



Surface activity and phytotoxicity of morpholinium herbicidal ionic liquids



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ARTICLE INFO

Article history:

Received 4 March 2022

Revised 20 June 2022

Accepted 27 June 2022

Available online 29 June 2022

Keywords:

Herbicidal ionic liquids

Surface active properties

Herbicides

Leaf wettability

Phytotoxicity

Weeds

ABSTRACT

The use of efficient synthesis methods to obtain novel herbicidal ionic liquids (HILs) with biological activity is extremely important because it can eliminate certain negative environmental impacts. The authors of this work succeeded in the experiment, which resulted in the synthesis of 18 novel ionic liquids with high yields. Furthermore, a number of physicochemical and biological properties have been investigated, including surface activity, thermal analysis, and phytotoxicity. In addition, it was proven that morpholinium ionic liquids with phenoxyacid anions were more effective against cress than HILs previously studied in the literature. To the best of our knowledge, this is the first report of surface-active ionic liquids with herbicidal anions where leaf surfaces were used for analysis. An important aspect of this work was to compare the wettability of the surfaces of wheat leaves and weeds. Moreover, it was shown that using paraffin as a reference surface was not sufficient to describe the wetting properties of HILs. The research reported here proved that morpholinium ionic liquids were effective in wetting weed surfaces while they do not adversely affect wheat leaf surfaces. Our results could be significant for meeting the environmental challenges and agricultural demands of the future.

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1. Introduction

One of the biggest challenges of modern agriculture is to satisfy the nutritional needs of a growing population without harming the environment [1,2]. The chemical intervention to overcome this problem is to use plant protection products that destroy weeds in agricultural fields. For this purpose, preparations called herbicides are used, often found in the form of salt, pure acid and ester [3]. However, because of their volatility and ability to drift, using herbicides can cause the movement of the volatile chemicals to other crop fields. Therefore, efforts are being made to synthesize new herbicidal structures that would meet the environmental standards of agriculture [1,4,5].

Recently, one of the most promising forms of herbicides has been herbicidal ionic liquids (HILs) [6–8]. HILs are organic salts with a melting point lower than 100 °C that contain at least one ion exhibiting herbicidal activity. Additionally, the most important advantage of HILs is their low volatility, which makes it possible to

reduce herbicide evaporation, increase the degree of surface wetting of weed leaves and reduce herbicide application rates per hectare [9]. Furthermore, the presence of a cation with surface properties in the structure of HILs reduces or completely eliminates the use of adjuvants traditionally included in commercial herbicides. Herbicidal ionic liquids with interfacial activity can be classified as surface-active ionic liquids (SAILs) [10,11].

The interfacial properties of SAILs have been gained attention in recent years. Surface-active ionic liquids, similar to surfactants, contain a hydrophilic head group and a hydrophobic tail (alkyl chain). In addition, ionic liquids with long alkyl chains are receiving special attention because they have the potential to serve as an alternative to conventional cationic surfactants. According to previous reports in the literature, these structures have been shown to have a fundamental influence on micellization and therefore the self-aggregation of SAIL monomers in water [12]. As the length of a hydrophobic chain increases, the CMC value decreases [13], which undoubtedly opens possibilities for the potentially greater application of SAILs in industry.

The surface activity is influenced not only by the alkyl chain length but also by the nature of the counterion since the anion is an integral part of the micelle. In addition, its hydrophobic nature

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contributes to the alteration of the thermal energy of the micellization process [11]. Surfactants that act as adjuvants reduce the interface tension between the leaf surface and the spray formulation since they are one of the primary components of applied herbicides [9]. To the best of our knowledge, the first studies that observed the effect of surfactant absorption on leaf surfaces were written in 1958 [14]. From a biological point of view, leaf surfaces are generally covered with a layer of cuticular wax, which itself comprises two layers of wax: amorphous and crystalline [15–17]. Each plant species contains a specific morphological structure; therefore, modification of the leaf surface properties of a plant is very difficult. The easiest way to improve leaf surface wetting is to modify the herbicide formulation. The theme of leaf surface wettability has become increasingly popular primarily due to the desire to minimize the number of adjuvants used.

In the present work, morpholine was selected as the source of the cation. In regard to the structure, morpholine contains two heteroatoms in its ring: nitrogen and oxygen; therefore, it has the ability to combine the features of a secondary amine and a cyclic ether. Cłapa et al. described the antimicrobial activity of ionic liquids with 4-decyl-4-ethylmorpholinium and 4,4-didecylmorpholinium cations combined with the same anions that were used in our study [18]. In the literature, the effects of elongating the alkyl chain length of ester-functionalized morpholinium-based SAILs is known [19–22]. Furthermore, to the best of our knowledge, there are reports on the micellization of morpholinium SAILs, but no study is based on morpholine cations with bromide as counter ions [19,22,23]. The surface activity of morpholinium ionic liquids with herbicidal anions has been described in scientific investigations. In this study, the influence of the surface-active properties of morpholinium herbicidal ionic liquids on their toxicity and biodegradability was evaluated [24].

However, structures derived from phenoxyacids have been used as herbicidal anions, including MCPA, MCP, 4-CPA, 2,4-D, benzoic acid (dicamba) and picolinic acid (clopyralid). Herbicide ionic liquids containing the abovementioned anions can be classified as synthetic auxins, which are used to control dicotyledonous weeds, such as cornflower (*Centaurea cyanus* L.), while simultaneously protecting cultivated cereals, such as winter wheat (*Triticum aestivum* L.).

The main aims of this study were to focus on newly synthesized morpholinium HILs with different alkyl chains in their cationic head groups and to observe the influence of the HILs on micellization. The objective of the present work is to explain the effect of aromatic counterions on the surface activity behavior of the analyzed HILs. Another important issue is to determine how the substitution of the aromatic herbicidal anion affects the composition of the surface and the biological activity of morpholinium ionic liquids.

The goals of this paper are to serve as an opportunity for new viewpoints on the topic of herbicidal ionic liquids and to motivate further research in the area of surface-active morpholinium ionic liquids.

2. Experimental

2.1. Materials

Morpholine 99%, 1-bromooctane 99%, 1-bromodecane 98%, 1-bromododecane 97%, benzyl chloride 99%, (2,4-dichlorophenoxy)acetic acid (2,4-D) 98%, active carbon and reagents for two-phase system titration (dimidium bromide 95%, patent blue V sodium salt 97%, sodium dodecylsulfate(VI) 98%) were purchased from Sigma-Aldrich. (4-Chlorophenoxy)acetic acid (4-CPA) 98% was purchased from Koch-Light Laboratories Ltd. (3,6-dichloro-2-methoxy)

benzoic acid (Dicamba) 95%, (4-Chloro-2-methylphenoxy)acetic acid (MCPA) 97% and (\pm)-2-(4-chloro-2-methylphenoxy)propionic acid (MCP) 96% and (3,6-dichloro)-2-picolinic acid 97% (Clopyralid) were purchased from Organika-Sarzyna (Poland). All solvents (acetonitrile, ethyl acetate, chloroform, toluene), NaHCO₃, and NaOH were purchased from Avantor and used without further purification. The herbicides used in the synthesis (4-CPA; 2,4-D; MCPA; MCP; Clopyralid and Dicamba) were first purified by dissolution in hot toluene, addition of activated carbon, filtration of the hot solution to remove colored impurities absorbed in activated carbon, and crystallization from cold toluene.

2.2. Synthesis

2.2.1. Preparation of 4-alkylmorpholines

Morpholine (0.25 mol) was dissolved in toluene (100 mL) and stirred with stoichiometric amounts of alkyl bromide and 0.3 mol of NaHCO₃. The reacting vessel was heated to the boiling point under a reflux condenser for 24 h. The produced NaBr was filtered and washed with toluene. Then, the toluene from the organic phase was removed by evaporation. Finally, the product was distilled under reduced pressure. The yields and boiling points under reduced pressure for each obtained 4-alkylmorpholine sample obtained are presented in Table A.1.

2.2.2. Preparation of 4-alkyl-4-benzylmorpholinium chlorides

Benzyl chloride (0.1 mol) was added to a round-bottomed flask that contained a vigorously stirred mixture of 50 mL of acetonitrile and 0.1 mol of 4-alkylmorpholine. The reaction mixture was stirred at its boiling point under a reflux condenser for 48 h. Subsequently, the acetonitrile was removed under reduced pressure, and 20 mL of ethyl acetate was added to the raw post-reaction mixture at a low temperature. The precipitate was filtered, washed with ethyl acetate, and dried at 60 °C under reduced pressure. The yields, surfactant content and melting point for each 4-alkyl-4-benzylmorpholinium chloride sample obtained are presented in Table A.2.

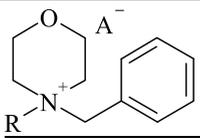
2.2.3. Preparation of 4-alkyl-4-benzylmorpholinium-based HILs

The reagent mixture consisting of 0.01 mol of the selected herbicide in acid form (4-CPA, 2,4-D, MCPA, MCP, clopyralid or dicamba), 20 mL of distilled water and 0.011 mol of a 10% aqueous solution of NaOH was mixed in a round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and an addition funnel. The mixture was heated at 50 °C until the solution became clear. Afterward, 0.01 mol of 4-alkyl-4-benzylmorpholinium chloride dissolved in 30 mL of water was added and stirred for 30 min at room temperature. In the case of 4-alkyl-4-benzylmorpholinium-based HILs, the product was extracted from the aqueous phase with 50 mL of chloroform and washed with distilled water until chloride ions were no longer detected using AgNO₃. After removing the chloroform, the product was dried under reduced pressure at 60 °C for 24 h. The yields and surfactant content for each HIL obtained are presented in Table 1.

2.3. Analysis

¹H NMR spectra were recorded on a Varian VNMR-S 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).

Table 1
4-alkyl-4-benzylmorpholinium ILs with herbicidal anions.



HIL	R	A ⁻	Abbreviation of IL	Surfactant content [%]	Yield [%]
1	C ₈ H ₁₇	4-CPA ⁻	[BenzOctMor][4-CPA]	92.5	81
2		2,4-D ⁻	[BenzOctMor][2,4-D]	93.5	82
3		MCPA ⁻	[BenzOctMor][MCPA]	94.5	91
4		MCPP ⁻	[BenzOctMor][MCPP]	97.5	90
5		Clopyralid ⁻	[BenzOctMor][Clopyralid]	96.0	86
6		Dicamba ⁻	[BenzOctMor][Dicamba]	96.5	81
7	C ₁₀ H ₂₁	4-CPA ⁻	[BenzDecMor][4-CPA]	97.0	94
8		2,4-D ⁻	[BenzDecMor][2,4-D]	98.5	92
9		MCPA ⁻	[BenzDecMor][MCPA]	98.0	92
10		MCPP ⁻	[BenzDecMor][MCPP]	98.5	91
11		Clopyralid ⁻	[BenzDecMor][Clopyralid]	99.5	89
12		Dicamba ⁻	[BenzDecMor][Dicamba]	98.5	90
13	C ₁₂ H ₂₅	4-CPA ⁻	[BenzDodecMor][4-CPA]	99.0	97
14		2,4-D ⁻	[BenzDodecMor][2,4-D]	98.0	98
15		MCPA ⁻	[BenzDodecMor][MCPA]	97.0	98
16		MCPP ⁻	[BenzDodecMor][MCPP]	99.0	98
17		Clopyralid ⁻	[BenzDodecMor][Clopyralid]	98.0	99
18		Dicamba ⁻	[BenzDodecMor][Dicamba]	98.5	99

2.4. Thermal analysis

The thermal transitions of the prepared salts were determined through differential scanning calorimetry (DSC) under nitrogen by using a Mettler Toledo Star^e TGA/DSC1 (Leicester, UK) unit. Samples with masses between 5 and 15 mg were placed in aluminum pans and heated from 25 to 120 °C at a rate of 10 °C min⁻¹ and cooled with an intercooler at a rate of -10 °C min⁻¹ to -100 °C min⁻¹. Thermogravimetric analysis was performed using a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples with masses between 2 and 10 mg were placed in aluminum pans and heated from 30 to 450 °C at a rate of 10 °C min⁻¹.

2.5. Phytotoxicity test

Phytotoxicity studies of synthesized 4-alkyl-4-benzylmorpholinium-based HILs in relation to dicotyledonous plants were carried out on the basis of measurements of shoot and root growth inhibition of the plant. The garden cress (*Lepidium sativum*) was used as a model dicotyledonous plant. Commercial herbicides in acid form with an equimolar amount of NaHCO₃ were used as reference samples. The tests were carried out using vertical plastic Phytotoxkit containers (Phytotoxkit, Tigret company, Belgium). Each container was filled with 130 ± 0.1 g of reference OECD soil for the Phytotoxkit tests (batch number OERS050419; composition: 85% air-dried quartz sand, 10% kaolin clay, 5% sphagnum peat, and calcium carbonate to obtain an initial pH of 6 ± 0.5). A 0.01 M sodium bicarbonate solution was prepared, then 0.25 mmols of the tested HIL, 5 mL of isopropanol, and 25 mL of sodium bicarbonate solution (0.01 M) were placed in a 100 mL graduated flask. Consequently, the initial solutions of the tested ionic liquids were prepared at a concentration of 2.5 mM, which contained 2.5 mM of sodium bicarbonate. Then, by dilution (10 mL of the initial solution was taken and diluted in a 100 mL volumetric flask before carrying out this tenfold dilution again), solutions of HILs were obtained with a concentration of 0.025 mM. Afterward, 25 mL of the prepared solutions were taken and used to water the soil in a container, which corresponded to 0.0048 mmol of the tested HIL per kg of soil. One of the containers was prepared as a "0" control,

which contained 25 mL of the same amounts of aqueous sodium bicarbonate and isopropanol used in all other containers. Next, 10 seeds of garden cress (*Lepidium sativum*) were planted in each container and incubated for 7 days at 25 °C. Seven days after sowing, the lengths of the shoots and roots were measured. The tests were performed according to the PN-ISO 11269-1 (1998) standard.

After terminating the germination tests, the impact of herbicides on root growth inhibition of garden cress was assessed. Based on the obtained data, the germination index (GI) was calculated according to the equation:

$$GI = \frac{G_s}{G_c} \cdot \frac{L_s}{L_c} \cdot 100 [\%]$$

G_s and G_c are the numbers of seeds germinated in the sample and control, respectively.

L_s and L_c are the lengths of the radicles in the sample and control, respectively.

2.6. Surface activity studies

By selecting a specific ion, some ionic liquids can be characterized by interfacial properties: critical micelle concentration (CMC), surface tension of the solution at the CMC (γ_{CMC}), adsorption efficiency (pC₂₀), contact angle at spray solution, contact angle at CMC concentration and Gibbs free energy of the adsorption (ΔG_{ads}⁰). The ΔG_{ads}⁰ values were calculated based on the equation found in the literature [19]. The herbicidal activity was also defined by the contact angle of the reference substance. The most important parameter of surface activity is surface tension (γ in mN m⁻¹), and the values of the surface tension were determined by using drop shape analysis (DSA 100, KRÜSS Germany accuracy ± 0.001 mN m⁻¹, at 25 °C). The surface tension was based on the drop shape method and calculated using the Laplace equation and specific software. The CMC and γ_{CMC} values were determined by the intersection of two straight lines drawn in the regions of low and high concentrations in surface tension using the linear regression analysis method. The pC₂₀ parameter represents the measure of adsorption in the interfacial spaces. The pC₂₀ values were determined according to the following equation:

$$pC_{20} = -\log C_{20}$$

pC_{20} is defined as the negative logarithm of the surfactant concentration in the bulk phase required to reduce the surface tension of the water by 20 mN m⁻¹, which represents the efficiency of surface adsorption on an air–water interface.

Gibbs energy (ΔG_{ads}^0), which characterizes the interactions between the bulk phase and the surface phase:

$$\Delta G_{\text{ads}}^0 = -RT \ln a$$

where:

R is the gas constant,

T is the absolute temperature.

a is a parameter of the Szyszkowski equation:

$$\gamma = \gamma_0 \left[1 - b \ln \left(\frac{C}{a} + 1 \right) \right]$$

where:

γ_0 is the surface tension of the solvent.

The wettability of the HILs studied was investigated by the contact angle, which was measured using the analyzed drop shape (DSA 100, KRÜSS Germany, accuracy ± 0.001 mN m⁻¹, at 25 °C). The contact angle values were determined by the sessile drop method. The sessile drop method involves placing a drop of liquid on the surface to be examined (paraffin or leaves) and then matching the image of the drop with its shape (the contour at the 3-phase contact point). In the same way, a drop of spray solution was analyzed. The Young-Laplace equation is one of the most complicated yet precise methods for determining contact angle values. In this study, paraffin (a model surface used in the laboratory) and biological systems: wheat winter (*Triticum aestivum* L.) and cornflower leaves (*Centaurea cyanus* L.) were taken as the solid phase.

2.7. Atomic Force Microscopy

The samples of the studied ionic liquids were dissolved in water, and then a small volume (5 μ l) of the studied solutions in different concentrations of ionic liquids (ILs) were deposited on freshly prepared mica substrates and dried. Topographic images were collected using a NanoWizard IV (JPK, Germany) atomic force microscope and Tap150AL AFM cantilevers (Ted Pella, Inc., Redding, USA). The experimental AFM data obtained for all studied ionic liquids were then processed and analyzed by the use of Gwyddion v2.58 image processing software [25].

2.8. Statistical analysis

For the statistical analysis, the SEM method is used, which involves the estimated standard errors of the mean. The SEM values were calculated on the basis of the equation below.

Equation of standard errors of mean (SEM) values.

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

SEM is the standard error of the mean,

s is the sample standard,

n is the number of replications.

3. Results and discussion

3.1. Synthesis

4-Alkyl-4-benzylmorpholine ionic liquids with herbicidal anions were designed and synthesized. With morpholine, alkyl bromide and benzyl chloride at our disposal, we used two main

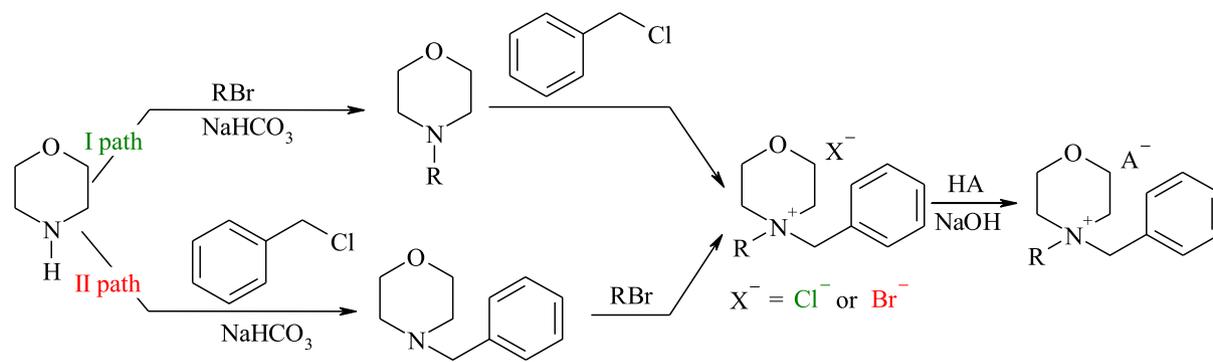
routes for the synthesis of 4-alkyl-4-benzylmorpholinium halides as precursors of HILs (Scheme 1). The first route was the alkylation of morpholine with an alkyl bromide followed by the quaternization of the resulting 4-alkylmorpholine with benzyl chloride. The second route was the alkylation of morpholine with benzyl chloride followed by the quaternization of 4-benzylmorpholine with alkyl bromide. In the first method, chlorides were obtained, and in the second, 4-alkyl-4-benzylmorpholinium bromides were obtained as precursors of the ionic liquids. The first synthesis path was chosen for many reasons. By analyzing the reactivity of morpholine and 4-substituted morpholine, it can be concluded that morpholine, as a secondary amine, is more reactive than 4-substituted morpholine (tertiary amine). In turn, benzyl chloride is a much more reactive reagent than alkyl bromide. Thus, in the first stage of the synthesis, it was decided to alkylate morpholine with a less reactive reagent, and in the second stage, the resulting less-reactive 4-substituted morpholine was quaternized with a reagent of greater reactivity. The second reason for choosing this synthesis path was the reactivity of the precursors of the ionic liquids. The chloride anion is more easily exchanged with a different anion than the bromide anion. Therefore, 4-alkyl-4-benzylmorpholinium chlorides could act as better precursors of ionic liquids than their counterparts with bromide anions. Table A.1 (in Supplementary Data) shows the obtained 4-alkylmorpholines, while Table A.2 (in Supplementary Data) shows the 4-alkyl-4-benzylmorpholinium chlorides. The content of cationic surface-active agents was determined by two-phase titration (EN ISO 2871–1.2: 2010).

The last stage of the synthesis was the ion exchange reaction that took place in the aqueous solution. Initially, the herbicide in the form of an appropriate acid was neutralized with a sodium hydroxide solution. The herbicides used in their acid form were relatively difficult to dissolve in water, while their sodium salt forms were highly soluble. The end of the acid-form herbicide neutralizing could be observed by the complete clarification of the reaction mixture. Thus, the prepared herbicides in the form of sodium salts reacted in the metathesis reaction with 4-benzyl-4-methylmorpholinium chlorides. The obtained 4-alkyl-4-benzylmorpholinium ionic liquids with herbicidal anions are presented in Table 1. The yield of the reaction increased with the elongation of the alkyl substituent. This relationship between the yield and substituent length was observed while washing the chloroform solution of the ionic liquid with water from the formed NaCl. Ionic liquids with a longer substituent are more difficult to transfer from chloroform to water, resulting in less loss of yield, which has also been observed in another work (Parus, et al., 2020) [26]. The obtained compounds could be classified as room temperature HILs. The content of cationic surfactant in ionic liquids, similar to the precursors, was determined by two-phase titration. The complement to 100% of the surfactant content is water, which is observed in the ¹H NMR spectra.

Analysis of the NMR spectra mentioned (Figures A.1–A.14. in Supplementary Data) confirmed that newly synthesized ILs were successfully obtained.

Fig. 1 shows the effect of the anion on the chemical shifts of protons located in close proximity to the quaternary nitrogen atom. The repositioning of the signals is seen in a series of two successive bonds, starting from the quaternary nitrogen atom. Analysis of the ¹H NMR spectra allowed us to rank the anions according to their increasing proton shielding capacities in the following order: [Cl] < [Cloparylid] < [4-CPA] < [Dicamba] < [MCP] < [2,4-D] < [MCPA].

The yields and surfactant content of the analyzed HILs are shown in Table 1.



R = C₈H₁₇, C₁₀H₂₁, C₁₂H₂₅

HA	R ¹	R ²	Herbicide	Abbreviation of anion
	H	H	4-CPA	[4-CPA]
	Cl	H	2,4-D	[2,4-D]
	CH ₃	H	MCPA	[MCPA]
	CH ₃	CH ₃	MCPP	[MCPP]
			Clopyralid	[Clopyralid]
			Dicamba	[Dicamba]

Scheme 1. Methods of synthesis of 4-alkyl-4-benzylmorpholinium-based HILs.

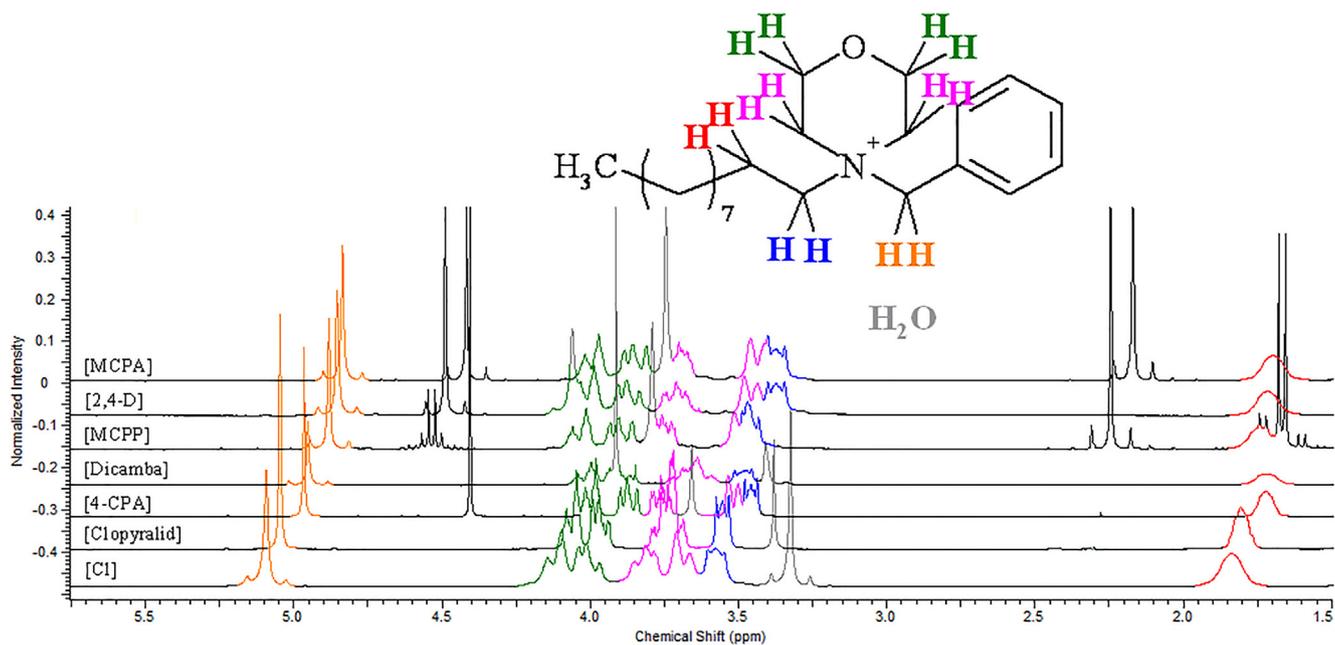


Fig. 1. Chemical shifts in proton signals.

Thermal analysis

The thermogravimetric properties obtained from tests, such as thermogravimetric analyses and differential scanning calorimetry, are presented in Table 2.

All the prepared compounds exhibited only a glass transition. For phenoxyacid anions with one chloride in the benzene ring (4-CPA anion), HILs **1**, **7** and **13** were in the range of approximately -18.0 to -11.0 °C. In the case of an anion with two chlorides in the aromatic ring (2,4-D), the glass transition temperature shifted to a higher value (from -8.1 to -0.5 °C) for compounds **8** and **2**, respectively. When compared to the 2,4-D anion exchange chlorine in the aromatic anion ring at position 2 in the methylene group, there was a small reduction in the glass transition temperature in the case of HILs with decyl substituent in the cation, but for substituents with eight and twelve carbon atoms in the alkyl chain, this reduction was greater and amounted to 6 °C. Replacement of the hydrogen atom in the MCPA anion with a methyl group for the MCPP anion resulted in a reduction of the glass transition temperature, but only for a compound with a long alkyl chain in the cation – HIL **16**. In the case of the pyridine derivative anion (clopalyridid), the lowest glass transition temperature was observed for the compound with an alkyl chain containing eight carbon atoms in the cation at -17.9 °C (HIL **5**). However, for the benzoic acid derivative (dicamba), increasing the alkyl chain reduced the glass transition temperature from 4.0 to -8.6 °C for compounds **6** and **18**, respectively.

The thermal stability of the prepared compounds is summarized in Table 2. Ionic liquids with morpholinium cation cores exhibited low thermal stability. In the case of the obtained salts, thermal decomposition was described with the parameters described in detail in the first phase of decomposition. In the literature, the thermal decomposition of ionic liquids is widely described with T_5 and T_{onset} parameters. As seen in Table 2 the tangential method T_{onset} is the temperature that describes decomposition with mass loss ranging from approximately 4 to 13%. This method, in comparison with a method such as T_5 , is less precise or even erroneous. In our opinion, the most accurate description

of thermal stability is based on the initial decomposition T_i , which describes the first mass deviation.

Based on a comparison of the initial decomposition from Table 2, it can be seen that the ionic liquids prepared based on phenoxyacetic acids (4-CPA, 2,4-D, MCPA and MCPP) were not thermally stable. For example, for the MCPP anion, the ionic liquid with [Dec-BenzMor] decomposed at 104.5 °C, while for the 2,4-D anion, these same cations decomposed at 114.5 °C. Generally, the influence of phenoxyacetates on thermal stability is ordered $MCPP < MCPA \approx 4-CPA < 2,4-D$. Higher thermal stability was observed for compounds with the benzoic acid derivative dicamba HILs **6**, **12** and **18** with decomposition temperatures of 125.1, 126.4, and 120.2 °C, respectively. The most thermally stable ionic liquids were salts with clopyralid anions that decomposed at approximately 130.9 °C.

Comparison data for the obtained ionic liquids with different alkyl substituents in the cation showed no significant difference. For example, in the case of T_i , MCPA anion elongation of the substituent from 8 to 12 carbon atoms caused a minor increase in thermal decomposition from 112.9 to 119.6 °C.

3.2. Phytotoxicity

The results of phytotoxicity tests against garden cress are shown in Fig. 2, and by considering the germination index in Table A.3 (in Supplementary Data) with Fig. 2, 4-benzyl-4-dodecylmorpholinium (4-chloro-2-methylphenoxy)acetate ([BenzDodecMor][MCPA]) and 4-benzyl-4-octylmorpholinium (4-chloro-2-methylphenoxy)acetate ([BenzOctMor][MCPA]) showed the highest phytotoxicity in relation to the model dicotyledonous plant. As shown in Fig. 2, in the case of the control, the root lengths were significantly greater than the stem lengths. In the case of plants growing in the substrate with added phytotoxic substances, the lengths of the roots were much shorter than those of the stems. The plants with added phytotoxins wanted to minimize the contact of their tissues with the toxic environment. For the same reason, some of the seedlings grew roots upward instead of downward. This behavior was observed in the case of soil saturated

Table 2
Thermal properties of 4-alkyl-4-benzylmorpholinium ILs with herbicidal anions.

HIL	T_g [°C] ^a	T_i [°C] ^b	T_1 [°C] ^c	T_2 [°C] ^d	T_5 [°C] ^e	T_{10} [°C] ^f	T_{onset} [°C] ^g	W_{onset} [%] ^h
1	-11.0	112.5	114.9	133.1	146.7	153.8	145.0	6.1
2	-0.5	118.9	120.3	137.7	148.0	156.7	152.2	6.7
3	-7.0	112.9	128.2	137.6	147.1	154.2	148.0	5.9
4	-0.2	107.1	120.2	129.6	140.4	148.7	141.3	5.4
5	-17.9	134.6	153.8	160.6	168.7	174.2	170.5	6.2
6	4.0	125.1	140.3	148.6	155.6	159.9	155.5	4.3
7	-18.0	112.2	124.4	137.2	150.1	159.1	152.4	6.4
8	-8.1	114.5	132.1	141.1	152.3	160.6	152.7	5.3
9	-9.9	107.0	117.1	133.7	149.3	159.8	153.2	6.5
10	-9.8	104.5	119.6	129.5	143.6	153.9	147.2	6.4
11	6.4	134.1	147.3	156.0	165.1	171.5	167.6	9.8
12	9.1	126.4	133.4	144.7	155.5	162.7	156.6	5.2
13	-14.8	114.4	128.6	143.8	159.0	169.3	157.1	4.0
14	-6.9	121.9	135.2	147.9	161.7	172.2	168.2	7.8
15	-12.9	119.6	140.8	148.5	160.3	169.3	174.3	12.9
16	-16.3	110.9	124.6	139.5	155.7	168.1	162.0	7.0
17	-0.6	130.9	149.7	156.1	165.0	172.2	166.2	5.6
18	-8.6	120.2	136.5	147.5	159.3	168.4	159.3	4.7

^a glass transition,

^b initial decomposition (temperature at which the derivative dm/dt is valued at 10^{-4}),

^c temperature at which a mass loss of 1% occurred,

^d temperature at which a mass loss of 2% occurred,

^e temperature at which a mass loss of 5% occurred,

^f temperature at which a mass loss of 10% occurred,

^g decomposition temperature based on the tangential method,

^h mass loss at T_{onset} .

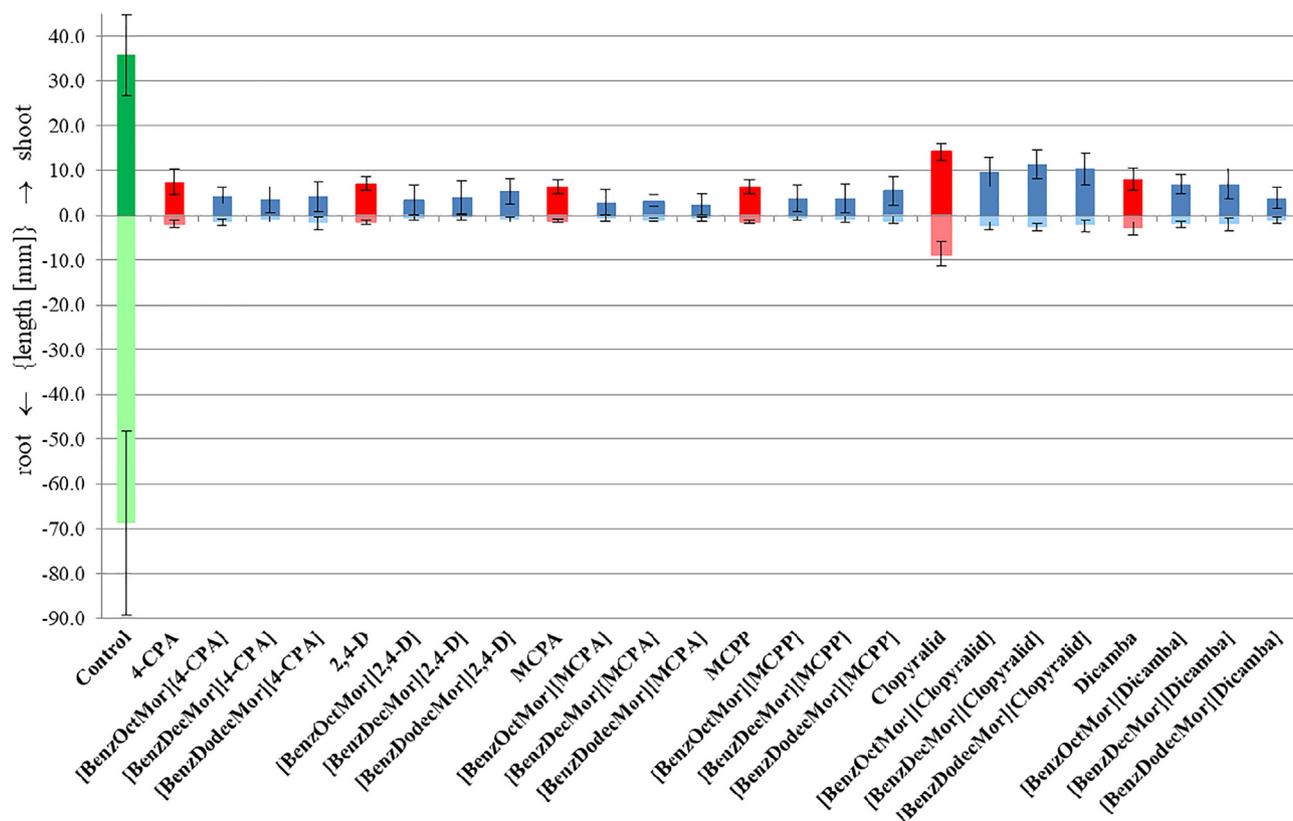


Fig. 2. Average root and shoot length for seedlings in soil with the addition of 4-alkyl-4-benzylmorpholinium-based HILs and reference herbicides.

with ionic liquid solutions with an octyl substituent and anions [MCPA] and [MCPP], as well as for all HILs with an alkyl substituent containing ten and twelve carbon atoms (except for 4-benzyl-4-decylmorpholinium (3,6-dichloro)-2-picolinate ([BenzDecMor][Clopyralid])). All synthesized ionic liquids proved to be more effective against garden cress than commercial herbicides. It can be seen that the ionic liquids with phenoxyacid anions were more effective against cress than HILs containing a benzoic acid or picolinic acid derivative in the anion. Compounds with clopyralid anions were the least effective, which was also confirmed by another work (Syguda et al., 2020) [26].

3.3. Surface activity

The surface properties of herbicidal morpholinium ionic liquids were established based on the surface tension measurements. The profiles of surfactants with different concentrations are shown in Fig. 3, Table 3 and Figure A.15 in the Supplementary Data.

Generally, for all of the morpholinium salts, the surface tension decreases with the increase in their concentration in the aqueous solution. When individual surfactant molecules start to form aggregates, a significant decrease in surface tension can be observed. This phenomenon consequently leads to a plateau. The salt concentration at which the addition of a compound to the solution does not cause a decrease in surface tension is called the CMC. The CMC is the main parameter used to determine the surface activity of the surfactants. The CMC is the basis for determining the other parameters described in the Experimental section (the values of the analyzed parameters are shown in Table 3).

According to the literature, the surface activity of cationic surfactants is determined by two factors: the number of carbon atoms in the alkyl chain and the nature of the salt polar head groups. For the studied HILs, the CMC values were between 1.02 mM for

[BenzDodecMor][2,4-D] and 75.02 mM for [BenzOctMor][Clopyralid]. Generally, for all of the amphiphilic compounds analyzed, the CMC values increased with alkyl chain elongation. The highest values were obtained for the cation with the decyl substituent, and the lowest values were observed in the case of the cation with the dodecyl substituent. These results demonstrated that the amount of carbon atoms within the hydrophobic cation chain had a significant influence on micelle aggregation in water. In addition, for ionic liquids with dodecyl substituent in the polar head, the obtained CMC values were similar to those of conventional ionic surfactants (approximately 2.2) [27]. In contrast, for the other ionic liquids with octyl and decyl substituents, the adsorption ability was much lower. Moreover, a detailed overview of the literature [11,12,19,21] suggests that the samples with the lowest tendency to form micelles among the studied morpholinium SAILs had alkyl imidazolium or alkyl pyridinium cations. Furthermore, there was an electronegative oxygen atom in the morpholinium cation that was involved in the formation of H bonds in the interaction with the aqueous medium, which affected the mode of aggregation of SAILs at the air/solution interface [19,27]. In Fig. 3, the relationship between surface tension and log C is shown.

As mentioned before, counterions also influence micellization. To analyze the effect of anions on surface activity, it was decided to divide the studied HILs into two groups. One of them was ionic liquids based on phenoxyacids, such as 2,4-D,4-CPA, MCPA, and MCPP. The second group included benzoic acid (dicamba) and picolinic acid (clopyralid) derivatives. Generally, the trend showed that all analyzed HILs with 4-CPA anions had the highest CMC values. Interestingly, the attachment of the chlorine atom to the aromatic ring of the 4-CPA anion caused an increase in the surface activity of the test salt. On the other hand, the value of the CMC parameter was slightly different for ionic liquids with MCPA and MCPP anions. This meant that the addition of the methyl group

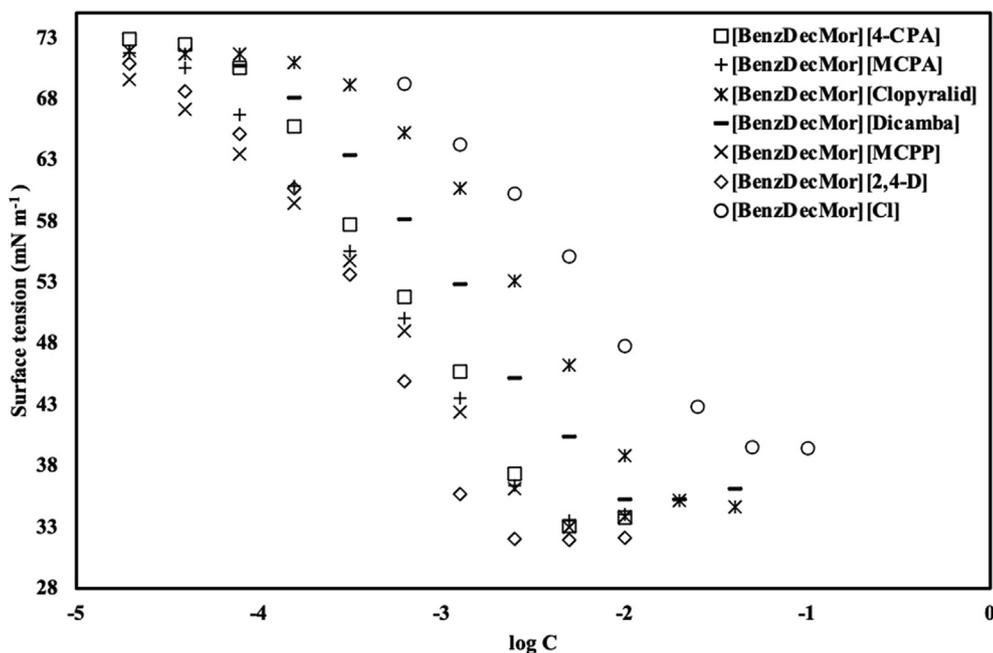


Fig. 3. Surface tension plot showing the variation of CMC with changing anions of studied HILs and their precursor.

Table 3

Surface properties of synthesized herbicidal ionic liquids.

HIL	CMC [mM]	γ_{CMC} [mN m^{-1}]	pC_{20}	ΔG_{ads}^0 [kJ mol^{-1}]
1	23.71	34.9	2.45	-17.9
2	18.29	34.2	2.83	-20.6
3	14.17	34.2	2.86	-20.6
4	13.80	34.9	2.86	-20.9
5	75.02	31.8	2.05	-14.7
6	26.18	34.5	2.50	-17.7
7	4.15	32.8	3.24	-20.7
8	2.40	32.0	3.55	-21.8
9	4.23	33.3	3.39	-22.7
10	5.33	33.1	3.49	-24.2
11	17.12	35.3	2.61	-17.4
12	9.69	35.1	2.94	-20.5
13	1.81	35.0	3.58	-22.9
14	1.02	33.8	3.85	-24.2
15	1.19	33.4	3.85	-24.6
16	1.27	33.8	3.86	-25.5
17	4.61	37.1	3.16	-21.5
18	3.06	35.1	3.44	-22.8

to the MCPP structure did not affect the adsorption capacity of the SAILs studied. Moreover, referring to the second group of salts, the highest CMC values were observed for ILs with clopyralid anions. Such results could be due to the presence of a nitrogen atom in the aromatic ring that exists in the ILs [BenzOctMor][Clopyralid], [BenzDecMor][Clopyralid], and [BenzDodecMor][Clopyralid]. Therefore, the structure of ILs with clopyralid anions determines the ability of micelles to aggregate into different forms [26].

Furthermore, as expected, HILs with an aromatic ring in the anion adsorb more readily at the interface than chlorides; this can be observed from the results obtained. The presented conclusion was determined because the aromatic ring is rich in electrons, which contributed to the higher adsorption efficiency [27].

The effectiveness of surface tension reduction is evaluated by γ_{CMC} . For the aqueous solution of the analyzed HILs, the surface tension decreased from 72.8 mN m^{-1} (value of the surface tension for pure water) to a minimum between 31.8 and 37.1 mN m^{-1} , at which a plateau was observed. In general, γ_{CMC} values differ slightly for all ionic liquids related to the specific structure of the

herbicides analyzed. Furthermore, analog values can be presented for ILs (belonging to typical herbicidal adjuvant groups) that reduce surface tension to the range of $25\text{--}40 \text{ mN m}^{-1}$ [26,28–30]. The surface adsorption efficiency at the air–water interface was correlated with the length of the alkyl chain presented in Fig. 4.

The pC_{20} of the analyzed ionic liquids ranged from 2.05 to 3.86; the lowest value was obtained for [BenzOctMor][Clopyralid] and the highest for ILs with MCPP anions. These results meant that [BenzDodecMor][MCPP] may better adsorb at the interface in comparison to the other studied HILs. In the case of the cations, the pC_{20} values increased linearly with elongation of the alkyl chain (Fig. 4). These results indicated that the adsorption efficiency of long-chain morpholinium ILs was similar to that of conventional herbicidal ionic surfactants [29,30]. An interesting relation was observed for [BenzOctMor][4-CPA] to [BenzMorDodec][MCPP]. For this group of herbicidal ionic liquids, the pC_{20} values were compared. Compounds with [2,4-D], [MCPP], [MCPA], and [4-CPA] anions are based on phenoxyacids with different substituents in

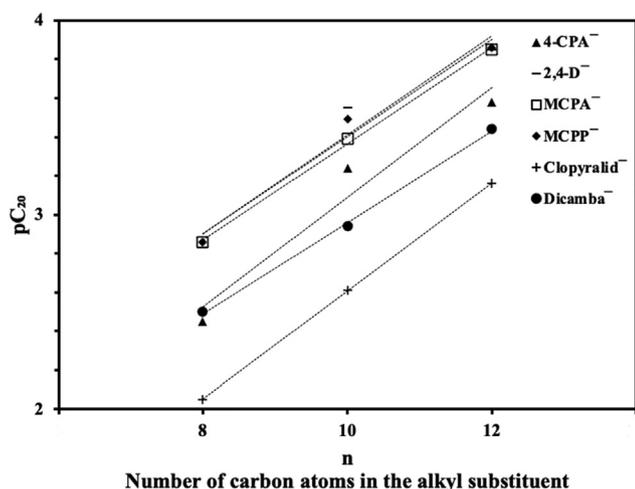


Fig. 4. Relationship between pC_{20} and the number of carbons in the cation substituent.

the cation, so they can impact the obtained results. In contrast, for ILs with clopyralid and dicamba anions, the pC_{20} values were lower than those for other herbicidal ionic liquids. In general, knowing the pC_{20} values of synthesized HILs is mainly important for designing novel herbicide formulations [26,30–32]. The standard free energy of adsorption ΔG_{ads}^0 was calculated, as seen in Table 3. The negative values of ΔG_{ads}^0 for all compounds indicate that the process proceeded spontaneously. Consequently, adsorption at the air-solution interface depends on the cation alkyl chain length [19].

3.4. Wettability of plant leaves

All morpholinium-based ionic liquids with dicamba anions were analyzed in terms of their surface activity according to two species of plants existing in fields of cornflower (*Centaurea cyanus* L.) and winter wheat (*Triticum aestivum* L.). Dicash, which is a commercially available product, was used as a reference substance since it contained an active substance analogous to the ILs tested. For example, Dicash contains dicamba dimethylammonium salt, 480 g L^{-1} .

For all solutions analyzed, the contact angle values ranged from 77.8° to 132.2° for the surface of winter wheat leaves and 45.5° to

93.0° for the surface of cornflower leaves (Fig. 5 and Table A.4 in the Supplementary Data). Thus, the results clearly show that the wettability of weed leaves is much higher than that of winter wheat leaves. Furthermore, it is confirmed that the investigated ionic liquids act selectively.

The contact angle values of the solutions studied were in the range of 62.2° to 109.6° for the paraffin surface (see Fig. 5 and Table A.4 in Supplementary Data). The CA values for winter wheat leaf area increased by approximately 20% in comparison to paraffin, while cornflower leaves decreased by approximately 30% relative to the model surface. The data show that although paraffin has a hydrophobic surface and is commonly used in the laboratory as a reference, it does not have the ability to imitate real leaves. Thus, it is confirmed that wettability is affected not only by the hydrophobic nature of the molecules that created a surface but also by the three-dimensional microstructure of the surface (for example, surface roughness). The interaction between the wetted surface and the liquid droplets is well reported in the literature [33–37].

It is well known that the adsorption of ionic liquid on a solid surface depends on the concentration of wetting substances [17,34], as shown in Figure A.16. and Table A.5, which are presented in the Supplementary Data. This analysis included two different concentrations at the CMC and the spray solution. The wettability values for HILs with concentration at the CMC were lower than those for the spray solution. Therefore, the contact angle values were within the range 58.5° to 61.1° for the concentration at the CMC and 62.2° to 94.3° for the spray solution. At this stage, it can be inferred that with increasing concentration, the wetting ability of the paraffin surface increases. In addition, for ionic liquids with dodecyl substituent in the cation, the contact angle values were on the same level for both concentrations. These results meant that the concentration at the CMC for HILs with [BenzDodecMor]⁺ could be used in the field just like the spray solution [36–39].

In addition, for all morpholinium-based ionic liquids, the CA values decreased linearly with alkyl chain elongation. One possible explanation for this observation was that the hydrophobic effect was a driving force for the formation of chemical compounds in the micelle [40]. Therefore, surfactants with long hydrophobic chains could be good candidates for herbicide formulations because they cover more surface area on the leaves, which could increase the penetration of the pesticides and result in greater weed control [9,35,41–45].

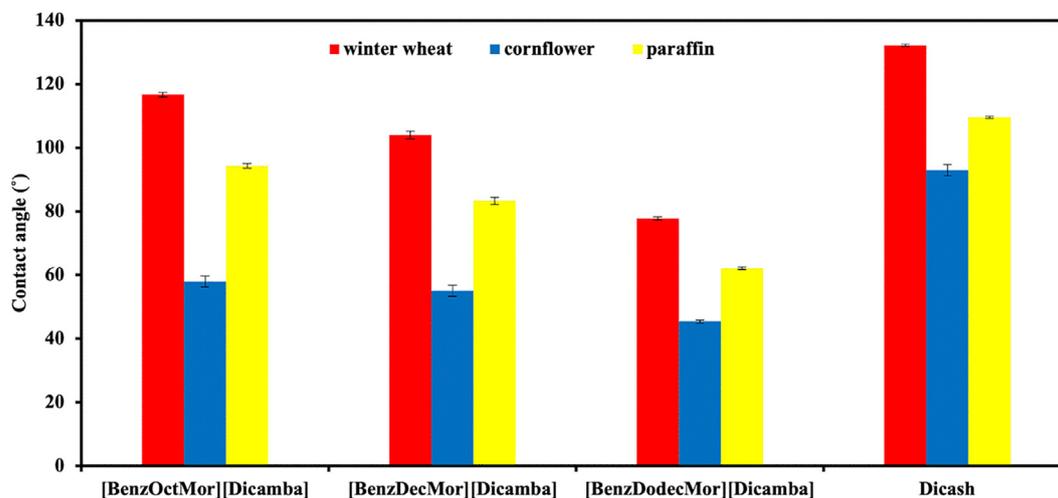


Fig. 5. Contact angle values of the ILs analyzed.

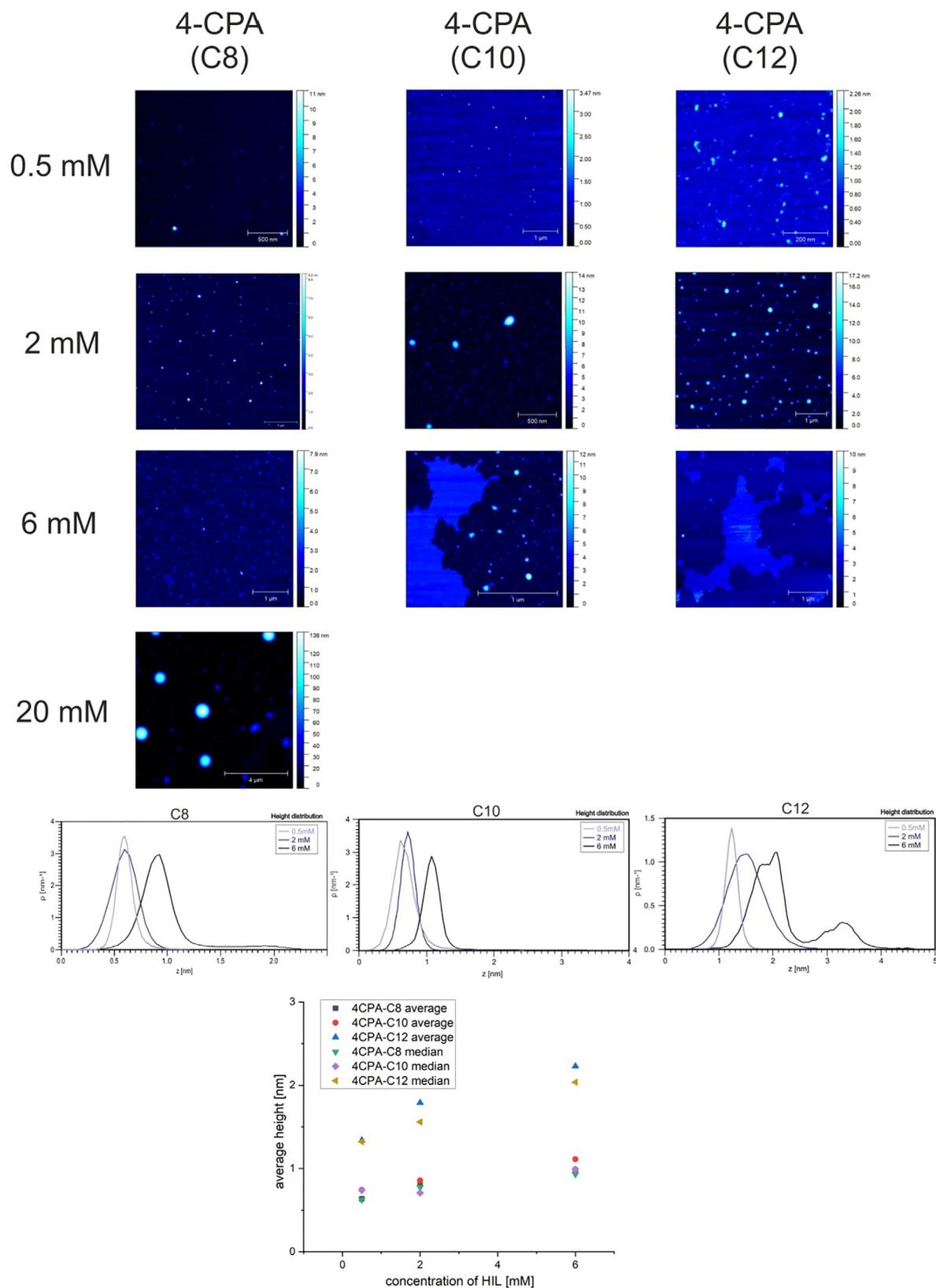


Fig. 6. AFM studies of 4CPA deposited on mica surface. The surface coverage by 4-CPA molecules with different alkyl chain lengths A) Topography of selected areas - the effect of concentration and length of alkyl chain (C₈, C₁₀ and C₁₂). B) The height distribution of selected samples depending on the surfactant concentration. C). Comparison of the mean heights and medians characterizing the tested sample areas.

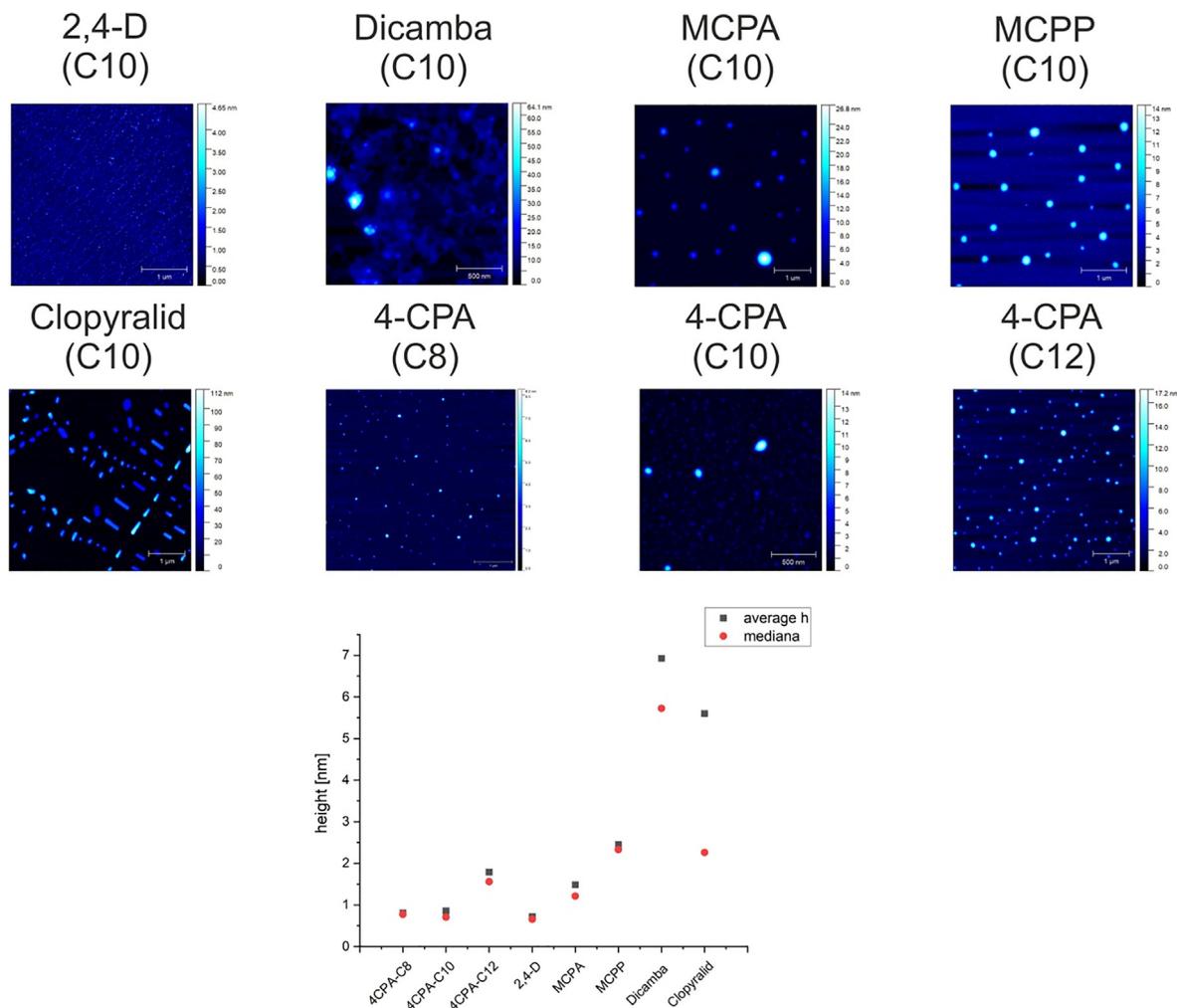


Fig. 7. A) Morphology of the microstructures formed by dried HIL samples for a concentration of 2 mM; B) Comparison of mean heights and medians for the surfaces imaged.

3.5. Topographic analysis

The potential applications of the studied surfactants in plant protection are determined by their physical properties, especially their ability to uniformly moisten and cover the surface of leaves. To characterize these features of the studied surfactants, we used atomic force microscopy, which allowed us to analyze the surface topography of the tested samples. The topography of ionic liquid samples deposited using atomic force microscopy is presented in the studied images in Figs. 6–9. Practically all studied samples form characteristic symmetric round-shaped deposits (micelles) or elongated rod-like forms. These deposits are usually formed in similar sizes within some compounds; however, there are significant differences between the studied compounds, their concentrations and their CMC values.

However, there is a clear connection between the topology of the created microstructures and the chemical structure of the tested compound, especially the size of the hydrophobic moiety and the CMC value. For the ionic liquids from the 4-CPA series, depending on the length of the alkyl chain and the CMC value, for 4-CPA C10 and C12 (CMC = 4.8 mM and CMC = 1.81 mM, respectively), the surfactant molecules deposited on the mica surface formed “islands” of uniform height. From the measurements of the height distribution of these microstructures (Fig. 6B), as well as the analysis of the mean heights or medians (Fig. 6C) for individual HILs differing in chain length, an increase in the height of the

microstructures formed was observed. The increased height correlated well with the increase in the alkyl chain length, and a better distribution of the surface coverage correlated well with an increase in the concentration of individual ionic liquids. Moreover, the best surface coverage could be observed for the ionic liquid with the longest C₁₂ alkyl chain at values above its CMC. In this case, homogeneous surface coverage by the dried ionic liquid in the form of “islands” (flat spilled surface) with an average height of 2 nm can be observed.

The analysis of the morphology of the surface covered by the ionic liquid can be crucial in the selection of the molecular geometry, as well as the optimal concentration of the ionic liquid for the production of plant protection products. The analysis of the surface coverage by the studied ionic liquids will allow the selection of the best substance that covers the leaf surface most effectively. Images of the morphology of the microstructures of the dried substances show the best and most effective surface coverage for 2,4-D, MCPA, MCPP, and dicamba. The formation of uniform layers of ionic liquid on the surface is mainly related to the surface tension (Fig. 8) and the efficiency of surface adsorption at the air–water interface (Fig. 9). MCPA and MCPP ionic liquids have a very similar arrangement, differing in the average height of the formed deposits by 1 nm. The distribution of these substances on the mica surface is similar. It is dominated by uniform larger micellar structures formed during drying, as well as evenly distributed smaller spherical structures resembling a substrate covered with 2,4-D liquid at

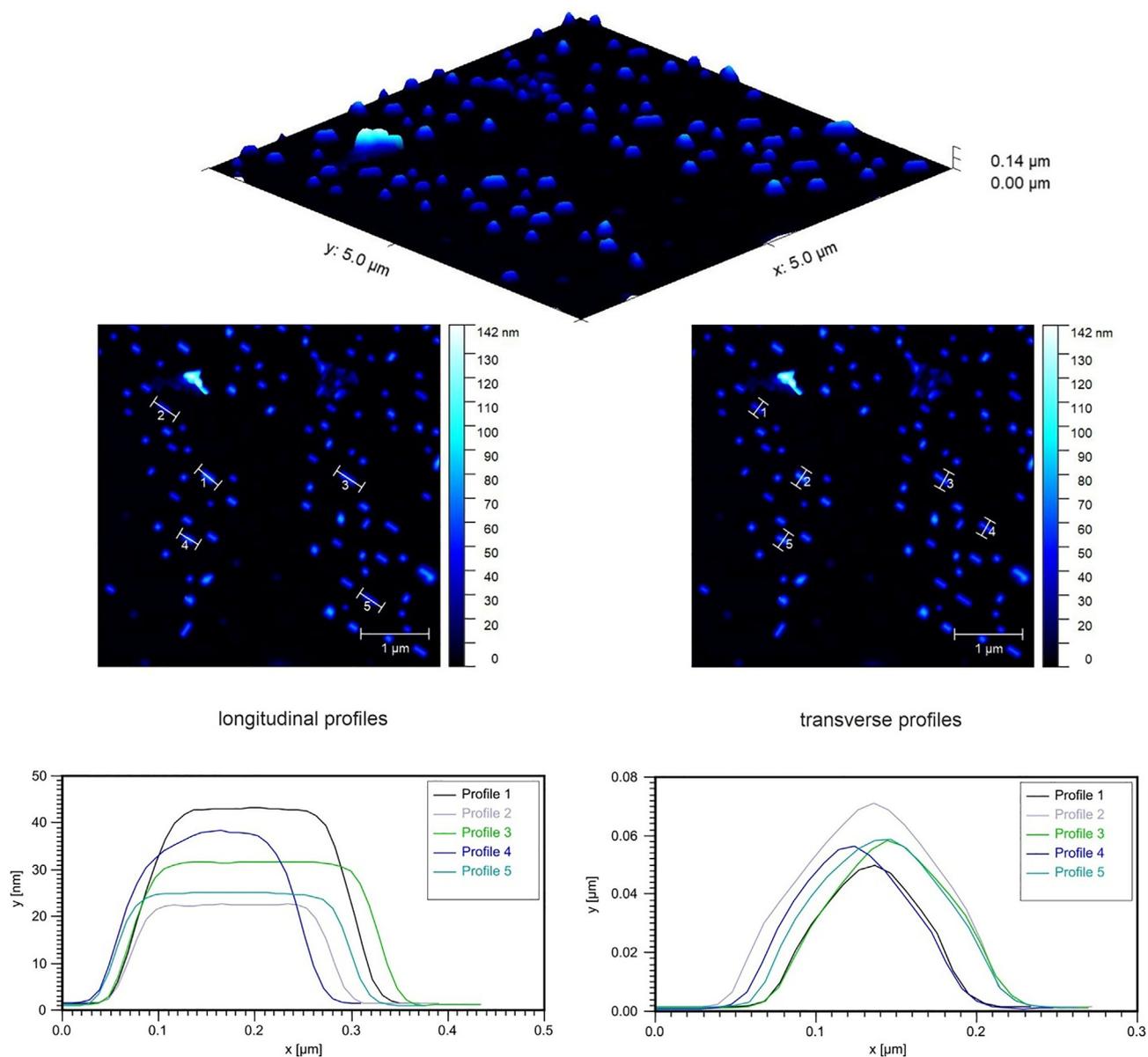


Fig. 8. The morphology of clopyralid microstructures formed on the silicon surface.

the same concentration. Therefore, one can speculate about their effective distribution on the mica surface.

The most significant differences in the deposit morphologies between anions such as 2,4-D, MCPP, MCPA, and 4-CPA and more complex anions, such as dicamba or clopyralid, can be seen in the height of the microstructures formed on the surface. The deposits of dicamba are evenly distributed over the entire mica surface, with an average height of 6–7 nm, which suggests its relatively large coverage area. Clopyralid, on the other hand, at the same concentration forms elongated, cylindrical micelles of different lengths. A comparison of the arrangement of clopyralid microstructures on the mica surface and the more hydrophobic silicon wafer is shown in Figs. 8 and 9, along with the cross-sections and longitudinal sections analyzed to determine the size of the microstructures formed.

The differences in morphology due to the deposition of clopyralid on different surfaces are rather slight. The individual structures formed on the mica are more elongated, but they are arranged the same on both surfaces so that their average distribution is comparable.

4. Conclusion

In this work, we described and investigated 18 novel ionic liquids with amphiphilic morpholinium cations and herbicidal anions based on phenoxyacids, benzoic acid derivatives, and picolinic acid derivatives. The main purpose of this dissertation was to show how the structure of the investigated ionic liquids will affect their physicochemical and biological properties. The methodology for the synthesis allowed all ionic liquids to be obtained in high yields (from 81% to 99%). Studies have shown that the structure of ionic liquids has a significant effect on physicochemical properties, such as surface activity, phase transitions, and thermal stability. The results established that all of the synthesized ionic liquids proved to be more effective against garden cress than commercial herbicides. Following the study of physicochemical properties, the greatest surface activity was observed to be characterized by salts with dodecyl substituent. This surface activity is caused by the elongation of the alkyl chain in the cation. The results indicated that paraffin, despite its hydrophobic properties, does not reflect biological surfaces. The values of the wetting angle measured for

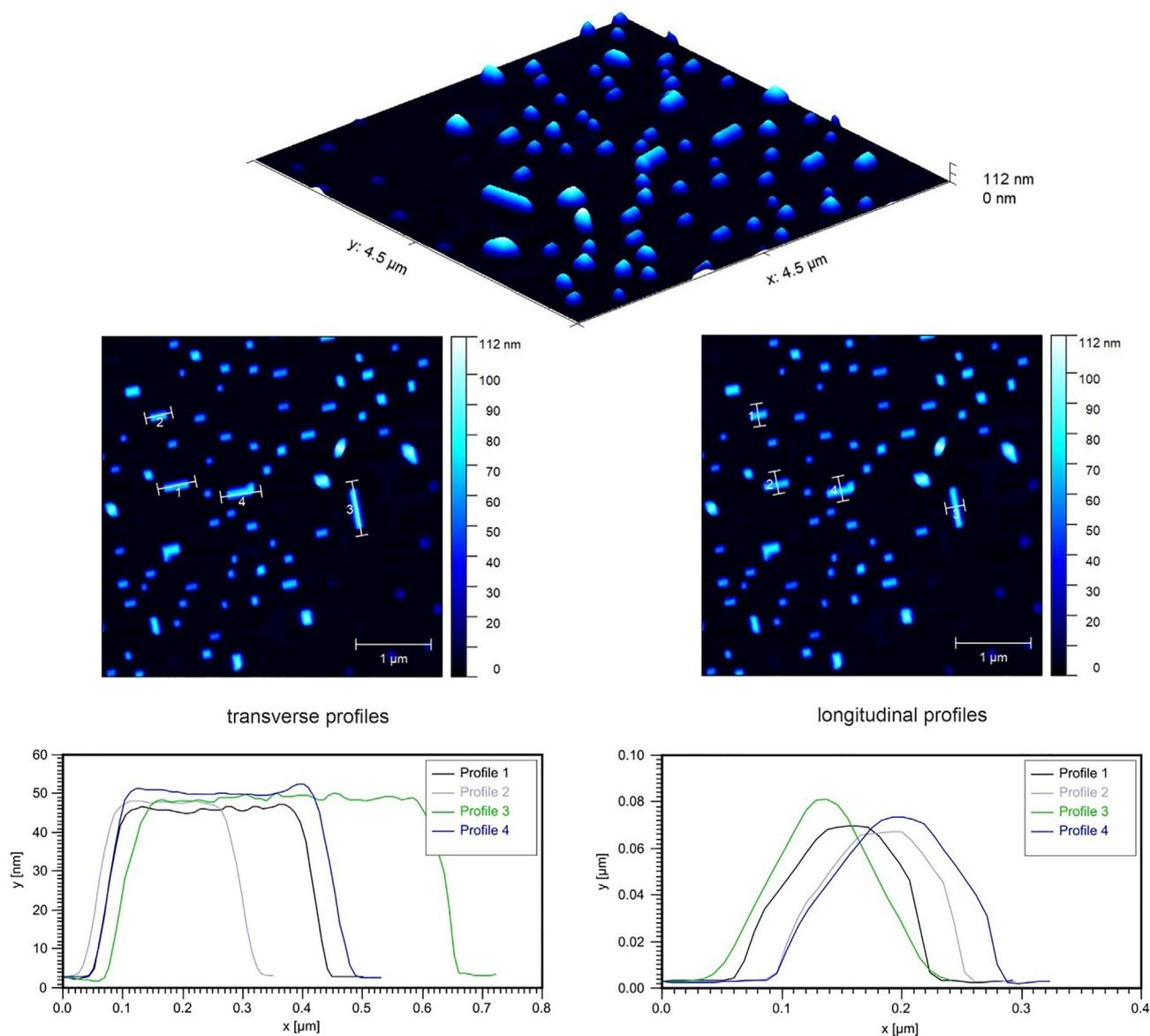


Fig. 9. The morphology of clopyralid microstructures formed on the mica surface.

the paraffin surface were between those achieved for the surfaces of the wheat and cornflower leaves. In addition, the primary advantage of morpholinium ionic liquids is the better wettability of the weed leaf surface compared to that of a commercial herbicide. There is a large difference in the amount of deposited microstructures between ionic liquids, and these differences are most visible for dicamba and clopyralid anions. The estimations of the surface coverage are compatible with the surface tension measurements and the surface adsorption efficiency at the air-water interface. We believe that the behavior of HIL droplets with surface activity is an interesting issue. In conclusion, the present study showed that morpholinium ionic liquids with herbicidal anions have high potential for use as weed control agents.

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.

Acknowledgments

This work was funded by the Polish Ministry of Education and Science as a subsidy to Poznan University of Technology, Poland (0912/SBAD/2208).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2022.119750>.

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