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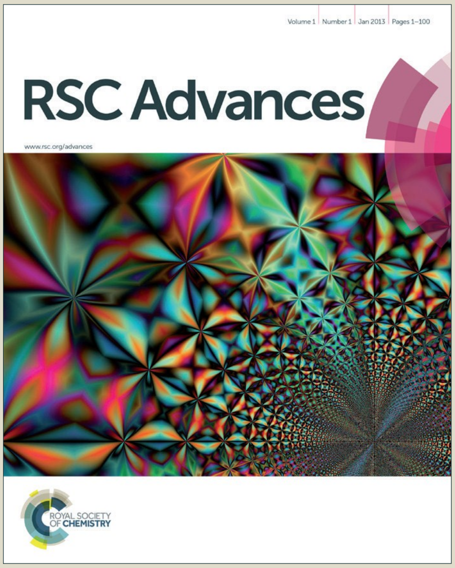

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Synthesis, properties and evaluation of biological activity of herbicidal ionic liquids with 4-(4-chloro-2-methylphenoxy)butanoate anion

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Abstract

In this study, fourteen new herbicidal ionic liquids (HILs) based on MCPB with 1-alkyl-1-methylpiperidinium cation were synthesized and characterized. The influence of alkyl chain length on physicochemical properties of HILs was described. Additionally, thermal analysis, solubility in ten representative solvents, and surface as well as herbicidal activity were determined. The herbicidal efficacy was tested in greenhouse experiments using common lambsquarters (*Chenopodium album L.)* and oilseed rape (*Brassica napus L.)* as test plants. The obtained ionic liquids proved to be more effective than the commercial herbicide. Moreover, the relationship between HILs surface activity and herbicidal efficiency was found.

1. Introduction

Herbicidal ionic liquids (HILs) are novel ionic liquids defined as organic compounds with a melting temperature below 100°C, which contain ions that exhibit herbicidal activity.[1] Their discovery in 2011 showed that it was possible to obtain new phytopharmaceuticals, which exhibit increased biological activity and multifunctional properties. This provided the opportunity to produce novel, effective formulations based on currently manufactured herbicides, such as the derivatives of phenoxyacetic acid (2,4-D, MCPA and MCPP)[1-4], benzoic acid (dicamba)[5], clopyralid[6], fomesafen[7], glyphosate[8], metsulfuron methyl (MS-M)[9], or bentazone[10]. It is also possible to synthesize HILs, which display two different biological functions: 2-chloroethyltrimethylammonium cation as a growth regulator with MCPA[11] or 2,4-D[12] anion. The first advantage of HILs compared to commercial herbicidal formulations is associated with their limited volatility.[5] This eliminates the problem of contamination through air emissions. The synthesis of HILs allows for a reduction of the herbicide dose per hectare, decrease of toxicity (toxic phenoxy herbicides may become nontoxic as HILs[1]) and introduction of unique physicochemical properties (thermal stability, solubility, and surface activity). Additionally, the chemical structure of the cation may be modified in order to directly regulate the environmental impact, toxicity and biodegradability.[13,14]

Furthermore, several novel reports show that ionic liquids may be used in order to improve the immunity of plants to pathogenic factors, e.g. by inducing plant systemic acquired resistance towards viral diseases[15,16] or fungi[17]. Recently protic ILs have been described as solvents for the solubilisation and stabilization of viruses.[18]

MCPB is a post emergent systemic hormone-type herbicide (phenoxy carboxylic acid) for early control of annual and perennial broad-leaved weeds. It is selective for cereals, clovers, sainfoin, peas, peanuts, and grassland. It is absorbed by the leaves and roots, then translocated into plant tissues. In susceptible plants, MCPB is metabolically transformed to the corresponding 2-methyl-4-chlorophenoxyacetic acid (MCPA) but in the resistant plants this process does not occur.[19] MCPB demonstrates high efficacy against cresses, docks, fathen, field bindweed, hedge mustard, redroot, sheperd's purse, thistles. It degrades relatively quickly in soil (DT_{50} c. 5-7 days) but it is moderately toxic to aquatic organisms. In the market, it is used mainly in combination with other herbicides. Many hormone-type herbicides, including MCPB, were discovered over 60 years ago, but they still play a major role in the herbicide resistance strategy and control of difficult weeds in cereal crops.[20]

Mepiquat chloride, widely used as a growth regulator, and its analogs can be used as sources of cations for synthesis of ionic liquids.

The main objective of our research was to synthesize the new MCPB-based ionic liquids with 1-alkyl-1-methylpiperidinium cation as potential novel herbicides. This paper shows the influence of the length of alkyl chain attached to the cation on physicochemical properties, solubility, thermal stability, and surface as well as biological activity of the obtained HILs. Furthermore, the correlation between the herbicidal efficiency and the adsorption parameter pC_{20} is also presented.

2. Experimental

2.1. Materials

Bromoethane 99%, 1-bromododecane 99%, 1-bromotetradecane 98%, 1-bromohexadecane 98,8% and 1-methylpiperidine 99% were purchased from Merck.1-Bromopropane 99%, 1-bromobutane 99%, 1-bromopentane 98%, 1-bromohexane 98%, 1-bromoheptane 99%, 1-bromooctane 99%, 1-bromononane 98%, 1-bromodecane 98%, 1-bromoundecane 98%, 1-bromooctadecane 97%, anion exchange resin Dowex-Monosphere 550A (OH), γ-butyrolactone 98%, 4-chloro-2-methylphenol 97% were purchased from

Sigma-Aldrich. All solvents (methanol, DMSO, acetonitrile, acetone, isopropanol, ethyl acetate, chloroform, toluene, hexane) and NaOH were purchased from Aldrich (European market, Poznan, Poland) and used without further purification.

2.2. Preparation of HILs

4-(4-Chloro-2-methylphenoxy)butanoic acid was prepared according to procedure described in patent.[21] 1-Alkyl-1-methylpiperidinium bromides were synthesized according to the previously described protocol.[22] The reaction times were longer (48 h) and were not optimized. The experiments were conducted under argon atmosphere. The crude product was dried under reduced pressure (20 mm Hg) at 50 °C for 10 h. An anion exchange resin (0.02 mol) and 200 mL of distilled water were placed in a 500 mL round-bottom flask equipped with a mechanical stirrer and the obtained suspension was vigorously stirred for 1 hour. Then, 1-alkyl-1-methylpiperidinium bromide (0.01 mol) was added and ion exchange reaction was conducted at room temperature for 5 hours. The resin was filtered off and rinsed with small amounts of distilled water. Next, the 4-(4-chloro-2-methylphenoxy)butanoic (MCPB) acid (0.01 mol) was gradually added to neutralize the obtained 1-alkyl-1-methylpiperidinium hydroxide solution. Afterwards, the water was removed using a rotary evaporator and the product was dried under reduced pressure (5 mm Hg) at 50 °C for 12 h.

2.3. Methods

General: ^{1}H NMR spectra were recorded on a Mercury Gemini 300 and Varian VNMR-S 400 MHz spectrometers operating at 300 MHz and 400 MHz with TMS as the internal standard. ^{13}C NMR spectra were obtained with the same instruments at 75 and 100 MHz, respectively. Elemental analyses (CHN) were performed at the Adam Mickiewicz University, Poznan

(Poland). The water content was determined by using an Aquastar volumetric Karl Fischer titration with Composite 5 solution as the titrant and anhydrous methanol as a solvent.

Density was determined using an Automatic Density Meter DDM2911 with a mechanical oscillator method. The density of the samples (approx. 2.0 mL) was measured with respect to temperature controlled conditions via Peltier, from 20 to 80 °C. The apparatus used was calibrated using deionized water as the reference substance. After each series of measurements, the densimeter was washed by two kinds of solvents (methanol and acetone) and dried. Viscosity was determined using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosity of the samples (approx. 1.5 mL) was measured with respect to temperature, from 20 to 80 °C. The uncertainty of the viscosity measurement was estimated to be less than 10^{-4} Pa·s. Refractive index was determined using Automatic Refractometer J357 with electronic temperature control.

Thermal Gravimetric Analysis (TGA): TGA was performed using a Mettler Toledo Star^{e} TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples (between 2 and 10 mg) were placed in aluminum pans and heated from 30 to 450 °C at a heating rate of 10°C/min.

Differential Scanning Calorimetry (DSC): Thermal transition temperature was determined by DSC, with 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 120 °C at a heating rate of 10 °C/min and cooled with an intracooler at a cooling rate of 10°C/min to -100 °C and then heated again to 120°C.

The cationic active substance content: The cationic active substance content was assayed by a direct two-phase titration according to EN ISO 2871-1:2010. The method is based on the titration in the water-chloroform biphasic system (or water-methanol-chloroform in the case of compounds with limited solubility in water) of the solution of ammonium salt by a standard solution of sodium dodecylsulphate(VI) in the presence of the mixed indicator (dimidium bromide indicator (CAS: 518-67-2) is used for determination of cationic active substances; and sulfan blue indicator (CAS: 129-17-9) is employed for determination of anionic active substances.

Solubilities: The solubilities of the prepared salts in ten representative solvents were determined according to the protocols described in Vogel's Textbook of Practical Organic Chemistry.[21] A 0.1 g sample of each salt was added to a certain volume of the tested solvent and the samples were thermostatted in Water Bath MEMMERT Model WNB 7 at 25 °C. Based on the volume of solvent used, 3 types of behaviors were recorded: 'soluble' applies to compounds which dissolved in 1 mL of the solvent, 'limited solubility' – applies to compounds that dissolved in 3 mL of the solvent, and 'not soluble' – applies to the compounds which did not dissolve in 3 mL of the solvent.

Surface activity: Surface tension and contact angle measurements were carried out by the use of a DSA 100 analyzer (Krüss, Germany, accuracy ±0.01 mN m^{-1}), at 25°C. The surface tension was determined using the shape drop method. Basically, the principle of this method is an axisymmetric drop at the tip of a needle. The image of the drop (3 mL) is taken from a CCD camera and digitized. The surface tension (g in mN m^{-1}) is calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy ±0.1 °C). The values of the critical micelle concentration (*CMC*) and the surface tension at the CMC (γ_{CMC}) were determined from the plot γ vs $log\ C$ using a linear regression analysis method.

Surface excess concentrations Γ_{max} were calculated using the Gibbs isotherm: $\Gamma_{\max} = -\frac{1}{RT} \cdot \frac{d\gamma}{d(\ln C)}$, where: Γ_{max} denotes the surface excess concentration at the saturated interface, R denotes gas constant and T the absolute temperature, C denotes concentration of salt. From Γ_{max}, the minimum surface occupied by a molecule at the interface A_{min} was calculated from equation: $A_{min} = \frac{1}{\Gamma_{max} N_A}$, where N_A denotes the Avogadro number.

The determination of the contact angle is based on the sessile drop method, i.e. drops of liquid are deposited on a solid surface (paraffin).

Greenhouse experiments: Common lambsquarters (*Chenopodium album L.*) and oilseed rape (*Brassica napus L.*) plants were grown in 0.5 L plastic pots containing commercial peat-based potting material. Within 10 days after emergence, the plants were thinned to five per pot and watered as needed. Greenhouse conditions were as follows: temperature of 20±2 °C, humidity at 60% and photoperiod of 16/8 day/night hours. Each experiment was arranged in a completely randomized design with at least four replications per treatment. Controls were included in all experiments.

The prepared salts were dissolved in water and the plants were treated with the solution only once, at the 6-8 leaves growth stage. The applications were conducted using a moving sprayer (APORO, Poznan, Poland) with a TeeJet® VP 110/02 (TeeJet Technologies, Wheaton, IL, USA) flat-fan nozzle capable of delivering 200 L ha^{-1} of spray solution at 0.2 MPa operating pressure. The sprayer was moved above the plants (40 cm distance) at a constant speed of 3.1 m/s. Fresh weight of plants was determined two weeks after treatment (2 WAT). Data were expressed as percent of fresh weight reduction compared with untreated plants. The program package ARM (Agriculture Research Management) was used for the statistical calculations. Only normally distributed data was analyzed by analysis of variance (ANOVA).

3. Results and discussion

3.1. Synthesis and physicochemical properties

Fourteen piperidinium salts presented in Table 1 were synthesized by using a two-step approach. The obtained products possessed 1-alkyl-1-methylpiperidinium cation, wherein alkyl varied from ethyl to octadecyl. The first step of synthesis involved utilizing an ion-exchange reaction in an ion-exchange column, wherein the halide anion was replaced by the hydroxide ion. The second step involved a direct acid-base reaction between the obtained hydroxides and MCPB free acid in 1:1 stoichiometric ratio (Scheme 1). Finally, the products were dried under vacuum at 50 °C for 24 h and stored over P_4O_{10}.

All salts were obtained in high yields exceeding 90%. The purity of salts with long alkyl chains (**7–14**) was determined *via* the direct two-phase titration technique, which proved to be very effective in defining the surface active substance content in the product. According to this method, the synthesized salts were characterized by high purities (Table 1) from 97% for **14** to 99% for **7**, **8** and **11**. Additionally, elemental analysis results allowed to validate the identity and purity of the synthesized salts.

Structures of the obtained new piperidinium salts were confirmed by ^1H and ^{13}C NMR spectroscopy. NMR spectra descriptions as well as elemental analysis results for salts **1-14** are provided in the Supporting Information (Fig. S1-S28). The water content in the product was determined by Karl-Fischer measurements and was found to be less than 1000 ppm for all salts. Furthermore, all products were stable in air and in contact with water and the tested organic solvents. The concentration and colour of solutions of synthesized salts were both constant during a period of two weeks.

Eight salts (**1-4**, **11-14)** were waxes and six (**5-10)** were liquids at room temperature. All of the synthesized salts did not undergo phase transfer to the solid state at 100 °C, therefore they could be classified as ionic liquids (ILs). Moreover, ILs **5-10** may be described as room temperature ionic liquids (RTILs) due to low melting points. Their physicochemical properties, such as viscosity, density and refractive index, were determined in range from 20 to 80 °C and presented in Figs. 1-4 (the collected physicochemical data are provided in the Supporting Information in Tables S1-S3).

The influence of temperature on the viscosity values for ILs **5-10** is presented on Fig. 1. At 20 °C the values of viscosity for the synthesized salts differ from 1.429 Pa·s for compound **5** to 13.094 Pa·s for **9**. Although several reports[24,25] show that the viscosity increases as the size of the non-polar part of the cations becomes larger, this phenomenon was not observed for the obtained ILs. All ILs exhibited similar viscosity values between 1.429 and 2.270 Pa·s, except **9**, which exhibited a viscosity value several times greater (Supporting Information, Table S1). Similar tendency has been already observed for HILs with other phenoxyacetate anion (MCPA). There was also no relationship between an increase in length of alkyl as well as alkoxymethyl chain in the ammonium cation and measured viscosities. Therefore, the highest values in homologous series possessed HILs with tetradecyl and octyloxymethyl substituents.[4] This specific behaviour may be connected with altered coordinating ability of phenoxycarboxylate anions compared to conventional, structurally simpler anions.

Furthermore, viscosity of the prepared ILs was relatively higher compared to most known piperidinium ILs. For example values ranging from 0.108 to 0.481 Pa·s (at 20 °C) were reported for bis(trifluoromethylsulfonyl)imides which were extensively studied for electrochemical applications.[26,27] As for other obtained ILs, the viscosity decreased nonlinearly with increasing temperature. Hence, an increase in temperature from 20 to 80 °C caused a rapid reduction of the analysed parameter, which finally ranged between 0.041 and 0.058 Pa·s.

The density of RTILs (**5-10**) was higher compared to the density of pure water (Fig. 2). Values determined at 20 °C ranged from 1.056 g cm^{-3} for **10** to 1.107 g cm^{-3} for **5** and were similar to other previously described ILs.[4,13] The values of density for the obtained ILs were temperature-dependent and linearly decreased with an increase in temperature . Hence, a temperature increase from 20 to 80 °C resulted in the reduction of this parameter by approx. 0.04 g cm^{-3} for all analysed salts (Supporting Information, Table S2). Moreover, Fig. 4 shows that density of the studied ILs linearly decreased with elongation of the alkyl chain. The chain extension by one carbon atom resulted in a slight decrease (approx. 0.01 g cm^{-3}) of density which is consistent with the literature data.[28,29]

ILs are often characterized by higher values of the refractive index as compared with conventional solvents. The measured indices mostly vary in the range from 1.40 to 2.20 depending on the structure of the cation and anion.[30-32]

Refractive index values of the synthesized ILs (**5-10**) at 20 °C ranged from 1.507 for **10** to 1.514 for **5** (Supporting Information, Table S3). Similar to density measurements, increase of temperature caused a linear and slight decrease of refractive index values, as shown in Fig. 3. Finally, at 80 °C the refractive indices were lower by approx. 0.018 and reached values below 1.500 for all compounds. Furthermore, the obtained results show that the elongation of alkyl substituent causes a decrease of index values (Fig. 4). This phenomenon was already observed and described in the literature, but mainly for imidazolium ILs.[32] Surprisingly, two linear relationships were found between refractive index at 20 °C and the chain length of the alkylpiperidinium ILs. The first one, characterized by a low slope of regression line ($y = -0.00028x + 1.516; R^2 = 0.99$) , refers to products comprising an even number of carbon atoms in the alkyl chain (ILs **5**, **7**, **9** with number of carbon atoms: 6, 8, and 10). The compounds with an odd number of carbon atoms (ILs **6**, **8**, **10** with number of carbon atoms: 7, 9, and 11) are represented by the second, more inclined line ($y = -0.00145x + 1.523; R^2 = 0.95$), which resulted in their lower values compared to ILs **5**, **7** and **9**. On the other side, only 3 points in regression line are not sufficient for us to unquestionably confirm mentioned hypothesis of linearity and the determined values might have arranged accidentally. However, an increase in alkyl length affect refractive index values differently than other physicochemical properties, which illustrates also that this dependence requires further research.

3.2. Thermal analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data for the ILs are presented in Table 2. Among all prepared ILs, six (**5-10)** were liquids below 20 °C. For three of them (**5**, **7**, **8)** neither melting nor crystallization events were observed in the analysed temperature range. The lowest melting point was noted for **10** (T_m = -27.3 °C), which additionally possessed a crystallization event during cooling at 23.0 °C. ILs with shorter (**1-4**) or longer (**11-14**) alkyl substituents melted at slightly higher temperatures between 36.5 °C for **11** and 64.3 °C for **3**.

This characteristic behaviour of ILs has been described repeatedly in the literature.[33,34] Nevertheless, all obtained salts exhibit a melting point below 100 °C and therefore all may be classified as ILs. The differences between crystallization temperatures of synthesized salts were small and ranged from -4.5 °C for **13** to 20.3 °C for **10**. However, the obtained results were diversified and did not allow to determine the effect of the alkyl chain length on this parameter. Surprisingly, two crystallization events (T_c = 6.1/19.5 °C) were observed during cooling of **14**. This phenomenon might be attributed to the presence of high molecular and long alkyl chain substituent attached to the ammonium cation, which may be connected with formation of two different crystalline structures.

Analysis of structure *vs* glass transition relationships revealed a known trend - the longer the alkyl chain substituent attached to the nitrogen atom, the lower the glass transition of the resulting IL. However, the changes of glass transition temperatures resulting from the difference in the length of the alkyl chain are generally much smaller than in case of the melting temperatures. It is believed that the rapid decrease of glass transition temperatures with increasing alkyl chain length was due to the elongation of the molecular chain, which disrupted the crystal packing and reduced the lattice energy.[35,36] The further increase of the alkyl chain length enhanced the attractive van der Waals interactions and then led to a significant increase of melting points as well as glass transitions, which was already reported for ammonium or imidazolium ILs.[33,37,38] Therefore, the lowest glass transition temperature (T_g = -43.8 °C) was observed for the **11** with the 1-dodecyl-1-methylpiperidinium cation and along with the increase of the alkyl chain length there is an increase of this phase transition. In consequence, the glass transition temperature for **12**, **13** and **14** was equal to -20.9, -12.1 and 1.6 °C, respectively.

Only ILs **1-4** comprising a short alkyl substituent exhibited simple thermal decomposition behaviour with a single decomposition step (Table 5). However, the other ILs were characterized by a two-, three- or even four-step decomposition, which is directly connected with the partial decomposition of alkyl chains attached to nitrogen atom. Thermograms of ILs **1** (1 deg. step), **5** (2 deg. steps), **9** (3 deg. steps) (**12**) (2 deg. steps), **14** (3 deg. steps) are presented in Fig. 5. The lowest decomposition temperatures $T_{onset5\%}$ were observed for both ILs with butyl (**4**) and pentyl (**5**) group: 158 °C and 154 °C, respectively. Moreover, the results demonstrated that $T_{onset5\%}$ values appear to be related with the length and molecular weight of the R substituent. Hence, temperatures exceeding 200 °C were observed for ILs possessing an undecyl or longer group.

This tendency is also visible in Fig. 5, where decomposition temperatures (T_{onset}) rise with the increase in length of alkyl chain. Generally, it is consistent with data collected for other HILs.[4] However, according to published reports, decomposition temperatures may be mainly independent on the alkyl chain length of the some ammonium or imidazolium ILs.[38,39]

Surprisingly, the lowest decomposition temperature (T_{onset}) was observed for IL with the octyl group (**7**) (T_{onset} = 224 °C), which was approximately 40 °C smaller than values obtained for other ILs with a medium-length alkyl chain (**6**, **8**). On the other hand, **13** and **14** exhibited the highest thermal stability, thus their T_{onset} values were equal to 347 and 367 °C, respectively.

3.3. Solubility

The solubilities of the prepared ILs were tested in ten representative solvents, varying from high polarity to low polarity. The solvents chosen for study were selected based on a decreasing order of polarity, expressed as the 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; hexane, 0.0. The results are presented in Table 3. As expected, almost all tested ILs were soluble in the most polar solvents such as water, methanol and DMSO. Nevertheless, only two ILs, possessing the longest alkyl substituents **13** and **14** were hydrophobic. It leads to conclusion that the presence of alkyl chain comprising more than 14 carbon atoms in MCPB-based HIL reduces the water solubility. This observation may particularly be useful from the point of view of controlling of groundwater mobility of a new herbicide.

Slightly less polar aprotic acetone and isopropanol also dissolved all ILs regardless of their carbon chain length. Interestingly, only ILs with alkyl group from pentyl to nonyl (**4-8**) were insoluble in acetonitrile. This means, that a decrease or increase of the alkyl chain length improves the affinity to this solvent. The opposite behaviour was found for ethyl acetate, which easily dissolved ILs comprising medium-length alkyl chains (**5-11**). Thus, IL **2**, **3** and **5** demonstrated limited solubility and the rest (**1**, **12-14)** was insoluble. Despite similar Snyder polarity index values (4.3) isopropanol and ethyl acetate demonstrated distinctly different influence of carbon alkyl length on solvent affinity. Due to the presence of ionic bond in the structure of IL, this alcohol as semipolar protic solvent appeared to be better diluent than tested aprotic semipolar ester of acetic acid.

The popular chlorinated solvent - chloroform, even though of relatively low polarity, dissolved all ILs. Moreover, all tested ILs were insoluble in nonpolar hexane and the majority of them (**5-14**) was soluble in toluene. The presence of a short-chain substituent attached to piperidinium cation hinders the solubility in this nonpolar solvent. The differences in solubility of HILs in three the least polar solvents, may find an explanation in their dielectric constant values. Obtained results confirm the hypothesis that ionic liquids are generally immiscible with liquids possessing low dielectric constants. Therefore, none of the obtained HILs dissolved in hexane (d.c. = 1.9) and the some of them were miscible with toluene (d.c. = 2.4). Chloroform as the solvent with the highest dielectric constant (d.c. = 4.8) dissolved HILs the most effectively.[23,40]

3.4. Surface activity

The surface-active properties of the prepared ILs are summarized in Table 4. Surface activity of ionic liquids can be evaluated by the γ_{CMC}, the effectiveness of surface tension reduction. For studied ILs aqueous solutions, the surface tension decreased from the water value to a minimum located between 33.5 to 42.9 mN m^{-1}. In the case of **1-6** the solutions manifested the highest γ_{CMC} values (from 40.8 to 42.9 mN m^{-1}). This demonstrated that the ILs with longer alkyl substituent exhibited more pronounced intermolecular hydrophobic interactions, making it easier to form aggregates in water (in parallel with the substituent elongation).

The *CMC* value decreased from **1** to **14** as expected from the increased hydrophobicity due to the elongation of hydrocarbon chain (Fig. 6). The values of area per molecule A_{min} were lowest for **10** and **11**, indicating that the molecules of the ILs **10** and **11** are more tightly packed at the water–air interface.

The adsorption efficiency, pC_{20} is defined as the negative logarithm of the surface active compound concentration in the bulk phase required to reduce the surface tension of the water by 20 mN m^{-1}. Thus, the greater the pC_{20} value, the higher the adsorption efficiency of the surface active compound. The efficiency of adsorption of a surface active compound at the surface, as measured by the pC_{20} value, was increased linearly with an increase in the number of carbon atoms in the hydrophobic chain.

In the case of wetting, the reduction of contact angle of the drop from 77.4 to 70.8 was observed for **1-6**, and to 62.5-52.4 for **7-14** (Table 4). Better wettability of paraffin surface, which is similar to the real surface of plants, observed for MCPB salts may be useful in future application of these ILs as herbicides.

3.5. Herbicidal activity

The greenhouse tests carried out with common lambsquarters and oilseed rape plants showed good efficacy of all ILs used at the dose equivalent of 600 g a.i. per 1 ha. Because MCPB is transformed to MCPA in the susceptible plants, the efficacy of tested ILs was compared with commercial product containing MCPA-salt. Data in Table 5 indicate that the level of weed control depended both on weed species and tested compound but in many cases the differences between HILs were not significant.

ILs with shorter aliphatic chain were characterized by a slightly lower activity as compared to those with longer alkyl chains, especially in the case of oilseed rape control. The most active compound was **9**, which exhibited the efficacy of 95%, but **10**, **12**, **13** and **14** also gave very good results. The statistical analysis showed that the differences between the above-mentioned compounds were not significant.

The biological activity of ILs was similar or better compared with commercial herbicide and therefore the tested homologous series of compounds can be classified as new herbicidal ionic liquids.

The effectiveness of ILs was dependent on their structure and weed species. Trends in the case common lambsquarters and oilseed rape are similar. In both cases a considerable improvement in the effectiveness can be observed when **9** was applied. It was established that this IL exhibited a significant decrease of the critical micelle concentration as compared to ILs of the shorter aliphatic chain. Surface tension is an important parameter influencing the surface properties of compounds. Low value of this parameter characterizes ILs with good surface properties. **9-14** exhibited the desired values of this parameter (33.6–35.8 mmol L^{-1}). High efficacy of these ILs can be observed in the case of oilseed rape. The herbicidal activity observed for oilseed rape as a function of the pC_{20} is shown in Fig. 7. The bulk liquid phase concentration of surfactant required to decrease the surface tension of the solvent by 20 mN m^{-1} is a good measure of the efficiency of adsorption of ILs. The efficiency of sorption of a given IL at the surface can be related to its herbicidal efficacy. It was observed that with increasing length of hydrophobic chain the herbicidal activity increased. For HILs with shortest chains a variation was observed in the form of higher values of the efficiency (for **1** and **2** than for **3-8)**. This can be explained mainly by the action of the anion and negligible impact of the cation on the relevant parameter. The maximum value of herbicidal efficacy was recorded for **9** ($R=C_{10}H_{21}$). For substituents containing more than 10 carbon atoms (**10** and **11),** the obtained results were surprisingly low, presumably due to excessive foaming. The reported values of efficacy for **12-14** were slightly lower than **9** (probably because of lower solubility in water), and remained stable at a similar high level (88-90%).

4. **Conclusions**

In this study, new MCPB-based ionic liquids with 1-alkyl-1-methylpiperidinium cation were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy. The studied physicochemical properties of the obtained salts (viscosity, density, refractive index values, and solubility) were influenced by the length of alkyl chain attached to the cation. The TGA and DSC analyzes confirmed that all the obtained salts were thermally stable and exhibited melting points below 100 °C. Furthermore, the herbicidal activity of all the obtained salts towards common lambsquarters and oilseed rape was similar or better compared to the commercial herbicide (MCPA – salt; herbicidal efficacy at 70%), therefore they can be classified as HILs. It was established that HILs comprising longer alkyl chains (C_{10}-C_{18}) exhibited higher herbicidal activity (80-95%), whereas those with shorter alkyl chains (C_2-C_9) were less efficient (70-80%), which was especially visible during tests on oilseed rape. The best results were obtained after treatment with HIL comprising the dodecyl chain ($R=C_{10}H_{21}$), which also displayed potent surface active properties. On this basis it was possible to correlate the herbicidal efficiency with the adsorption parameter pC_{20}. These findings provide structural and functional fundaments for the synthesis of efficient crop protection agents for future applications.

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Table 1 Synthesized piperidinium salts

Salts	R	Yield (%)	Purity (%)	State at 25 °C
1	C_2H_5	93	---	Wax
2	C_3H_7	94	---	Wax
3	C_4H_9	96	---	Wax
4	C_5H_{11}	95	---	Wax
5	C_6H_{13}	92	---	Liquid
6	C_7H_{15}	91	---	Liquid
7	C_8H_{17}	93	99	Liquid
8	C_9H_{19}	92	99	Liquid
9	$C_{10}H_{21}$	91	98	Liquid
10	$C_{11}H_{23}$	94	98	Liquid
11	$C_{12}H_{25}$	93	99	Wax
12	$C_{14}H_{29}$	91	98	Wax
13	$C_{16}H_{33}$	93	98	Wax
14	$C_{18}H_{27}$	92	97	Wax

Table 2 Thermal properties of the obtained ILs

ILs	R	T_m[a] (°C)	T_c[b] (°C)	T_g[c] (°C)	Steps of degradation	$T_{onset5\%}$[d] (°C)	T_{onset}[e] (°C)
1	C_2H_5	40.3	-2.7	-31.2	1	187	254
2	C_3H_7	59.6	16.2	-32.8	1	184	252
3	C_4H_9	64.3	7.5	-29.2	1	158	243
4	C_5H_{11}	39.9	-2.8	-36.1	1	154	252
5	C_6H_{13}	---	---	-35.4	2	197	260
6	C_7H_{15}	19.7	4.5	-32.1	2	190	262
7	C_8H_{17}	---	---	-42.1	2	170	224
8	C_9H_{19}	---	---	-41.2	3	196	272
9	$C_{10}H_{21}$	18.6	17.4	-40.0	3	188	284
10	$C_{11}H_{23}$	-27.3	23.0	-39.7	4	205	305
11	$C_{12}H_{25}$	36.5	8.9	-43.8	4	215	327
12	$C_{14}H_{29}$	59.9	11.4	-20.9	2	197	314
13	$C_{16}H_{33}$	46.4	-4.5	-12.1	2	210	347
14	$C_{18}H_{27}$	46.3	6.1/19.5	1.6	3	213	367

[a] T_m – melting point; [b] T_c – temperature of crystallization; [c] T_g– glass transition temperature; [d] $T_{onset5\%}$ – decomposition temperature of 5% sample; [e] T_{onset} – decomposition temperature

Table 3 Solubility of prepared ILs (+: soluble. ±: limited solubility. –: not soluble)

ILs	Water	Methanol	DMSO	Acetonitrile	Acetone	Isopropanol	Ethyl acetate	Chloroform	Toluene	Hexane
1	+	+	+	+	+	+	–	+	–	–
2	+	+	+	±	+	+	±	+	–	–
3	+	+	+	±	+	+	±	+	–	–
4	+	+	+	–	+	+	±	+	±	–
5	+	+	+	–	+	+	+	+	+	–
6	+	+	+	–	+	+	+	+	+	–
7	+	+	+	–	+	+	+	+	+	–
8	+	+	+	–	+	+	+	+	+	–
9	+	+	+	+	+	+	+	+	+	–
10	+	+	+	+	+	+	+	+	+	–
11	+	+	+	+	+	+	+	+	+	–
12	+	+	+	+	+	+	–	+	+	–
13	±	+	+	+	+	+	–	+	+	–
14	–	+	+	+	+	+	–	+	+	–

Table 4 Surface activity parameters of synthesized ILs

ILs	***CMC*** **(mmol L^{-1})**	γ_{CMC} **(mN m^{-1})**	$\Gamma_{max}\times10^6$ **(mol m^{-2})**	$A_{min}\times10^{19}$ **(m^2)**	***CA*** **(°)**	pC_{20}
1	31.4	42.9	5.25	3.28	77.4	2.0
2	29.7	41.2	5.85	3.09	74.2	2.2
3	28.3	40.8	6.03	2.75	76.6	2.3
4	27.7	42.7	6.86	2.42	72.2	2.5
5	23.5	41.6	6.75	2.14	75.8	2.7
6	22.1	41.2	6.43	1.96	70.8	2.9
7	19.9	37.1	6.47	2.27	62.5	3.1
8	5.01	36.1	6.53	2.41	59.6	3.2
9	3.16	35.0	6.62	2.21	56.0	3.4
10	2.00	34.4	8.47	1.96	55.3	3.6
11	1.00	33.5	9.86	1.68	53.0	3.9
12	0.32	33.6	7.91	2.11	52.4	4.2
13	0.10	35.5	6.84	2.43	53.1	4.5
14	0.08	35.8	7.11	2.34	52.5	4.6

Table 5 Herbicidal activity of the studied ILs (2 WAT)

ILs	**R***	**Efficacy [%]**		
		Common lambsquarters	**Oilseed rape**	
1	C_2H_5	83	73	cd
2	C_3H_7	73	71	cd
3	C_4H_9	71	70	d
4	C_5H_{11}	77	70	d
5	C_6H_{13}	79	70	d
6	C_7H_{15}	81	70	d
7	C_8H_{17}	79	78	bcd
8	C_9H_{19}	77	80	bcd
9	$C_{10}H_{21}$	88	95	a
10	$C_{11}H_{23}$	82	83	abc
11	$C_{12}H_{25}$	85	82	bcd
12	$C_{14}H_{29}$	86	88	ab
13	$C_{16}H_{33}$	80	90	ab
14	$C_{18}H_{27}$	75	90	ab
	MCPA - salt	70	70	d

*all compounds were used at a dose of 600 g of active ingredient per 1 ha; the same letter in the column means no statistically significant differences

Figure captions:

Scheme 1. Synthesis of 1-alkyl-1-methylpiperidinium 4-(4-chloro-2-methylphenoxy)-butanoates.

Fig. 1. Influence of temperature on the viscosity values for ILs (**5-10**).

Fig. 2. Influence of temperature on the density values for ILs (**5-10**).

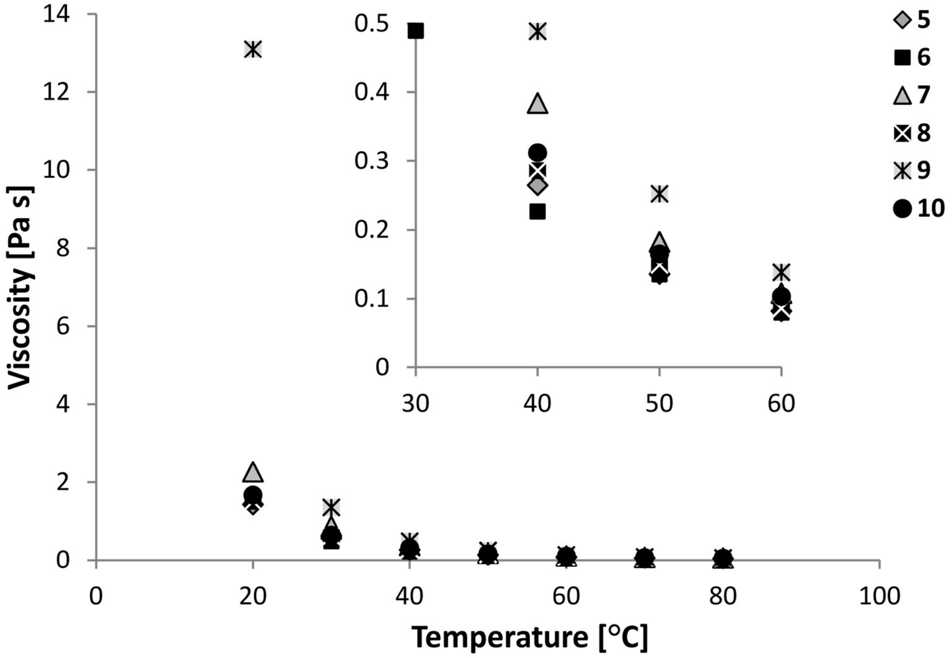
Fig. 3. Influence of temperature on the refractive index values for ILs (**5-10**).

Fig. 4. Relationship between density (▲) or refractive index (●) and the chain length of obtained ILs (**5-10**), at 20°C.

Fig. 5. TGA thermogram of obtained ILs, where (——) – **1** (T_{onset}: 254 °C)**;** (**……**) – **5** (T_{onset}: 260 °C)**;** (**– –**) – **9** (T_{onset}: 284 °C)**;** (**—— .**) – **12** (T_{onset}: 314 °C)**;** (**----**) – **14** (T_{onset}: 367 °C)**.**

Fig. 6. Relationship between log *CMC* and the number of carbon atoms in the alkyl substituent (**7-14**).

Fig. 7. Relationship between the herbicidal efficacy and pC_{20} (oilseed rape).



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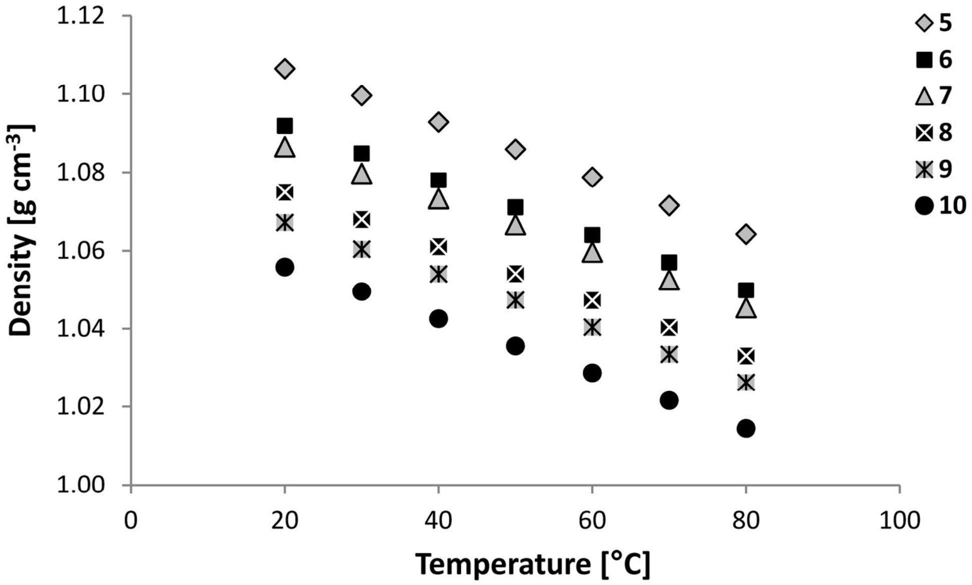

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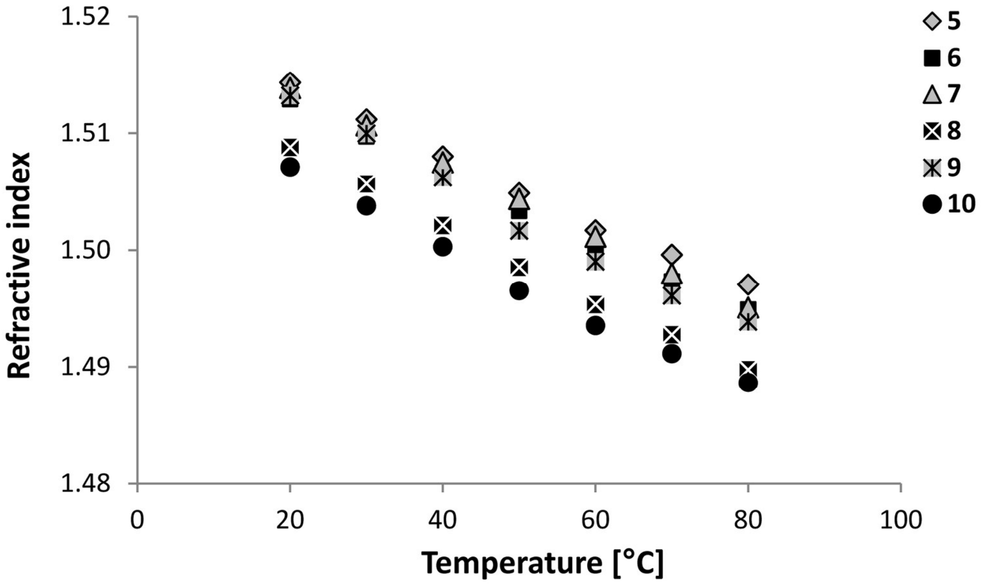

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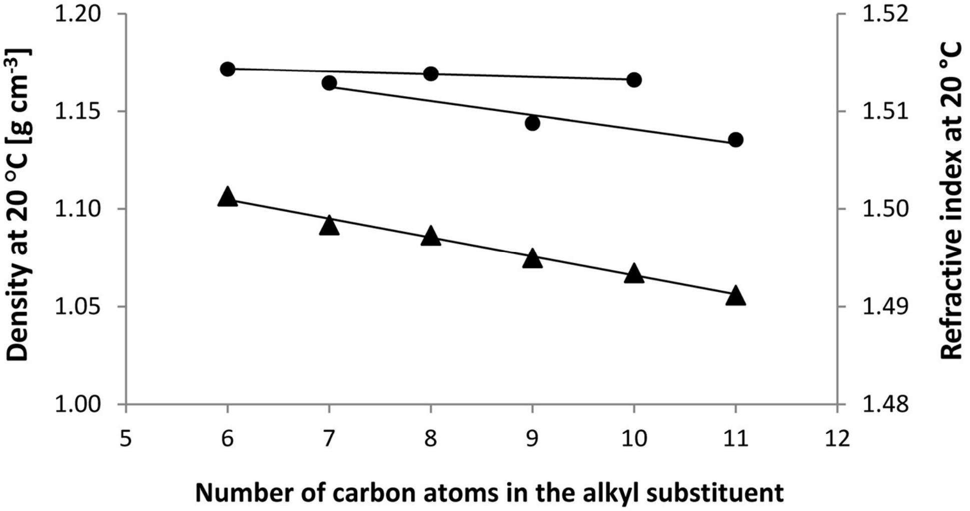

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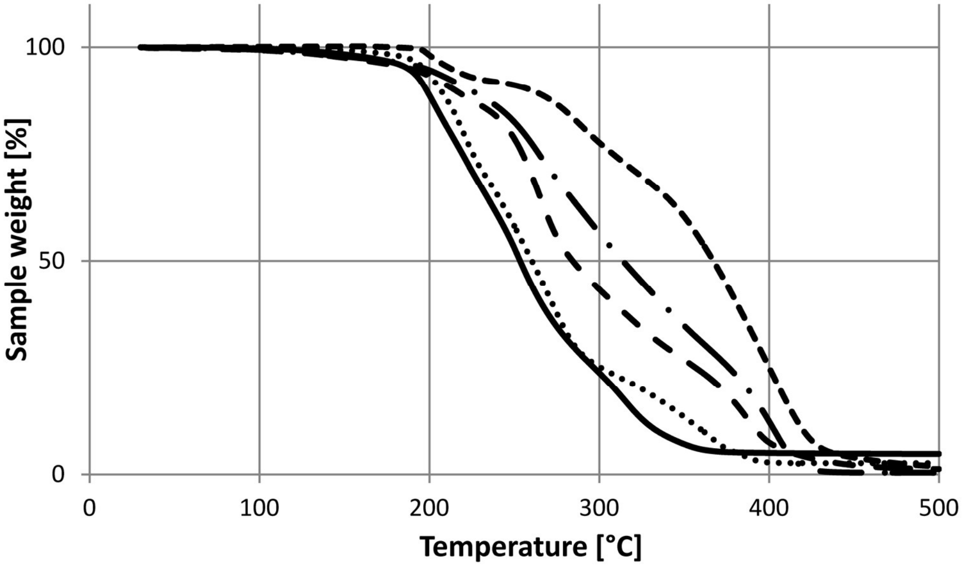

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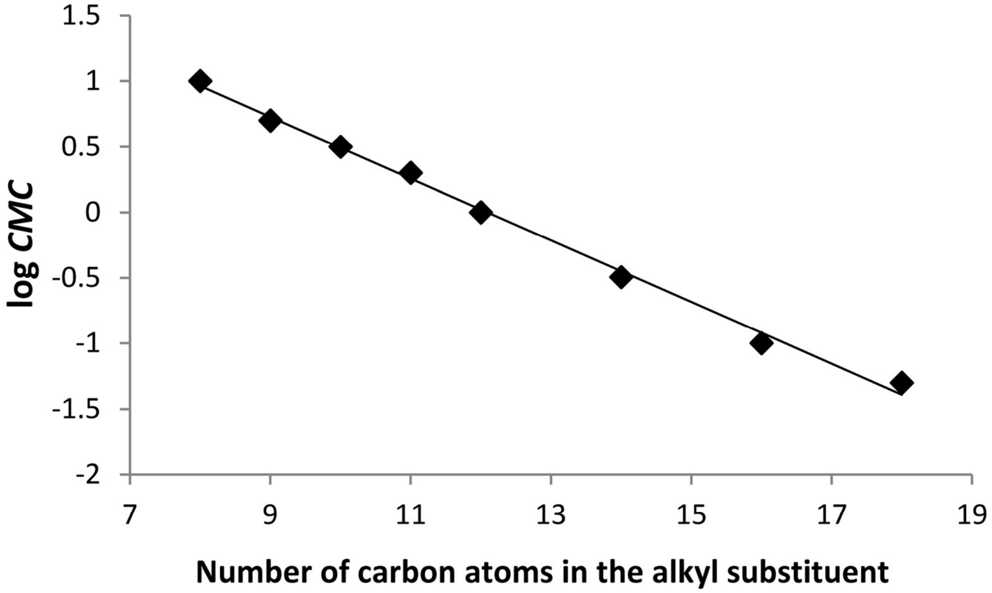

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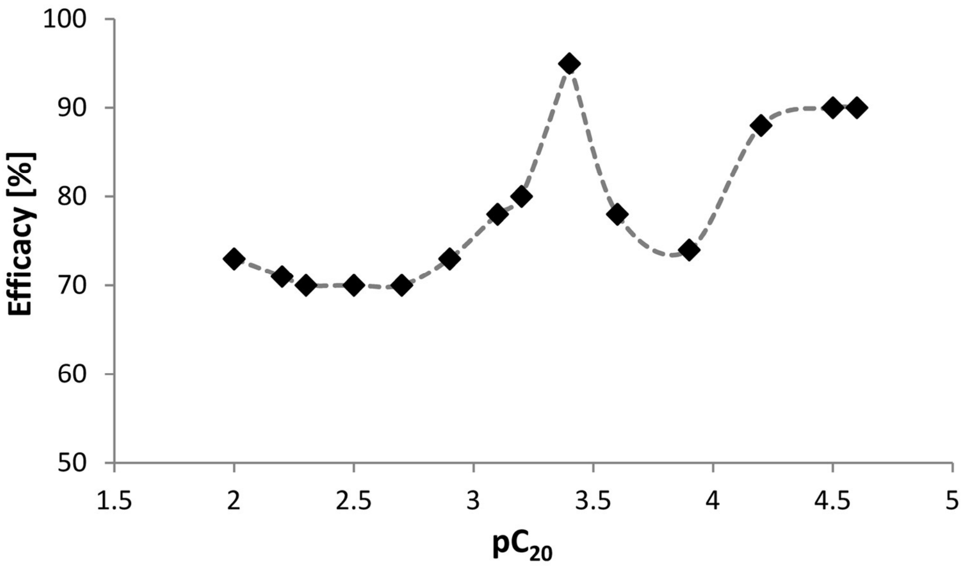

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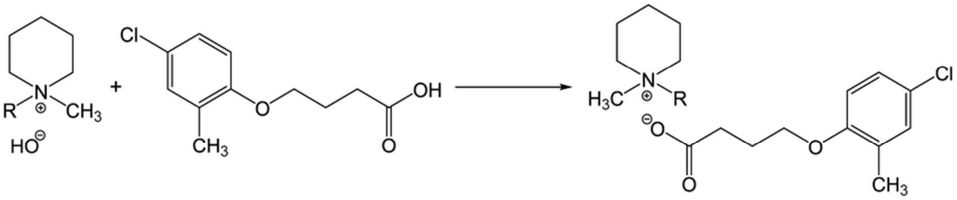

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