Multifunctional long-alkyl-chain quaternary ammonium azolate based ionic liquids†

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A new group of quaternary ammonium ionic liquids with azolate (benzotriazolate, 1,2,4-triazolate, 4-nitroimidazolate, 2-methyl-4-nitroimidazolate) anions was prepared and characterized. The synthetic method employed was easy and quick, and required a polar solvent. The obtained ionic liquids were tested as anti-microbial and anti-fungal plant protection agents. Additionally, the surface-active properties and the phytotoxicity of the quaternary ammonium azolates were also studied. These clearly defined ionic liquids were found to be very effective anti-bacterial and anti-fungal agents.

Introduction

Ionic liquids (ILs) have received marked attention in recent years due to their potential applications.[1–4] Their unique chemical properties such as low melting point, wide liquid range, high thermal and chemical stability make them excellent substitutes for the conventional solvents. The huge number of cation-anion combinations allow appropriate salts to be designed for the process. All of these properties brought a multitude of applications of ILs in the industrial scale (*e.g.*, BASIL).[5] Recently, the use of ILs as active pharmaceutical ingredients has been discussed as a possible future application.[6,7]

A group of ILs with azole anions (imidazolate, triazolate, tetrazolate) have been reported to be energetic materials.[8–11] Ionic salts containing a large number of nitrogen atoms form a unique class of energetic materials, the energy of which is derived from their very high heats of formation. For example, 1,2,4-triazole and 1,2,3-triazole have positive heats of formation of 1580 J g^{-1} and 3940 J g^{-1} respectively.[8] Over the past few years several publications have appeared describing energetic ILs. Shreeve *et al.*[12–15] reported a wide range of energetic azolate salts based on 4,5-dinitroimidazolate and 3,5-dinitro-1,2,4-triazolate anions with melting points approaching the definition of ILs and with high heats of formation. Moreover, Ohno *et al.*[16,17] described the preparation and electrochemical properties of 1-ethyl-3-methylimidazolium tetrazolate and triazolate. Tetraalkylammonium and tetraalkylphosphonium 1,2,4-triazolates and imidazolates were studied as solvents and highly active catalysts for oligomerization of isocyanates.[18] Furthermore, Searcey *et al.*[19] described tetrabutylammonium 4-nitroimidazolate as an intermediate for the synthesis of 1-alkyl-4-nitroimidazoles. Additionally, Liotta *et al.*[20] disclosed a method for formation of an energetic IL comprised of a tetrazolate anion and a tetrazolium cation. Rogers *et al.*[9,21] showed that salts with a wide range of heterocyclic azolate anions with 1-butyl-3-methylimidazolium cation gave several examples of room temperature ILs. Recently, Rogers and co-workers have reported the synthesis and characterization of organic salts based on tetraalkylammonium, 1,3-dialkylimidazolium, pyridinium, and phosphonium cations combined with energetically-substituted tetrazolate, triazolate, imidazolate, benzimidazolate, and benzotriazolate anions.[22] Generally, the azolates were surprisingly stable in the systems explored and IL behavior was observed with all combinations of the 1-butyl-3-methylimidazolium cation and the heterocyclic azolate anions studied.

Here, we report the synthesis and characterization of novel organic salts based on didecyldimethylammonium, benzalkonium, domiphen, and hexadecyltrimethylammonium cations combined with benzotriazolate, 1,2,4-triazolate, 4-nitroimidazolate, and 2-methyl-4-nitroimidazolate anions. In this paper we present their properties and potential applications.

Results and discussion

Synthesis and characterization

Benzotriazolate [**Bt**], 1,2,4-triazolate [**Tr**], 4-nitroimidazolate [**4-NO_2Im**], and 2-methyl-4-nitroimidazolate [**2-Me-4-NO_2Im**] (Scheme 1) were prepared by *in situ* deprotonation of corresponding azoles with sodium or potassium hydroxide in methanol and mixed with an equimolar amount of commercially inexpensive and widely used quaternary ammonium halides, dissolved in methanol. Sodium or potassium halide as a by-product was removed with success from an anhydrous acetone solution. The products were dried in vacuum at 80 °C for 24 h and stored over P_4O_{10}. The synthesized azolates contained high ammonium cation presented in Scheme 2 (didecyldimethylammonium – [**DDA**], benzalkonium with alkyl

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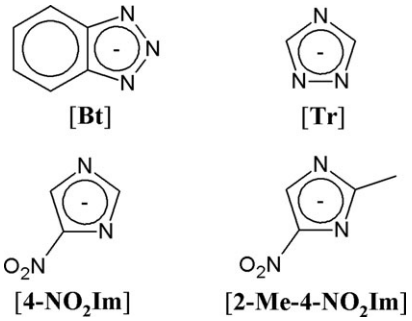
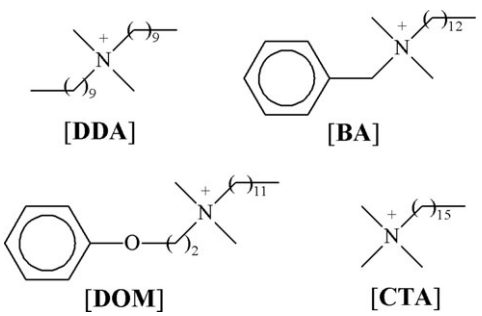


Scheme 1 Structure of anions.

group $C_{12}H_{25}$ and $C_{14}H_{29}$ equal to 60 and 40%, respectively – [**BA**], domiphen – [**DOM**], and hexadecyltrimethylammonium – [**CTA**]) are summarized in Table 1. The method used in synthesis of azolates is easy and quick (after mixing substrates the inorganic halides were formed immediately), and required a polar solvent, methanol. The products were obtained with good yields of over 87%. Benzotriazolates (**1**, **5**, **9** and **13**) were obtained as a wax and as solid matter, 1,2,4-triazolates (**2**, **6** and **14**) were liquid at room temperature. All of the hexadecyltrihexylammonium azolates (**9–12**) were solids. In the case of domiphen azolates only benzotriazolate salts (**13**) were solid, the rest of the studied salts were liquid.

The water content of obtained compounds, determined by Karl-Fischer measurements, was found to be less than 500 ppm. The prepared salts were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. In the ^{1}H spectra for benzotriazolates (**1**, **9** and **13**) typically two doublets at 7.02–7.11 and 7.78–7.85 ppm and in the ^{13}C spectra signals of aromatic carbons at 116, 121 and 145 ppm were observed. These symmetrical patterns for aromatic proton and carbon signals indicate the 2-isomer.

The octanol-water coefficient was tested, commonly used as a parameter for assessing the environmental fate of organic chemicals. The solubility of azolates in octanol and water provided data for calculation of the partition coefficients in the octan-1-ol/water system. As previously described, there is some influence of solubility in pure and mutually saturated solvents, so the second evaluation was used in the experiments. Experimental values for partition coefficient for obtained azolates were in range −0.96 to 1.4 (Table 1) which makes these compounds potential biologically active agents, according Lipinski's rules. Some known ILs also show negative values for logP.[23–25] Generally, the triazolates showed the lowest



Scheme 2 Structure of cations.

Table 1 Prepared ILs with azolate anion

IL	Cation	Anion	Yield [%]	Form	Log *P*
1	**[DDA]**	**[Bt]**	92	Solid	−0.84
2	**[DDA]**	**[Tr]**	96	Liquid	−0.69
3	**[DDA]**	**[4-NO$_2$Im]**	91	Liquid	0.64
4	**[DDA]**	**[2-Me-4-NO$_2$Im]**	95	Liquid	0.54
5	**[BA]**	**[Bt]**	89	Wax	−0.96
6	**[BA]**	**[Tr]**	97	Liquid	−0.37
7	**[BA]**	**[4-NO$_2$Im]**	90	Liquid	0.49
8	**[BA]**	**[2-Me-4-NO$_2$Im]**	97	Liquid	0.30
9	**[CTA]**	**[Bt]**	96	Solid	−0.29
10	**[CTA]**	**[Tr]**	99	Solid	−0.26
11	**[CTA]**	**[4-NO$_2$Im]**	97	Solid	−0.04
12	**[CTA]**	**[2-Me-4-NO$_2$Im]**	94	Solid	1.40
13	**[DOM]**	**[Bt]**	92	Solid	0.48
14	**[DOM]**	**[Tr]**	87	Liquid	−0.77
15	**[DOM]**	**[4-NO$_2$Im]**	95	Liquid	−0.20
16	**[DOM]**	**[2-Me-4-NO$_2$Im]**	99	Liquid	0.38

value of logP, and they were the most hydrophilic compounds. It was found that nitroimidazolates were the most hydrophobic salts.

DSC and TGA analyses

The results are presented in Table 2. The glass transition for azolates [**DDA**] (**1–4**) and [**BA**] (**5–8**) increased in the following order: [**Tr**] < [**4-NO$_2$Im**] < [**Bt**] < [**2-Me-4-NO$_2$Im**]. Crystallization was observed mostly for benzotriazolates [**DDA**] (**1**) −23.6 °C, [**BA**] (**5**) −17.4 °C and for [**DOM**] (**13**) 8.4 °C. A lower melting point was observed for triazolates (**2**, **10**, **14**), and in the case of [**BA**][**Tr**] (**6**) only glass transition was observed. The thermal stability of azolate based ILs was greater than 160 °C. The observed thermal decomposition for [**2-Me-4-NO$_2$Im**] with four different cations is shown in Fig. 1. The benzotriazolates [**DDA**] (**1**) and [**DOM**] (**13**) showed stepwise decomposition, with 48 and 77% of decomposed matter respectively. The nitroimidazolates (**7**, **8** and **12**) showed stepwise decomposition with 68, 64, and 77% of decomposition at 283, 265 and 260 °C respectively. Only [**DDA**][**Tr**] (**2**) exhibited three-step decomposition with 20 and 46% decomposed matter after the first and second step. The most thermally stable were nitroimidazolate salts as well as [**4-NO$_2$Im**] and [**2-Me-4-NO$_2$Im**]. The thermal stability of cations decreased in the following order: [**DOM**] > [**DDA**] > [**CTA**] > [**BA**] and, in the case of anions, [**2-Me-4-NO$_2$Im**] ≈ [**4-NO$_2$Im**] > [**Bt**] > [**Tr**].

The obtained results allow us to classify all the synthesized azolates to ILs of a high viscosity.

In thermal decomposition of nitroimidazolates exoenergetic phenomena were observed. Surprisingly, in the case of [**2-Me-4-NO$_2$Im**] these effects were two times more extensive than for [**4-NO$_2$Im**] anion. For [**DOM**][**2-Me-4-NO$_2$Im**] and [**DOM**][**4-NO$_2$Im**] heats were equal to 356.11 J g^{-1} and 180.87 J g^{-1} respectively (Fig. 2).

Biological activity

Azoles are commonly known as anti-microbial compounds. Many of them (*e.g.*, fluconazole, posaconazole, ravuconazole, econazole, ketoconazole, voriconazole, and itraconazole) are used as anti-fungal drugs in the treatment and prevention of

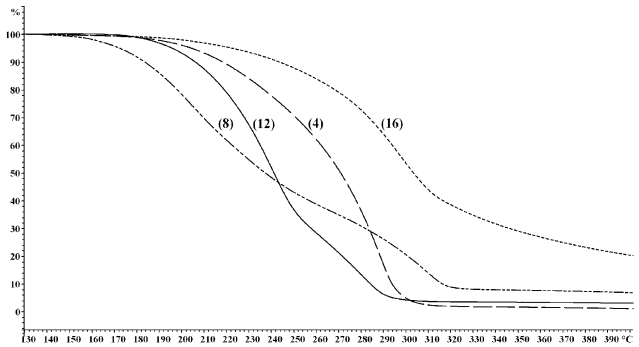


Fig. 1 Examples of the observed thermal decomposition for 2-methyl-4-nitroimidazolates with **[DDA]** – (**4**), **[BA]** – (**8**), **[CTA]** – (**12**) and **[DOM]** – (**16**).

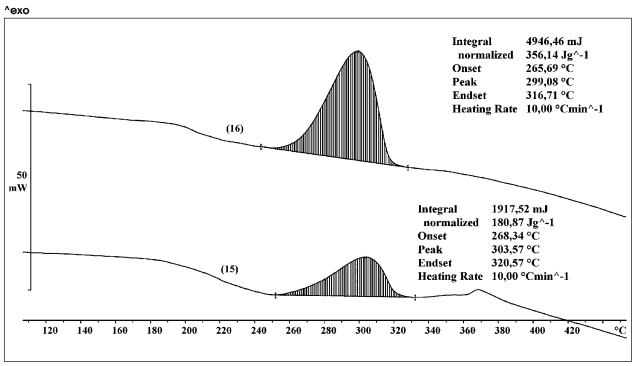


Fig. 2 Exoenergetic effect of thermal decomposition of **[DOM][4-NO$_2$Im]** – (**15**) and of **[DOM][2-Me-4-NO$_2$Im]** – (**16**).

superficial and systemic fungal infection. Recently, many papers[26–40] have reported that ILs obtained from a biologically active cation or anion retain this activity on the same or higher level. For this reason, we decided to examine the biological activity of the synthesized ILs.

The anti-microbial activity was tested against clinically important microorganisms. The minimum inhibitory concentration (MIC) and minimum bactericidal or fungicidal concentration (MBC) were established for ILs soluble in water (1–8 and 13–16) against Gram-positive cocci, Gram-negative rods and fungi. MIC and MBC values are shown in Table 3. The results demonstrate that the synthesized ILs were very effective bactericidal and fungicidal agents. The activity was more pronounced than that of the original benzalkonium chloride [BA][Cl]. In general, the studied [DDA] ILs exhibited the most amplified antimicrobial activity (the reduction in average MIC and MBC values is presented in Fig. 3) against all strains tested. The impact of organic anion on biological activity was noticeable. The very low values of MIC and MBC obtained demonstrate the extensive potential of these products for use in disinfection.

Table 2 Thermal properties of obtained azolate ammonium ILs

IL	T_g[a]/°C	T_c[b]/°C	T_m[c]/°C	$T_{onset(5\%)}$[d]/°C	T_{onset}[e]/T_{onset2}[f]/T_{onset3}[g]/°C
1	−67.7	−23.6	29.4	190	260/250 (48)
2	−77.8	—	−18.6	170	260/203 (20)/248 (46)
3	−71.6	—	—	210	275
4	−66.7	—	—	210	270
5	−44.6	−17.4	22.1	170	220
6	−59.3	—	—	170	222
7	−48.9	—	—	178	230/283 (68)
8	−41.1	—	—	175	232/265 (64)
9	—	—	101	193	237
10	−45.7	—	36.6	168	229/195 (17)
11	—	—	34	205	230
12	—	—	45	200	240/260 (77)
13	−38.2	8.4	48.9	190	282/253 (40)
14	−58.1	—	2.3	195	267
15	−57.6	−3.8	14.0	220	290
16	−44.0	—	5.8	225	287

[a] The glass transition temperature (T_g) was determined by DSC on heating. [b] The crystallization temperature (T_c) was determined by DSC on heating. [c] The melting point (T_m) was determined by DSC on heating. [d] The decomposition temperature ($T_{onset\ (5\%)}$) was determined from the onset of 5% mass loss. [e] The decomposition temperature (T_{onset}) was determined from the onset of 50% mass loss. [f] Second step of decomposition. [g] Third step of decomposition. Values in parentheses – percent of decomposition.

Wood preservation

The exceptional results obtained in microbiological studies stimulated us to test the prepared azolates in wood preservation. Fungal growth was first determined by the agar-plate method for the fungal strains *S. pityophila*, *T. versicolor* and *C. puteana*. The toxicity data (ED_{50}, ED_{100} and LD) of azolates (**2**, **6**, **7** and **8**) are presented in Table 4. The results showed that studied ILs were poor anti-fungal agents when tested *versus T. versicolor* and *C. puteana*. In the case of *S. pityophila* two ILs (**7** and **8**) were exceptionally effective. Their effectiveness, measured by ED_{100} and LD values, was several times higher than that of didecyldimethylammonium chloride **[DDA][Cl]**. Such a pronounced activity was related to an anion which contained a nitro group in the imidazole ring **[4-NO$_2$Im]** and **[2-Me-4-NO$_2$Im]**.

Antifungal activity

It was found that all tested substances showed fungistatic activity against *F. culmorum* and *S. sclerotiorum*. Both species are important pathogens of cereals and oil seed rape, respectively. Significant differences were observed in fungistatic

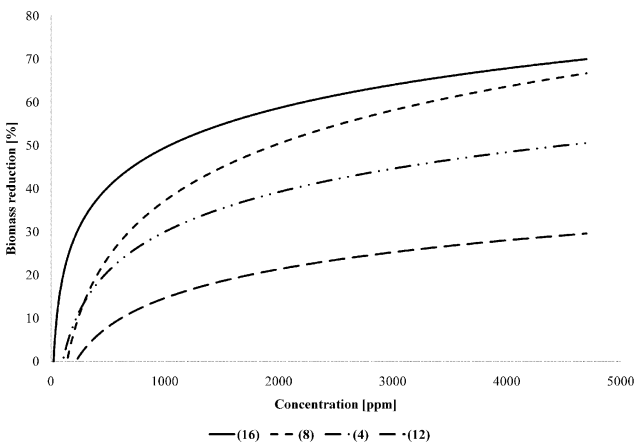


Fig. 3 Mean MIC and MBC values for obtained azolate ILs with **[DDA]** (**1–4**).

Table 3 MIC and MBC values[a] for prepared azolate ILs

Strain		ILs												
		1	2	3	4	5	6	7	8	13	14	15	16	BA[b]
M. luteus	MIC	0.4	1.3	1.1	0.2	0.2	0.3	2.3	0.4	0.4	2.5	0.2	0.2	1.4
	MBC	0.4	5.1	1.1	1.1	0.5	1.3	4.6	2.2	1.1	9.9	0.2	0.4	11.2
S. aureus	MIC	0.4	2.5	0.2	0.4	1.1	0.3	1.2	0.2	0.4	2.5	1.1	2.2	5.6
	MBC	9	5.1	1.1	2.2	1.1	5.1	4.6	1.1	8.8	2.5	17.9	2.2	22.5
S. epidermidis	MIC	0.2	0.5	0.2	0.2	2.3	0.3	0.2	0.2	0.4	0.2	2.2	1.1	1.4
	MBC	0.4	1.3	1.1	2.2	4.6	0.3	0.5	0.4	2.2	0.2	9	4.3	5.6
E. feacium	MIC	0.2	5.1	0.5	2.2	2.3	0.3	1.2	2.2	1.1	2.5	2.2	1.1	5.6
	MBC	36	5.1	9.1	17.7	4.6	5.1	2.3	4.5	68.5	5	4.5	2.2	22.5
M. catarhalis	MIC	0.2	0.3	0.5	0.2	9.1	0.3	0.5	2.2	1.1	0.2	2.2	0.4	0.6
	MBC	0.2	5.1	0.5	0.4	18.2	0.3	4.6	4.5	8.8	9.9	17.9	4.3	1.4
E. coli	MIC	0.2	1.3	1.1	2.2	0.5	0.3	0.5	4.5	1.1	5	2.2	1.1	5.6
	MBC	0.2	5.1	2.3	2.2	4.6	1.3	18.5	4.5	2.2	77	2.2	4.3	5.6
S. marcescens	MIC	139	40.5	70.7	35.3	70.7	79.8	143	69.4	68.5	77	69.4	34.7	174
	MBC	281	78.6	141	137	141	322	143	139	137	77	139	67.3	174
P. vulgaris	MIC	18	20.3	36.5	35.3	70.7	79.8	71.6	35.8	35.3	39.7	35.8	34.7	87.1
	MBC	36	78.6	141	35.3	141	322	71.6	139	137	154	69.4	67.3	87.1
P. aeruginosa	MIC	36	40.5	70.7	68.5	141	160	143	280	68.5	154	35.8	67.3	174
	MBC	69.7	78.6	70.7	137	285	160	289	280	137	310	69.4	135	174
B. subtilis	MIC	1.1	0.3	0.5	2.2	9.1	0.5	0.2	0.4	1.1	0.5	1.1	1.1	5.6
	MBC	2.2	1.3	1.1	2.2	9.1	0.5	0.5	2.2	2.2	2.5	1.1	1.1	5.6
C. albicans	MIC	2.2	10.1	18.2	4.4	9.1	10.3	9.2	17.9	8.8	9.9	4.5	17.4	11.2
	MBC	4.5	20.3	36.5	17.7	70.7	20.6	71.6	139	35.3	9.9	4.5	17.4	87.1
R. rubra	MIC	1.1	10.1	18.2	4.4	9.1	10.3	9.2	4.5	8.8	9.9	4.5	17.4	22.5
	MBC	9	10.1	141	17.7	36.5	20.6	71.6	35.8	17.7	19.9	4.5	17.4	87.1

[a] In μM, the number of microorganism in 1 mL range from 10^4 to 10^5. [b] **[BA][Cl]**.

activity of the preparations. However, the degree of inhibition depended on the compound used, its concentration and also on the examined fungal species. Generally, the tested ILs were more effective in higher concentrations, especially in the case of *F. culmorum*. *S. sclerotiorum* was more sensitive to active substances. All examined azolates effectively inhibited growth of these fungi in concentrations of 100 as well as 10 ppm. The obtained results (summed up in Table 5) revealed that the strongest inhibition of mycelium growth was induced by preparations designated as azolates **2**, **15** and **16**. Also ILs **6**, **7**, **8** and **14** showed high effectiveness in the growth inhibition of *S. sclerotiorum*, but they were less efficient towards *F. culmorum*.

Table 4 The effective dose ED and the lethal dose LD of azolate ILs against *C. puteana*, *T. versicolor* and *S. Pityophila*

IL	ED_{50}	ED_{100}	LD
	C. puteana		
2	25	2500	2500
6	250	2500	2500
7	250	2500	2500
8	250	2500	2500
[DDA][Cl]	50	5000	5000
	T. versicolor		
2	25	2500	2500
6	50	750	2500
7	25	2500	2500
8	50	2500	2500
[DDA][Cl]	25	2500	2500
	S. pityophila		
2	25	500	2500
6	10	250	1000
7	25	100	750
8	25	100	250
[DDA][Cl]	10	750	2500

Phytotoxicity

Plant response to tested ILs was determined on the basis of garden cress (*Lepidium sativum*) seedling growth inhibition. ED_{50} of four ILs groups are presented in Table 6, arranged according to increasing values of this parameter. The tested ILs demonstrated a broad spectrum of ED_{50} values. Low ED_{50} indicates a strong phytototoxic effect. Benzotriazolates (**1**, **5** and **9**), 1,2,4-triazolates (**2**, **6** and **10**) with **[DDA]**, **[CTA]** and **[BA]** cations were the most phytotoxic to garden cress seedlings. However, benzotriazolate and 1,2,4-triazolate with **[DOM]** cation were significantly less toxic. Anions such as **[4-NO_2Im]** and **[2-Me-4-NO_2Im]** with NO_2 group were also less toxic to tested plants. **[CTA][2-Me-4-NO_2Im]** demonstrated lower phytotoxicity compared to the other **[2-Me-4-NO_2Im]** ILs (Fig. 4). The results show that it is very difficult to determine the relationships between chemical structure of tested azolates and their phytotoxic properties.

Surface activity

Surface excess concentrations Γ_{max} were calculated from the slope of the linear portion of the γ–log *c* plots using the Gibbs isotherm:

$$\Gamma_{max} = -\frac{1}{RT} \cdot \frac{d\gamma}{d(\ln c)}$$

where: Γ_{max} is the surface excess concentration at the saturated interface, *R* is gas constant, *T* the absolute temperature and c is concentration.

From Γ_{max}, the minimum surface occupied by a molecule at the interface A_{min} can be calculated from the equation: $A_{min} = \frac{1}{\Gamma_{max} N_A}$, where: N_A is the Avogadro number.

Table 5 The influence of tested compounds on the growth inhibition of *Fusarium culmorum* and *Sclerotinia sclerotiorum* mycelium

	Growth inhibition [I%]			
IL	Concentration 10 ppm *F. culmorum*	Concentration 100 ppm	Concentration 10 ppm *S. sclerotiorum*	Concentration 100 ppm
2	46.3	73.5	61.0	75.1
6	28.3	56.8	69.8	77.0
7	36.1	54.7	66.1	74.3
8	35.5	57.9	61.3	74.7
10	29.2	36.0	48.2	69.6
11	27.9	34.8	48.7	62.7
12	32.2	33.4	34.9	56.0
14	34.1	60.0	66.1	74.2
15	36.9	56.7	65.2	73.2
16	37.9	59.0	62.1	73.8
$LSD_{(0.05)}$	0.45	0.33	1.3	0.54

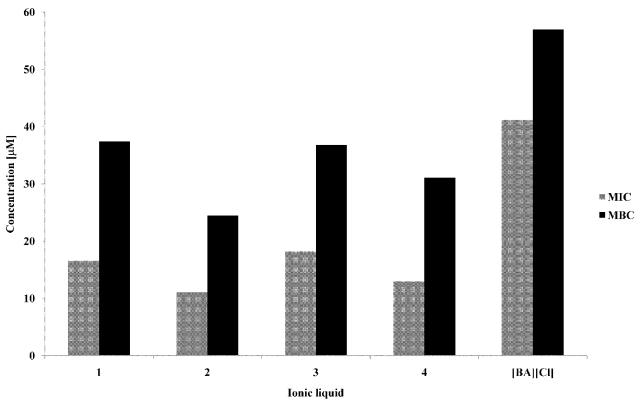


Fig. 4 The response of *Lepidium sativum* seedlings to ILs with [**2-Me-4-NO_2Im**] anion used at different concentrations.

Critical micelle concentration (CMC) and the corresponding surface tension (γ_{CMC}), the surface excess Γ_{max} and area per molecule A_{min}, are summed up in Table 7.

For studied ILs aqueous solutions, the surface tension decreased from the water value to a minimum located between 25.2 to 35.1 mN m^{-1}. After this point, the surface tension reached the plateau region. In the case of azolates **15** and **16**, the solutions manifested the highest values of 34.2 and 35.1 mN m^{-1}, respectively. This demonstrated that [**DDA**] exhibited more pronounced intermolecular hydrophobic interactions, making it easier to form aggregates in water than it was in the case of [**DOM**]. As far as γ_{CMC} values are concerned, they were dependent on the cation form in the IL. For [**DDA**] γ_{CMC} values were lower than for [**DOM**] azolates. The area per molecule A_{min} of both [**DDA**] and [**DOM**] forms with [**2-Me-4-NO_2Im**] was higher than that of the corresponding [**Bt**] form, indicating that the IL molecules containing [**Bt**] are more tightly packed at the water–air interface. [**DDA**][**Bt**] had a lower CMC value and a lower γ_{CMC}, resulting in better surface properties than [**DOM**][**Bt**]. However, both CMC and γ_{CMC} values of aqueous solutions of [**DDA**] and [**DOM**] are of the same order as the CMC of cationic surfactants. For instance, the CMC of hexyldecyltrimethylammonium bromide [**CTA**][**Br**] is 0.9 mmol L^{-1}.[41] These results indicate that [**DDA**] and [**DOM**] azolates self-assemble easily in aqueous solutions.

Table 6 The effective dose (ED_{50}) of prepared ILs for *Lepidium satiwum*

			Parameters for equation ED = $A\times$ lnC − B [ppm]		
IL	Cation	ED_{50} [ppm]	A	B	$ED_{50}/\mu M$
			Benzotriazolates		
1	[**DDA**]	320	11.694	17.289	707
9	[**CTA**]	330	8.7849	1.0017	752
5	[**BA**]	410	16.267	47.883	906
13	[**DOM**]	61000	8.5896	44.63	141646
			1,2,4-Triazolates		
10	[**CTA**]	390	12.834	26.673	893
2	[**DDA**]	490	13.653	34.569	1217
6	[**BA**]	840	15.243	52.551	2382
14	[**DOM**]	1020	12.87	39.146	2484
			4-Nitroimidazolates		
15	[**DOM**]	980	12.2	34.021	2471
3	[**DDA**]	5330	9.9812	35.644	11934
11	[**CTA**]	9210	15.723	93.519	20712
7	[**BA**]	12160	11.79	60.891	31450
			2-Methyl-4-nitroimidazolates		
16	[**DOM**]	1040	13.243	42.049	2583
8	[**BA**]	1960	19.059	94.494	4407
4	[**DDA**]	4510	13.294	61.862	9791
12	[**CTA**]	39090	9.6518	52.054	99042

Table 7 The CMC, surface tension (γ_{CMC}), surface excess concentration (Γ_{max}), and area per molecule (A_{min}) of the prepared azolates in aqueous solution at 25 °C

IL	CMC/mmol L^{-1}	γ_{CMC}/mN m^{-1}	$\Gamma_{max}/10^{-6}$ mol m^{-2}	$A_{min}/10^{-19}$ m^2	ΔG^0_{ads}/kJ mol^{-1}
1	0.501	25.2	5.371	3.091	−27.2
2	2.512	27.0	4.387	3.784	−26.4
3	1.259	26.1	3.862	4.299	−27.0
4	2.344	26.1	2.610	6.361	−31.3
13	0.398	29.2	1.548	1.073	−19.4
14	0.631	31.1	7.916	2.097	−23.0
15	1.259	34.2	5.812	2.856	−22.0
16	1.514	35.1	4.562	3.639	−23.9

Experimental section

^{1}H NMR spectra were recorded on the Mercury Gemini 300 spectrometer operating at 300 MHz with TMS as the internal standard. ^{13}C NMR spectra were obtained with the same instrument at 75 MHz. CHN elemental analyses 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 solvent.

General procedure for preparation of azolate salt

Equimolar amounts of azole and sodium or potassium hydroxide were dissolved in a methanol. Once dissolved, an equimolar amount of **[DDA][Cl]** or **[BA][Cl]** or **[DOM][Cl]** or **[CTA][Cl]** in methanol was added. After overnight stirring in room temperature the precipitate was removed. From the remaining solution, the methanol was evaporated and anhydrous acetone was added. After removal of the rest of the inorganic salt, the solvent was evaporated and the residue was dried overnight in a vacuum at 80 °C.

Didecyldimethylammonium benzotriazolate (1)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.89 (t, *J* 6.8 Hz, 6 H), 1.07 (m, 32 H), 2.78 (m, 10 H), 7.02 (dd, *J* 6.21, 3.06 Hz, 2 H), 7.78 (dd, *J* 6.26, 3.01 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0, 22.4, 22.6, 25.9, 29.0, 29.1, 29.2, 29.3, 31.7, 50.4, 63.3, 116.1, 120.4, 145.4; elemental analysis found (%): C 75.37, H 11.49, N 16.28; calc. for $C_{28}H_{52}N_4$ (444.74): C 75.62, H 11.79, N 12.60.

Didecyldimethylammonium 1,2,4-triazolate (2)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* 6.7 Hz, 6 H), 1.26 (m, 28 H), 1.5 (m, 4 H), 2.9 (s, 6 H), 3.03 (t, *J* 8.5 Hz, 4 H), 8.0 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9, 22.3, 22.4, 25.9, 28.9, 29.0, 29.08, 29.1, 31.6, 50.5, 63.4, 149.4; elemental analysis found (%): C 73.38, H 13.1, N 13.98; calc. for $C_{24}H_{50}N_4$ (394.68): C 73.04, H 12.77, N 14.20.

Didecyldimethylammonium 4-nitroimidazolate (3)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* 6.7 Hz, 6 H), 1.26 (m, 28 H), 1.64 (m, 4 H), 3.16 (s, 6 H), 3.2 (t, *J* 8.5 Hz, 4 H), 7.36 (s, 1 H), 7.96 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9, 22.5, 26.0, 28.9, 29.0, 29.1, 31.4, 31.6, 50.6, 64.0, 131.1, 145.5, 148.1; elemental analysis found (%): C 68.22, H 11.26, N 12.38; calc. for $C_{25}H_{50}N_4O_2$ (438.69): C 68.45, H 11.49, N 12.77.

Didecyldimethylammonium 2-methyl-4-nitroimiodazolate (4)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* 6.7 Hz, 6 H), 1.26 (m, 28 H), 1.64 (m, 4 H), 2.35 (s, 3 H), 3.09 (s, 6 H), 3.2 (t, *J* 8.5 Hz, 4 H), 7.92 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0, 17.2, 22.5, 26.0, 28.8, 28.9, 29.0, 29.1, 29.2, 31.6, 50.7, 64.1, 132.8, 147.3, 155.0; elemental analysis found (%): C 69.13, H 11.79, N 12.69; calc. for $C_{26}H_{52}N_4O_2$ (452.72): C 68.98, H 11.58, N 12.38.

Benzalkonium benzotriazolate (5)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.87 (t, *J* 6.7 Hz, 3 H), 1.14 (m, 22 H), 2.84 (m, 8 H), 4.38 (s, 2 H), 7.04 (m, 2 H), 7.2 (m, 5 H), 7.82 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0, 22.4, 25.9, 29.0, 29.23, 29.25, 29.3, 29.5, 29.55, 29.6, 31.8, 49.3, 62.8, 67.3, 116.4, 121.0, 127.2, 128.9, 130.3, 132.9, 145.4.

Benzalkonium 1,2,4-triazolate (6)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* 6.7 Hz, 3 H), 1.26 (m, 22 H), 1.82 (m, 2 H), 3.05 (s, 6 H), 3.3 (t, *J* 8.4 Hz, 2 H), 4.7 (s, 2 H), 7.37 (m, 5 H), 8.1 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.6, 22.1, 22.2, 25.7, 28.6, 28.7, 28.75, 28.8, 29.1, 31.3, 48.8, 63.2, 67.0, 126.7, 128.6, 130.1, 132.5, 148.3.

Benzalkonium 4-nitroimidazolate (7)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.85 (t, *J* 6.7 Hz, 3 H), 1.17 (m, 22 H), 1.75 (m, 2 H), 3.06 (s, 6 H), 3.26 (t, *J* 8.5 Hz, 2 H), 4.6 (s, 2 H), 7.36 (m, 6 H), 7.98 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 22.4, 22.5, 26.0, 28.9, 29.0, 29.1, 29.16, 29.3, 29.35, 29.4, 31.6, 49.4, 63.9, 67.8, 126.5, 129.1, 130.2, 130.7, 132.6, 144.7, 148.0.

Benzalkonium 2-methyl-4-nitroimidazolate (8)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.86 (t, *J* 6.7 Hz, 3 H), 1.26 (m, 22 H), 1.75 (m, 2 H), 2.35(s, 3H), 3.06 (s, 6 H), 3.3 (t, *J* 8.4 Hz, 2 H), 4.6 (s, 2 H), 7.43 (m, 5 H), 7.97 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.9, 17.1, 22.5, 22.6, 26.0, 28.9, 29.1, 29.13, 29.2, 29.4, 29.42, 29.5, 31.67, 31.7, 49.4, 64.0, 68.1, 126.5, 129.3, 130.9, 132.6, 133.0, 147.5, 155.2.

Hexadecyltrimethylammonium benzotriazolate (9)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* 6.7 Hz, 3 H), 1.26 (m, 28 H), 2.77 (t, *J* 8.5 Hz, 2 H), 2.94 (s, 9 H), 7.06 (dd, *J* 3.05, 6.23 Hz, 2 H), 7.81 (dd, *J* 3.0, 6.28 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.2, 22.8, 22.9, 26.0, 29.1, 29.37, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0, 52.7, 66.5, 116.3, 121.0, 145.26;

elemental analysis found (%): C 74.17, H 11.13, N 13.58; calc. for $C_{25}H_{46}N_4$ (402.66): C 74.57, H 11.51, N 13.91.

Hexadecyltrimethylammonium 1,2,4-triazolate (10)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.86 (t, J 6.7 Hz, 3 H), 1.18 (m, 28 H), 3.11 (s, 9 H), 3.19 (t, J 8.5 Hz, 2 H) 8.05 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.7, 22.2, 22.6, 25.7, 28.7, 28.9, 28.94, 29.1, 29.16, 29.2, 29.25, 31.5, 52.6, 66.3, 148.8; elemental analysis found (%): C 71.33, H 12.28, N 15.66; calc. for $C_{21}H_{44}N_4$ (352.6): C 71.53, H 12.58, N 15.89.

Hexadecyltrimethylammonium 4-nitroimidazolate (11)

^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.83 (t, J 6.7 Hz, 3 H), 1.24 (m, 26 H), 1.65 (m, 2H), 3.04 (s, 9 H), 3.23 (t, J 8.5 Hz, 2 H) 7.22 (s, 1 H), 7.81 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 14.0, 22.0, 22.1, 25.8, 28.5, 28.7, 28.8, 28.83, 28.97, 29.0, 29.1, 31.3, 52.1, 65.3, 129.3, 144.2; elemental analysis found (%): C 66.41, H 11.36, N 14.01; calc. for $C_{22}H_{44}N_4O_2$ (396.61): C 66.62, H 11.18, N 14.13.

Hexadecyltrimethylammonium 2-methyl-4-nitroimidazolate (12)

^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.88 (t, J 6.6 Hz, 3 H), 1.17 (m, 26 H), 1.71 (m, 2H), 2.36 (s, 3H), 3.22 (s, 9 H), 3.32 (t, J 8.5 Hz, 2 H), 7.92 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 14.0, 16.7, 22.6, 23.0, 26.0, 29.0, 29.21, 29.23, 29.3, 29.4, 29.52, 29.53, 29.56, 29.57, 29.58, 29.6, 31.8, 53.2, 67.1, 130.9, 147.4, 153.8; elemental analysis found (%): C 67.17, H 11.13, N 13.58; calc. for $C_{23}H_{46}N_4O_2$ (410.64): C 67.27, H 11.29, N 13.64.

Domiphen benzotriazolate (13)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, J 6.7 Hz, 3 H), 1.26 (m, 18 H), 1.52 (m, 2 H), 3.11 (m, 8 H), 3.67 (t, J 4.3 Hz, 2 H), 4.11 (t, J 4.0 Hz, 2 H), 6.77 (m, 2 H), 7.0 (t, J 7.4 Hz, 1 H), 7. 11 (dd, J 3.0, 6.2 Hz, 2 H), 7.26 (m, 2 H), 7.85 (dd, J 3.0, 6.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.1, 22.7, 26.1, 29.1, 29.3, 29.34, 29.4, 29.5, 29.56, 29.6, 31.9, 51.5, 61.6, 62.0, 65.7, 114.1, 116.2, 121.4, 121.9, 129.6, 144.6, 156.6; elemental analysis found (%): C 73.91, H 9.63, N 12.19; calc. for $C_{28}H_{44}N_4O$ (452.66): C 74.29, H 9.80, N 12.38.

Domiphen 1,2,4-triazolate (14)

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.86 (t, J 6.7 Hz, 3 H), 1.17 (m, 18 H), 1.78 (m, 2 H), 3.4 (m, 6 H), 3.56 (t, J 4.3 Hz, 2 H), 4.08 (t, J 4.3 Hz, 2 H), 4.43 (t, J 4.3 Hz, 2 H), 6.9 (m, 2 H), 7. 13 (m, 1 H), 7.27 (m, 2 H), 8.13 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 13.8, 22.3, 22.6, 25.9, 28.8, 28.9, 29.0, 29.1, 29.2, 31.5, 51.7, 61.6, 62.0, 65.7, 114.0, 121.9, 129.6, 147.0, 156.6; elemental analysis found (%): C 71.45, H 10.33, N 13.69; calc. for $C_{24}H_{42}N_4O$ (402.62): C 71.60, H 10.51, N 13.92.

Domiphen 4-nitroimidazolate (15)

^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.85 (t, J 6.7 Hz, 3 H), 1.25 (m, 10 H), 1.71 (m, 2 H), 3.19 (s, 6 H), 3.42 (t, J 4.3 Hz, 2 H), 3.82 (t, J 4.3 Hz, 2 H), 4.46 (t, J 4.1 Hz, 2 H), 7.0 (m, 3 H), 7. 32 (m, 2 H), 7.44 (s, 1 H), 7.99 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 14.0, 21.9, 22.8, 25.8, 28.5, 28.7, 28.8, 28.9, 29.0, 31.3, 50.8, 61.3, 61.8, 64.0, 114.3, 121.3, 126.1, 129.5, 141.6, 147.9, 157.4; elemental analysis found (%): C 67.19, H 9.63, N 12.19; calc. for $C_{25}H_{42}N_4O_3$ (446.63): C 67.23, H 9.48, N 12.54.

Domiphen 2-methyl-4-nitroimidazolate (16)

^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.85 (t, J 6.7 Hz, 3 H), 1.17 (m, 18 H), 1.74 (m, 2 H), 2.25 (s, 3H), 3.23 (s, 6 H), 3.45 (t, J 4.3 Hz, 2 H), 3.86 (t, J 4.3 Hz, 2 H), 4.48 (t, J 4.1 Hz, 2 H), 6.98 (m, 3 H), 7. 31 (m, 2 H), 7.89 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 13.9, 16.0, 21.9, 22.1, 25.8, 28.6, 28.7, 28.9, 28.98, 29.0, 31.3, 50.8, 61.4, 61.8, 64.0, 114.6, 121.2, 128.0, 129.5, 147.1, 150.9, 157.4; elemental analysis found (%): C 67.52, H 9.76, N 12.25; calc. for $C_{26}H_{44}N_4O_3$ (460.65): C 67.79, H 9.63, N 12.16.

LogP

The partition coefficients were calculated using solubility of azolate ionic liquids in mutually saturated octanol and water. The solubility was checked visually. 0.1 mL of solvents were added to 0.5 g of pure ILs. When the solutions became transparent, the densities were measured.

Thermal analyses

Melting points were determined (DSC) using a Mettler Toledo DSC Instruments model cooled with an intracooler. The calorimeter was calibrated for temperature and cell constants using indium (melting point 156.61 °C, ΔH 28.71 J g^{-1}). Data were collected at constant atmospheric pressure, using samples between 10–40 mg in aluminium sample pans. Experiments were performed at a heating rate of 10 °C min^{-1}. An empty sample pan was used as reference.

Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA (TA Instruments 2950) under air atmosphere. Samples between 2–10 mg were heated from 40–500 °C under constant heating at 10 °C min^{-1}. Decomposition temperatures ($T_{onset(5\%)}$ and T_{onset}) were determined from onset to 5% mass loss and 50% mass loss respectively, under nitrogen.

Antimicrobial activity

The following microorganisms were used: *Micrococcus luteus* NCTC 7743, *Staphylococcus aureus* NCTC 4163, *Staphylococcus epidermidis* ATCC 49134, *Enterococcus faecium* ATCC 49474, *Moraxella catarrhalis* ATCC 25238, *Escherichia coli* ATCC 25922, *Serratia marcescens* ATCC 8100, *Proteus vulgaris* NCTC 4635, *Pseudomonas aeruginosa* NCTC 6749, *Bacillus subtilis* ATCC 6633, *Candida albicans* ATCC 10231, *Rhodothorula rubra* (Demml 1889, Lodder 1934). Standard strains were supplied by the National Collection of Type Cultures (NCTC) London and American Type Culture Collection (ATCC). *Rhodothorula rubra* was obtained from the Department of Pharmaceutical Bacteriology, University of Medical Sciences, Poznan. Antimicrobial activity was determined by the tube dilution method. Bacteria strains were cultured on a Müller-Hinton broth for 24 h, and fungi on Sabouraud agar for 48 h. A suspension of the microorganisms at a concentration of 10^6 cfu mL^{-1} was prepared from each culture. This suspension was then used to inoculate

each dilution of the broth medium at a 1 : 1 ratio. Growth of the microorganisms (or lack thereof) was determined visually after incubation for 24 h at 35 °C (bacteria) or 48 h at 22 °C (fungi).

The lowest concentration at which there was no visible growth (turbidity) was taken as the MIC (minimal inhibitory concentration). Then, an aliquot taken from each tube in a sample loop was cultured in an agar medium with inactivates (0.3% lecithin, 3% polysorbate 80, and 0.1% cysteine L) and incubated for 48 h at 37 °C (bacteria) or for 5 d at 29 °C (fungi). The lowest concentration of the studied salt supporting no colony formation was defined as the MBC (minimum bactericidal or fungicidal concentration).

Antifungal efficacy

The fungal growth rates were measured in 90 mm Petri dishes using the agar dilution test. Ten concentrations of the compounds were studied in a geometric progression from 10 to 5000 μg mL^{-1}. Stock solutions of each concentration of the studied chemicals were produced in sterile malt agar (1.5% agar and 4% maltextract), 20 mL of which was added to each Petri dish. Three replicate plates of each concentration of each compound were centrally inoculated with a 5 mm diameter disc taken from the submargin of 10-day-old cultures of the desired test fungus grown on malt agar. The plates were incubated at (22 ± 1) °C in darkness. The duration of the test was either determined by waiting for complete plate coverage by growing mycelium or 12 days for *Sclerophoma pityophila* and *Coniophora puteana* fungi and 6 days for *Trametes versicolor* fungus (for which growth rates were higher than for the two earlier mentioned fungi). If growth on the preservative-containing agar had not begun after 12 days or 6 days, respectively, the inoculum was removed and transferred to a fresh malt agar plate for determination of the fungal viability.

The results were used to calculate ED_{50} (preservative concentrations retarding the fungal growth rate by 50 percent in comparison with plates where the toxic agent was omitted), the effective dose ED_{100} (preservative concentrations retarding the fungal growth rate by 100 percent in comparison with plates where the toxic agent was omitted), and LD (concentrations causing death of fungus inoculum) of the examined salts. The strains used for the tests, *Sclerophoma pityophila* (Corda) v.Höhn, strain S 231, *Coniophora puteana* (Schum.:Fr.) Karst. strain BAM 15, and *Trametes versicolor* (L.:Fr.) Pilát strain CTB, were obtained from the collection of the Institute of Wood Technology, Poznan, Poland.

Assay of biological activity as potential fungicides

Two species of fungi were used: *Fusarium culmorum* and *Sclerotinia sclerotiorum* (Institute of Plant Protection-PIB collection). ILs were dissolved in 10 mL of water and ethanol solution (1 : 1) and then added to sterile medium (PDA—Potato Dextrose Agar, Difco™), cooled to 50 °C.[42] The concentration of IL in the medium was established on 10 and 100 ppm. Liquid medium with preparations was overlaid on the Petri dishes. The 5 mm disks of the examined fungi were placed in the center of the Petri dish. At the control plates fungi were grown on PDA with water. The plates were incubated at a temperature of 21 °C until the control reached the edge of the Petri dish. Then a diameter of mycelium growth was measured. All assays were performed in eight replications and the presented results are means of all replications. The results were subjected to Student-Newman-Keuls's *t*-test at $p < 0.05$ to test for significant differences between control and samples with addition of active substances.

Phytotoxicity

The influence of new azolate compounds on growth of garden cress (*Lepidium sativum*) was examined using test tube agar method described by Mathur and Kondsdal[43] with our modifications. 10 mL of 1% water agar was poured into each test tube (16 mm × 160 mm) using an automatic dispenser. The tubes covered with aluminium foil were placed into containers and autoclaved at 121 °C for 20 min. After solidification of agar, 1 seed of garden cress and 50 μL of water solution of tested compounds were dropped in each tube. ILs were tested at 8 concentrations (36, 73, 146, 292, 584, 1167, 2335 and 4670 ppm). The homogenous seeds of garden cress (1.25–1.5 mm of diameter) were treated with 5% solution of sodium hypochlorite for 3 min and placed in Petri dishes for germination 20 h before pouring was done. The test tubes were arranged in racks and placed in a growth chamber at 20 °C, 80% of humidity and 16/8 h day/night photoperiod. After 7 days plants were removed from tubes and fresh mass was measured using laboratory scales (Kern, Germany, accuracy 0.0001 g). The test was carried out at six replications.

Statistical analysis

Two-way analysis of variance of fresh weight reduction of garden cress plants was carried out to determine the main effects of compound and concentration and the effect of compound × concentration interaction. Least significant differences for fresh weight reduction were calculated. Homogeneous groups for the analyzed trait were determined on the basis of least significant differences. The best model for every relationship between compound and concentration was estimated and ED_{50} were calculated.

Surface activity

Surface tension 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 to form an axisymmetric drop at the tip of a needle of a syringe. The image of the drop (3 μL) is taken from a CCD camera and digitized. The surface tension (γ in mN m^{-1}) is calculated by analyzing the profile of the drop according to the Laplace equation. Temperature was controlled using a Fisherbrand FBH604 thermostatic bath (Fisher, Germany, accuracy ±0.1 °C). The values of the critical micelle concentration (CMC) and the surface tension at the CMC (γ_{CMC}) were determined from the intersection of the two straight lines drawn in low and high concentration regions in surface tension curves (γ-log *C* curves) using a linear regression analysis method.

Conclusion

A novel group of quaternary ammonium azolate based ionic liquids were synthesized and investigated. These salts were obtained with combinations of didecyldimethylammonium, benzalkonium, domiphen, and hexadecyltrimethylammonium cations and benzotriazolate, 1,2,4-triazolate, 4-nitroimidazolate, and 2-methyl-4-nitroimidazolate anions. It was found that the studied ionic liquids were very effective anti-bacterial and anti-fungal agents. Their activities were comparable or higher than those of the original benzalkonium chloride. Phytotoxicity of synthesized azolates depended on cation and anion. Benzalkonium 4-nitroimidazolate, hexadecyltrimethylammonium 2-methyl-4-nitroimidazolate and dominphen benzotriazolate demonstrated lower phytotoxicity. In addition, our results indicated that these salts self-assemble easily in aqueous solutions. The obtained results of CMC were similar or lower than values of classical cationic surfactants in aqueous solutions. We believe these multifunctional quaternary ammonium azolate based ionic liquids are of high practical importance.

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