantly impacts the CMC values. In the case of octyl derivatives, the formation of a two-anion DSHIL reduces the CMC value to 9.13 mmol dm⁻³, and the addition of dicamba anion causes a further reduction of 40%. A similar phenomenon can be observed for hexadecyl derivatives; however, the introduction of dicamba anion does not cause further reduction. Therefore, the addition of a third anion may improve the surface activity of a DSIL, but this is not a rule. The causes of this phenomenon should be explored more thoroughly.

The pC_{20} parameter describes the effectiveness of the surface tension reduction compared to that of pure water. The pC_{20} values are listed in Table A.4. ([Supplementary Data](#)). For the analyzed compounds, this parameter increased with the number of carbon atoms in the hydrophobic chain. Therefore, greater pC_{20} values for the **1b–5b** systems than in **1a–5a** indicate a better tendency of hexadecyl derivatives to adsorb at the air–water interface. According to the calculated pC_{20} results, the formation of two-anion and three-anion DSHILs does not cause a more effective reduction in the water surface tension by 20 mN m⁻¹.

3.5. Herbicidal activity

All obtained single-anion HILs as well as DSHILs **5a** and **5b** were analyzed in terms of their herbicidal activity toward two common species of weeds widespread in Polish fields: cornflower (*Centaurea cyanus*) and winter rapeseed (*Brassica napus*). Commercially avail-

able products containing the active substances corresponding to the ILs tested were used as reference substances. The HILs with dicamba anion (**3a** and **3b**) were compared to Dicash (dicamba dimethylammonium salt, 480 g dm⁻³), while the results for the HILs based on both phenoxy acids (**1a, 2a, 1b** and **2b**) were referenced to the results obtained for Chwastox Extra 300 SL (MCPA sodium and potassium salts, 300 g dm⁻³) since there is no formula available on the Polish market containing mecoprop-P as the only active substance. Single-anion ILs and reference substances with MCPA or mecoprop-P anions were applied at a dose of 400 g ha⁻¹, while herbicides involving dicamba were used at a dose of 200 g ha⁻¹. Considering the results of previous studies with DSHILs, which have been characterized by synergistic effects and better performance compared to single-anion HILs [27,28], systems **5a** and **5b** were applied in quantities such that the MCPA dose was equal to 200 g ha⁻¹–4.5 times less than the recommended dose. In analogous amounts, a reference substance was used: commercially available Chwastox® New Trio 390 SL containing the same active substances in the same mass ratio as in **5a** and **5b**. Overall, the dose of agents containing more than one synthetic auxin was 390 g ha⁻¹, corresponding to MCPA, mecoprop-P and dicamba doses of 200, 150 and 40 g ha⁻¹, respectively. The exact results recorded in the experiments are provided in the [Supplementary Data](#) (Table A.5).

It should be noted that although cornflower plants show relatively high susceptibility to synthetic auxins [66], winter rapeseed is significantly less susceptible to these agents and requires higher doses [28]. Regardless of the plant species and the tested active ingredient, the use of HILs has resulted in a significantly higher effectiveness compared to commercially available preparations containing the same active ingredients (Fig. 7). Furthermore, in the experiments conducted on rapeseed plants (Fig. 7B), the use of reference herbicides at the reduced dose resulted in uncontrolled growth of the plants, which was observed as an increase in fresh weight of the plants compared with untreated controls. It should be emphasized that this phenomenon, resulting from the limited susceptibility of winter rapeseed to synthetic auxins, did not occur after the application of HILs. The superior HIL activity is most likely associated with more effective penetration of auxins into plant tissues due to the introduction of an amphiphilic counterion [14].

However, the results of the experiment were highly dependent on the structure of the herbicide anion. Of the tested HILs involving a single anion, the compound comprising the MCPA anion and a hexadecyl substituent in cation (**1b**) exhibited the highest effi-

cacy—its use resulted in fresh weight reductions of 94 and 80% (cornflower and winter rapeseed, respectively). Compounds **2a** and **2b** with mecoprop-P-derived anions were approximately half as active as HILs **1a** and **1b** containing MCPA anions, respectively. It was also noted that despite the transformation into the IL form, HILs **3a** and **3b** with dicamba anions did not show any activity against winter rapeseed plants. The respective differences between the use of single-anion ILs with octyl (**1a**, **2a**, **3a**) and hexadecyl (**1b**, **2b**, **3b**) substituents did not exceed 14%, despite a significant change in the length of the alkyl substituent. This is consistent with previous reports indicating that most surface-active HILs exhibit biological activity at similar levels when their pC_{20} values exceed 3 [18,28]. For DSHILs **5a** and **5b**, which involved three anions derived from synthetic auxins, the application of the “DSHIL strategy” allowed satisfactory levels of fresh weight reduction to be obtained. It should be noted that the herbicidal efficacy of **5a** and **5b** toward both species of weeds was significantly better than those for all HILs containing only mecoprop-P (**2a**, **2b**) or only dicamba (**3a**, **3b**). Moreover, although the dose of MCPA (the most efficient of the tested active ingredients) was twice as low as doses for **1a** and **1b** applied in the same experiment, the DSHILs were in most cases characterized by biological activity similar to that of MCPA-based HILs. In the experiments conducted on cornflower plants, compounds **1a** and **5a** were almost equally effective (93 and 91% of fresh weight reduction, respectively), and **5b** was only slightly less active toward this species (by 9%) compared to single-anion **1b**. As observed in previous experiments on less susceptible winter rapeseed plants [28], the elongation of alkyl substituents crucially impacted the intensification of the synergy among active ingredients in DSHILs. The test results obtained show that the use of DSHIL with a shorter substituent (**5a**) resulted in a reduction of 49% (16% less than **1a**), while the analogous compound containing a hexadecyl substituent (**5b**) exhibited one and a half times higher activity (76%) and was as effective as its MCPA-only counterpart (**1b**). This phenomenon is a clear indication that a decrease in the dose of highly active HILs (with MCPA anion) may be successfully compensated by the synergistic effect originating from the interactions with different HILs containing anions of other synthetic auxins. Thus, the application of DSHILs permits broadening of the spectrum of action against other weeds [27,33,37,67] and counteracts the acquisition of resistance [2,29,68,69] due to the use of more than one herbicide while maintaining favorable biological activity of the most potent active ingredient.

To evaluate the behavior of the spray solutions of HILs and DSHILs on the leaf surfaces of test plants, we measured their contact angles (CAs) on paraffin, which is considered a model of a

hydrophobic leaf surface [70], as well as on the adaxial surfaces of cornflower and rapeseed leaves. The obtained values (Fig. 8) reflect the hydrophobic or hydrophilic affinity of the analyzed systems toward the leaf surfaces of weeds. The exact values are provided in Table A.6 (Supplementary Data).

High surface activity of the obtained HIL and DSHIL systems allowed the reduction of the CA to values in the range from 64° to 119° for ILs comprising a cation with an octyl substituent (**1a–5a**) and from 43° to 92° for their analogs with hexadecyl substituents (**1b–5b**). Basically, we observed that the introduction of two different herbicidal anions into the structure of a DSHIL does not influence the wettability of either the paraffin or leaf surfaces compared to their single-anion counterparts involving either MCPA or mecoprop-P. In addition, the highest contact angle values were recorded for dicamba-based HILs **3a** and **3b**, which were also characterized by the highest CMC values. Therefore, the use of the obtained ILs resulted in a significant increase in the wettability of the leaf surface [71–73] with the respective spray solutions (down to CA values of less than 100° in almost all cases, with the exception of a single IL **3a**).

It should also be noted that the CA values of spray solutions on winter rapeseed leaves were significantly higher (by up to approximately 40° for **1b** spray solution) than the angles recorded on the surfaces of cornflower leaves or paraffin. The observed discrepancy in wettability of leaf surfaces results from the differences in the morphological structure of wetted surfaces, as well as the chemical and hydrophobic properties of the plants' superficial waxes [74,75]. Since favorable wettability of the leaf surface is correlated with a better penetration of the active substance into the plant tissue [70], higher CA values recorded for rapeseed leaves may explain the difference in the susceptibility of cornflower and winter rapeseed plants observed in greenhouse experiments. Moreover, the obtained results show that the synthesized HILs and DSHILs can be successfully used without any addition of commercial surface-active herbicide adjuvants.

4. Conclusions

In this study, six HILs with amphiphilic cations analogous to choline and anions derived from herbicidal synthetic auxins were synthesized and subsequently transformed into novel DSHILs involving two or three herbicidal anions. The developed three-step process allowed the final products to be obtained in a time-efficient manner, with very satisfactory purity and near-theoretical yield (>99%), using ethanol derived from natural

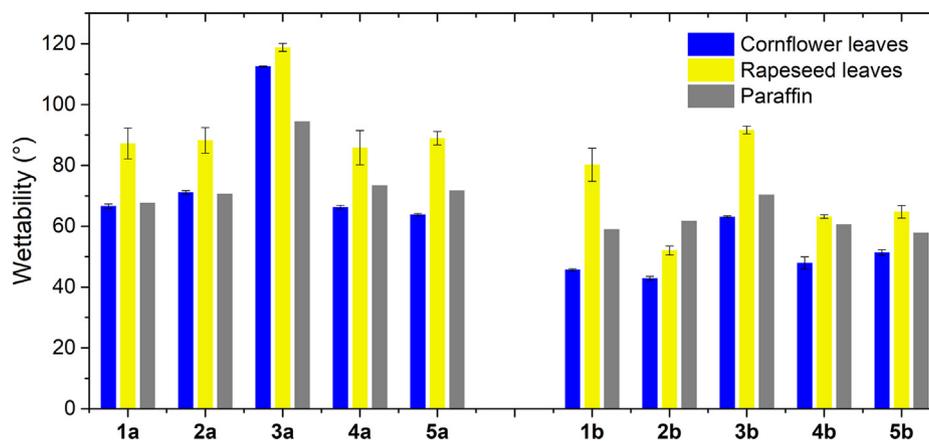


Fig. 8. Contact angle values of analyzed ILs.

sources as the only solvent. On the basis of the spectral analyses, we confirmed the chemical structures of the obtained compounds and that they are chemically stable under aerobic conditions. In addition, in the ^1H NMR spectra of DSHILs, significant deshielding effects on the CH_2 groups in the MCPA and mecoprop-P anions were observed, which indicates the presence of unique competitive interactions between two or three herbicidal anions in the same compound.

According to the study of physicochemical properties, we observed that the greatest differences in density, refractive index and surface properties are caused by a significant elongation of the alkyl substituent (from octyl to hexadecyl), while viscosity of HILs and DSHILs depends mainly on the interaction of cation with a specific anion or anions. The results of the conducted analyses also confirmed that the synthesis of DSHILs comprising both MCPA and mecoprop-P anions in many cases resulted in the occurrence of unexpected deviation of the values of the physicochemical parameters from the theoretical values predicted according to the mixing laws. Thus, it was possible to synthesize a DSHIL with a viscosity lower than both of its single-anion counterparts (by 46% and 84%, respectively), which indicates the possibility of obtaining significant technological benefits as a result of synthesis of ILs containing more than 2 ions. Moreover, the two-anion DSHILs were characterized by superior surface activity in aqueous solutions compared to their respective parent HILs. Interestingly, in the majority of cases, the introduction of the dicamba anion to the structure of a DSHIL did not result in a further escalation of the abovementioned deviations. This phenomenon implies that the presence of three anions in the structure of the same compound does not cause a greater structural disturbance compared to two-ion DSHILs.

Of all single-anion HILs tested in greenhouse experiments, the compounds involving MCPA anions were characterized by the most satisfactory herbicidal efficacy. Similar levels of biological activity toward weeds have also been noticed for three-anion DSHILs applied in an analogous dose, although they contained twice as little MCPA as single-anion HILs. The observed results confirm a hypothesis regarding the occurrence of synergy among the anions of more and less potent active ingredients, previously observed only for the two-anion DSHILs. Based on the results of the experiment on winter rapeseed plants, we can also assume that the presence of a long alkyl substituent in the three-anion DSHIL common cation intensifies this effect. Thus, it can be concluded that the application of the strategy of merging two or more synthetic auxins into a single IL allows highly efficient plant protection products to be obtained while simultaneously maintaining crucial advantages resulting from the use of more than one herbicide.

CRediT authorship contribution statement

Tomasz Rzemieniecki: Conceptualization, Data curation, Investigation, Methodology, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Marta Wojcieszak:** Data curation, Investigation, Methodology, Writing - original draft. **Katarzyna Materna:** Methodology, Validation, Writing - review & editing. **Tadeusz Praczyk:** Investigation, Methodology, Resources. **Juliusz Pernak:** Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.116452>.

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