Ionic Liquids with Symmetrical Dialkoxymethyl-Substituted Imidazolium Cations

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Abstract: A new one-step procedure is described for the synthesis of disubstituted imidazolium chlorides. 1,3-Dialkoxymethylimidazolium chlorides thus obtained can be employed as synthetic precursors of symmetrical ILs. The salts have been found to exhibit antimicrobial activity and an antielectrostatic effect. Their densities and viscosities have been determined and are reported herein. It has also been demonstrated that the ILs can be decomposed using an aqueous solution of $KMnO_4$. For each IL, the permanganate index (I_{Mn}) has been estimated, which varies with the structure of cation. The only limitation of I_{Mn} is the degree to which the IL dissolves in water.

Keywords: alkoxymethylation • imidazolium salts • ionic liquids • structure–activity relationships • synthetic methods

Introduction

Among the ionic liquids (ILs) described in the literature, the most widely known are those that contain an imidazolium cation. Particular attention has been devoted to asymmetrically disubstituted imidazolium salts. These have been utilized in many areas of synthetic organic chemistry as solvents and catalysts, and also in separation science.[1–7] Biocatalysis in ILs has only recently been considered.[8] ILs have even been successfully used for embalming and tissue preservation.[9]

The most frequently encountered cations are 1-alkyl-3-methylimidazolium ions, with limited structural variation in the alkyl group.[10–17] The precursors of the ILs are disubstituted imidazolium halides, which have a hygroscopic or deliquescent nature. The reported preparations of 1-alkyl-3-methylimidazolium chlorides, starting from 1-methylimidazole and an alkyl chloride and based on the conventional method of heating in refluxing solvents, require long reaction times (from hours to days).[18,19] A significant shortening of the reaction time can be achieved by using an alkyl bromide as the alkylating agent.[20] An efficient method for the preparation of the halides makes use of microwave irradiation as the energy source under solvent-free conditions.[21,22] Application of this technique leads to dramatically reduced reaction times. Another procedure, using sonochemical activation, has also been described for solvent-free preparations of 1-alkyl-3-methylimidazolium halides by reaction of 1-methylimidazole with alkyl halides.[23] An efficient microwave-based protocol has been described for the preparation of ILs consisting of dialkylimidazolium cations and BF_4^- anions.[24] The asymmetry of the 1-alkyl-3-methylimidazolium cations is believed to be responsible for the low melting points of the resulting ILs.[25,26] Even symmetrically substituted 1,3-dialkylimidazolium hexafluorophosphates with dibutyl, dipentyl, dioctyl, dinonyl, and didecyl substituents are found to be ILs.[27] Howarth and co-workers have described the use of symmetrical chiral imidazolium bromides in Diels–Alder reactions.[28] Symmetrical disubstituted 1,3-dialkoxymethyl imidazolium cations provided the subject for our studies.

Results and Discussion

Our synthesis started from imidazole (freshly recrystallized from benzene; m.p. 90–91 °C) and chloromethyl alkyl ethers. The type of solvent employed was found to play a significant role in determining the course of the reaction: only in anhydrous DMF was a single product obtained, namely a 1,3-dialkoxymethylimidazolium chloride, $[(C_nOm)_2im][Cl]$ (Scheme 1). Deprotonation took place in the absence of alkali, in parallel to the quaternization reaction. The total efficiency of the two reactions reached 85 %. If the process was attempted in any other anhydrous solvent, such as acetone, toluene, or DMSO, the reaction product contained three salts: the 1,3-dialkoxymethylimidazolium chloride, the

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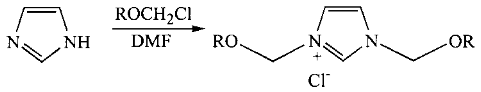
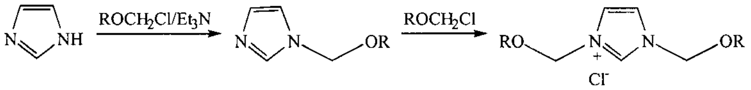


Scheme 1.

1-alkoxymethylimidazolium hydrochloride, and imidazolium hydrochloride, the separation of which was practically impossible. A similar mixture was obtained under neat reaction conditions. When DMF was used, the medium served not only as a solvent but also played the role of a proton-trapping base. The initially generated imidazolium anion rapidly reacted with the $ROCH_2^+$ cation at each of the nitrogen atoms at the same rate. On the other hand, no reaction of the $ROCH_2^+$ cation with DMF was observed, reflecting the difficult access of the cation to the free electron pair of the nitrogen atom. The new one-step approach for the synthesis of symmetrical disubstituted imidazolium chlorides described herein proved to be very effective.

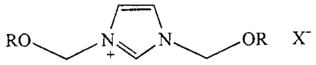
1,3-Dialkoxymethylimidazolium chlorides were also obtained in a two-step procedure (Scheme 2). In the first step, toluene was used as solvent for an N-alkoxymethylation of imidazole with the appropriate (alkoxymethyl)triethylammonium chloride. This reaction constitutes a new approach, which is better than deprotonation and nucleophilic displacement.[29] The 1-alkoxymethylimidazole, formed in 70–80 % yield, was distilled from the reaction mixture, and then a Menschutkin reaction was performed to afford a quaternized product in 75–90 % yield. $ROCH_2Cl$ is an effective quaternization substrate in the Menschutkin reaction, but its use required that anhydrous conditions were maintained. The presence of water induces hydrolysis of $ROCH_2Cl$ with the formation of HCl, which, in turn, forms amine hydrochlorides.



Scheme 2.

The purities of the chloride salts, $[(C_nOm)_2im][Cl]$, containing more than six carbon atoms in the alkoxy substituent were determined by a direct two-phase titration technique (EN ISO 2871-2:1994) and ranged from 92 to 96 %. The remainder was essentially water since the chloride salts were strongly hygroscopic. The chlorides were then employed as synthetic precursors for ILs. The metathesis reactions were conducted in aqueous solutions using the salts $NaBF_4$, KPF_6, and $LiNTf_2$, and gave high yields (89–95 %). The precursor and product salts are listed in Table 1. All of the $[BF_4]$ and $[NTf_2]$ salts, as well as eight out of ten $[PF_6]$ salts, proved to be ILs (m.p. $< 100\,°C$), but at room temperature only three $[BF_4]$, no $[PF_6]$, and six out of ten $[NTf_2]$ salts were liquid. Thus, out of 28 potential ILs, only nine proved to be room temperature ionic liquids (RTILs). The symmetrically substituted cation had an impact on the solid nature of the salts, but not as much as has been suggested in the literature. The type of anion rather than the cation symmetry played a key role in formation of the RTILs.

Table 1. Structure and melting points of prepared salts of the series $[(C_nOm)_2im][X]$.



Salt	R	Cl m.p. [°C]	BF_4 m.p. [°C]	PF_6 m.p. [°C]	NTf_2 m.p. [°C]
$[(C_3Om)_2im][X]$	C_3H_7	oil	liquid	69–73	liquid
$[(C_4Om)_2im][X]$	C_4H_9	oil	liquid	53–56	liquid
$[(C_5Om)_2im][X]$	C_5H_{11}	grease	liquid	50–54	liquid
$[(C_6Om)_2im][X]$	C_6H_{13}	grease	42–43	60–62	liquid
$[(C_7Om)_2im][X]$	C_7H_{15}	grease	39–40	63–66	liquid
$[(C_8Om)_2im][X]$	C_8H_{17}	93–96	53–54	77–80	liquid
$[(C_9Om)_2im][X]$	C_9H_{19}	94–98	55–58	84–87	26–30
$[(C_{10}Om)_2im][X]$	$C_{10}H_{21}$	99–102	67–70	97–99	31–32
$[(C_{11}Om)_2im][X]$	$C_{11}H_{22}$	104–106	70–72	103–105	45–46
$[(C_{12}Om)_2im][X]$	$C_{12}H_{25}$	108–110.5	78–80	104–107	44–45

The new 1,3-dialkoxymethylimidazolium salts were characterized by ^1H and ^{13}C NMR and by elemental analysis. The ^1H NMR spectra of the precursors and the resulting $[BF_4]$, $[PF_6]$, and $[NTf_2]$ salts indicated different chemical shifts for the imidazolium ring protons and the two methylene groups adjacent to the oxygen atoms. No such differences were noted in the ^{13}C NMR spectra. Chemical shift data are reported in Table 2. The strong effect of the anion is evident. The most marked shift differences were observed for the proton in the 2-position of the ring, and these shifts can serve as a parameter to classify the type of salt. Similar observations concerning the ring protons were made by Fannin and co-workers for 1-alkyl-3-methylimidazolium salts $[Al_xCl_{3x+1}]$.[30]

Anhydrous ILs were obtained by heating the samples at 80 °C in vacuum (8 mmHg) for 10 h. Karl–Fischer measurements showed the water content of the dried salts to be < 500 ppm. Moreover, no bands associated with water were observed in the near-infrared spectrum at 1910 nm. These anhydrous ILs quickly absorb water when they are exposed to air. In 10 h, $[(C_nOm)_2im][NTf_2]$ can absorb up to around 0.5 % of its weight in water. All of the salts were found to be stable in air, in water, and in common organic solvents such as $CHCl_3$, ethyl acetate, and ethanol. The RTILs showed high solubility in common alcohols, DMSO, ethyl acetate, and $CHCl_3$, but were visually immiscible with hexane. $[(C_3Om)_2im][BF_4]$ was found to be miscible with

Table 2. Characteristic proton chemical shifts[a] of the prepared salts.

Salt	Imidazole NCHN Singlet	Imidazole NCHCHN Doublet	NCH_2O Singlet	OCH_2CH_2 Triplet
$[(C_nOm)_2im][Cl]$	10.85	7.75 (J = 1.4 Hz)	5.84	3.61 (J = 6.5 Hz)
$[(C_nOm)_2im][BF_4]$	9.12	7.48 (J = 1.6 Hz)	5.59	3.56 (J = 6.5 Hz)
$[(C_nOm)_2im][PF_6]$	8.79	7.48 (J = 1.4 Hz)	5.54	3.54 (J = 6.5 Hz)
$[(C_nOm)_2im][NTf_2]$	9.04	7.53 (J = 1.4 Hz)	5.57	3.53 (J = 6.5 Hz)

[a] In $CDCl_3$.

water, while $[(C_4Om)_2im][BF_4]$ and $[(C_5Om)_2im][BF_4]$ were only partially miscible. On the other hand, the $[(C_nOm)_2im][NTf_2]$ ILs proved to be immiscible with water; only those with propoxymethyl and butoxymethyl substituents demonstrated slight solubility in water at 80 °C.

Some physical properties of the new RTILs were studied. All of the RTILs were found to be denser than water. Density values at 25 °C are presented in Table 3. The densities ranged from 1.105 to 1.391 $g\,mL^{-1}$. The $[(C_nOm)_2im][NTf_2]$ ILs were significantly denser than their $[(C_nOm)_2im][BF_4]$ counterparts. As is typical for RTILs with a range of alkyl chain lengths, increasing chain length is associated with a decrease in density. In the range 20–30 °C, temperature had only a slight effect on density, which did not exceed 2 %.

Table 3. Density, viscosity, and thermal degradation temperature (T_d) of prepared RTILs.

Entry	Salt	Density[a] [$g\,mL^{-1}$]	Viscosity[a] [mPa s]	T_d [°C]
1	$[(C_3Om)_2im][BF_4]$	1.194	165.7	210
2	$[(C_4Om)_2im][BF_4]$	1.137	313.6	220
3	$[(C_5Om)_2im][BF_4]$	1.105	$>$ 400	200
4	$[(C_3Om)_2im][NTf_2]$	1.391	82.6	235
5	$[(C_4Om)_2im][NTf_2]$	1.338	86.7	240
6	$[(C_5Om)_2im][NTf_2]$	1.277	95.0	230
7	$[(C_6Om)_2im][NTf_2]$	1.249	115.0	230
8	$[(C_7Om)_2im][NTf_2]$	1.226	144.9	240
9	$[(C_8Om)_2im][NTf_2]$	1.205	154.0	235

[a] At 25 °C.

Viscosity data at 25 °C are also presented in Table 3. The viscosity/chain length relationship showed the inverse trend to the density/chain length relationship: thus, viscosity increased with increasing alkyl chain length of the cation. The values were also found to be strongly affected by humidity and temperature. A decrease in temperature of 5 °C (from 25 to 20 °C) was found to be accompanied by an increase in viscosity of 15–30 %. We observed that the $[NTf_2]$ salts had lower viscosities than the $[BF_4]$ salts. From the presented data, it could be concluded that the most favorable lower viscosities were found for RTILs having $[NTf_2]$ anions and propoxymethyl, butoxymethyl, and pentyloxymethyl substituents on the cation. The low viscosities of these RTILs is an important issue in some applications.

The prepared RTILs could not purified by distillation due to their involatile character. However, their thermal degradation temperatures could be estimated by using a Büchi model B-545 automatic boiling point apparatus. The thermal stabilities of the RTILs ranged from 200 to 240 °C, as shown in Table 3. TG analysis showed that the degradation process took place at 210–220 °C for the $[(C_nOm)_2im][BF_4]$ salts and at 230–240 °C for the $[(C_nOm)_2im][NTf_2]$ salts, thus confirming the results in Table 3. In the case of imidazolium salts with two alkoxymethyl substituents, a significantly lowered thermal degradation temperature was noted as compared to analogues with alkyl groups, for example, 1-alkyl-3-methylimidazolium $[NTf_2]$, which are stable up to 400 °C.[18] This is a reflection of the presence of two oxygen atoms in the symmetrical substituents.

The solid-phase behavior of two RTILs was analyzed by differential scanning calorimetry (DSC). $[(C_4Om)_2im][BF_4]$ exhibited multiple solid phases below its melting point. It displayed a glass transition at −49 °C, followed by a crystallization at −29 °C, seen as an exothermic transition, followed by a large endothermic solid–solid transition at −11 and −5 °C and the final melt at 8 °C. The DSC trace of a $[(C_nOm)_2im][NTf_2]$ salt showed only a glass transition. These materials are good glass-formers, that is, they can be cooled from the liquid state down to low temperatures without crystallizing. The glass transitions for the $[NTf_2]$ series are as follows: $[(C_3Om)_2im]$ −40 °C, $[(C_4Om)_2im]$ −39 °C, $[(C_5Om)_2im]$ −41 °C, $[(C_6Om)_2im]$ −44 °C, $[(C_7Om)_2im]$ −43 °C, and $[(C_8Om)_2im]$ −42 °C.

The prepared chlorides were tested for antimicrobial activity against rods, cocci, and fungi. The tube dilution method used showed the lowest concentration of a chloride required to inhibit cell multiplication (minimal inhibitory concentration; MIC). Mean MIC values for cocci, rods, and fungi are presented in Figure 1. Chlorides $[(C_7Om)_2im][Cl]$, $[(C_8Om)_2im][Cl]$, and $[(C_9Om)_2im][Cl]$ proved to be effective against the microbes, and their activity remained at a level typical for

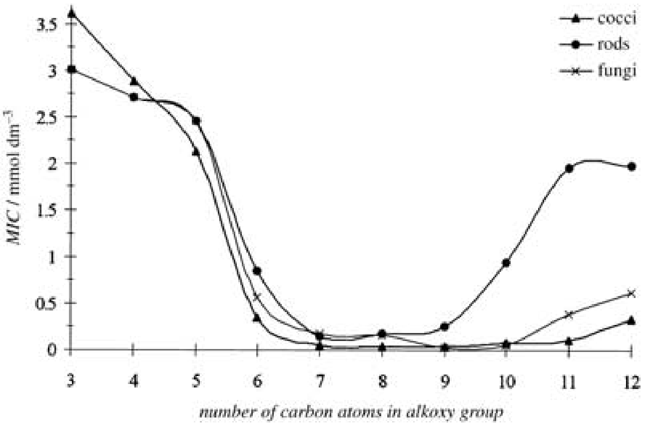


Figure 1. Mean MIC values for microorganisms.

commercially available benzalkonium chloride (BAC). The optimal relationship between the measured activity and compound structure was noted for *Micrococcus luteus*, and a simplified Hansch equation was constructed [Eq. (1)]:

$$\log RBR = a + b \cdot C\log P + c \cdot C\log P^2 \tag{1}$$

where *RBR* (relative biological response) is represented by 1/MIC and *P* is the 1-octanol/water partition coefficient.

For chlorides $[(C_nOm)_2im][Cl]$, values of $a = 0.6384$ (± 0.1109), $b = 0.5287(\pm 0.6010)$, and $c = -0.0696(\pm 0.0118)$ were obtained, with the relevant statistical data as follows: correlation coefficient $r = 0.9635$, predicted value of equation $r^2 = 0.9282$, standard error of estimation $s = 0.2610$, significance level of regression equation $p < 0.00010$, and apex of the parabola $C\log P_o = 3.798$. The statistically significant correlation of the QSAR equation obtained confirmed that lipophilicity, expressed by $C\log P$, was the main conditioning factor of antimicrobial activity.

The $[(C_nOm)_2im][BF_4]$ and $[NTf_2]$ ILs could also be expected to be effective to the same extent, in line with earlier studies that demonstrated that the anion exerted negligible effect on antimicrobial activity.[31] The data were significant with regard to the selection of the synthesized RTILs as solvents for enzymatic reactions with participation of microbes. The RTILs that could be safely used were found to include three $[BF_4]$ salts and three $[NTf_2]$ salts with propoxymethyl, butoxymethyl, and pentyloxymethyl groups.

The antielectrostatic properties of the synthesized salts were also examined. The antielectrostatic effect is dependent on two quantities: the surface resistance and the half-charge decay time. The surface resistance was calculated from the formula:

$$R_s = \frac{U \cdot l}{i \cdot s}\,[\Omega] \tag{2}$$

where U is the applied voltage ($U = 100$ V), l is the length of the electrodes ($l = 100$ mm), i is the measured current intensity, and s is the distance between the electrodes ($s = 10$ mm).

The half-charge decay time was obtained from the relationship:

$$\tau = \sqrt{\frac{\tau_+^2 + \tau_-^2}{2}}[s] \tag{3}$$

where τ_+ and τ_- are the mean half-decay times of positive and negative charges, respectively.

The antielectrostatic effect was determined according to the criteria listed in Table 4 and the findings are presented in Table 5. Of ten chlorides studied, eight showed an excellent antielectrostatic effect. These chlorides contained three to ten carbon atoms in their alkoxy chains. The use of alkoxymethyl substituents longer than the decyloxymethyl group caused the chlorides to lose their antielectrostatic properties. Substitution of the anion in the studied chlorides demonstrated its strong effect on the antielectrostatic properties of the compounds: the $[(C_nOm)_2im][PF_6]$ ILs obtained lost their potential for draining the charge and showed no antielectrostatic properties. In the case of the $[(C_nOm)_2im]$ $[BF_4]$ series, only three salts with a short substituent, containing three, four, and five carbon atoms in the alkoxy group, demonstrated an excellent antielectrostatic effect. $[(C_nOm)_2im][BF_4]$ ILs with seven, eight or nine carbon atoms behaved untypically, giving a high R_s value and a low $\tau_{1/2}$ value. In terms of the the applied evaluation scale, these compounds could not be unequivocally categorized. A similar situation was encountered with $[(C_5Om)_2im][PF_6]$, $[(C_6Om)_2im][PF_6]$, $[(C_7Om)_2im][PF_6]$, and $[(C_8Om)_2im]$ $[PF_6]$. On the other hand, in the case of the $[(C_nOm)_2im]$ $[NTf_2]$ series, as seen for their synthetic precursors, the first eight salts demonstrated an excellent effect. The groups of salts showed an acute transition from salts with an excellent effect to those with no effect. The type of anion was also found to be significant for the potential to drain the charge. Because of the delocalization of the negative charge within the S–N–S core, the NTf_2^- anion is probably less associated with the cation and more mobile than PF_6^- or BF_4^-. At the same time, it proved possible to synthesize ILs which, similarly to their synthetic precursors, demonstrated an excellent antielectrostatic effect. It is also worth nothing that all of the obtained RTILs demonstrated excellent antielectrostatic properties.

Table 4. Criteria for the estimation of the antielectrostatic effect based on the surface resistance R_s [Ω] and half-charge decay time $\tau_{1/2}$ [s].

$\log R_s$	$\tau_{1/2}$	Antielectrostatic effect
< 9	< 0.5	excellent
9–9.99	0.51–2	very good
10–10.99	2.1–10	good
11–11.99	10.1–100	sufficient
12–12.99	> 100	insufficient
> 13	> 600	lack of antielectrostatic properties

The dynamically growing application of ILs induces misgivings as to their utilization. We regard their oxidation in an aqueous solution of $KMnO_4$ as an effective solution. This proved to offer a hitherto unknown safe way of utilizing them. The cation was ultimately oxidized to CO_2 and H_2O. Under such conditions, the anion was not oxidized. For each IL we were able to investigate the permanganate index (I_{Mn}), which exhibited a range of values. The values of I_{Mn} for the synthesized and some commercially available ILs are listed in Table 6. Solubility in water represented the only limitation. In the case of the $[(C_nOm)_2im][NTf_2]$ ILs, which are immiscible with water, no such index could be estimated. The risk that used ILs could pollute the environment as non-decomposable agents was found to be groundless.

We decided to check whether the RTILs exhibited phytotoxic activity and to examine their influence on soil flora by the measurement of root growth inhibition. The investigations followed the International Standard ISO 11269-1 protocol and were performed using $[(C_nOm)_2im][BF_4]$. The tested representative plant was barley, *Hordeum vulgare L.* All $[(C_nOm)_2im][BF_4]$ salts introduced to the soil at a con-

Table 5. Surface resistance R_s [Ω], half-charge decay time $\tau_{1/2}$ [s], and antielectrostatic effect for the prepared salts.

Salt	$\log R_s$	$\tau_{1/2}$	Effect	Salt	$\log R_s$	$\tau_{1/2}$	Effect
$[(C_3Om)_2im][Cl]$	7.35	< 0.1	excellent	$[(C_3Om)_2im][PF_6]$	13.20	> 600	lack
$[(C_4Om)_2im][Cl]$	7.08	< 0.1	excellent	$[(C_4Om)_2im][PF_6]$	13.11	> 600	lack
$[(C_5Om)_2im][Cl]$	6.63	< 0.1	excellent	$[(C_5Om)_2im][PF_6]$	12.72	0.55	
$[(C_6Om)_2im][Cl]$	6.72	< 0.1	excellent	$[(C_6Om)_2im][PF_6]$	12.95	2.10	
$[(C_7Om)_2im][Cl]$	6.79	< 0.1	excellent	$[(C_7Om)_2im][PF_6]$	12.20	2.60	
$[(C_8Om)_2im][Cl]$	6.77	0.45	excellent	$[(C_8Om)_2im][PF_6]$	12.99	2.05	
$[(C_9Om)_2im][Cl]$	7.04	0.35	excellent	$[(C_9Om)_2im][PF_6]$	13.20	> 600	lack
$[(C_{10}Om)_2im][Cl]$	8.04	0.35	excellent	$[(C_{10}Om)_2im][PF_6]$	13.36	> 600	lack
$[(C_{11}Om)_2im][Cl]$	9.43	0.55	very good	$[(C_{11}Om)_2im][PF_6]$	13.11	> 600	lack
$[(C_{12}Om)_2im][Cl]$	10.57	2.05	good	$[(C_{12}Om)_2im][PF_6]$	13.08	> 600	lack
$[(C_3Om)_2im][BF_4]$	7.58	< 0.1	excellent	$[(C_3Om)_2im][NTf_2]$	8.41	<0.1	excellent
$[(C_4Om)_2im][BF_4]$	8.15	< 0.1	excellent	$[(C_4Om)_2im][NTf_2]$	8.60	<0.1	excellent
$[(C_5Om)_2im][BF_4]$	8.11	< 0.1	excellent	$[(C_5Om)_2im][NTf_2]$	8.56	<0.1	excellent
$[(C_6Om)_2im][BF_4]$	9.63	0.17	very good	$[(C_6Om)_2im][NTf_2]$	8.58	<0.1	excellent
$[(C_7Om)_2im][BF_4]$	10.04	0.25		$[(C_7Om)_2im][NTf_2]$	8.80	<0.1	excellent
$[(C_8Om)_2im][BF_4]$	11.34	0.40		$[(C_8Om)_2im][NTf_2]$	8.73	<0.1	excellent
$[(C_9Om)_2im][BF_4]$	11.28	0.45		$[(C_9Om)_2im][NTf_2]$	8.11	0.30	excellent
$[(C_{10}Om)_2im][BF_4]$	13.00	> 600	lack	$[(C_{10}Om)_2im][NTf_2]$	8.36	0.35	excellent
$[(C_{11}Om)_2im][BF_4]$	13.08	> 600	lack	$[(C_{11}Om)_2im][NTf_2]$	13.20	> 600	lack
$[(C_{12}Om)_2im][BF_4]$	13.00	> 600	lack	$[(C_{12}Om)_2im][NTf_2]$	13.18	> 600	lack

Table 6. Permanganate indices (I_{Mn}) for the prepared and some commercial ILs.

IL	I_{Mn}	IL	I_{Mn}
$[(C_3Om)_2im][BF_4]$	8.4	$[C_4mim][PF_6]$[a]	3.1
$[(C_4Om)_2im][BF_4]$	8.7	$[C_4mpyr][BF_4]$[a]	1.4
$[(C_5Om)_2im][BF_4]$	11.1	$[C_8mim][BF_4]$	4.7
$[(C_3Om)_2im][NTf_2]$	6.5	$[C_{10}mim][BF_4]$	6.0
$[(C_4Om)_2im][NTf_2]$	8.5	$[C_7Omim][BF_4]$	8.8
$[C_2mim][BF_4]$[a]	5.6	$[C_8Omim][BF_4]$	9.3
$[C_4mim][BF_4]$[a]	3.6	$[C_9Omim][BF_4]$	9.5
$[C_2mim][NTf_2]$[a]	5.2		

[a] Product from Fluka; $[C_nmim]$ = 1-alkyl-3-methylimidazolium; $[C_4mpyr]$ = 1-butyl-4-methylpyridinium; $[C_nOmim]$ = 1-alkoxymethyl-3-methylimidazolium.

centration of 1 g kg^{-1}, or 0.1 g kg^{-1} dry mass of soil, were found to exert a phytotoxic effect on monocotyledonous plants. On the other hand, at a concentration of 0.01 g kg^{-1} no such effect was noted on the growth of the roots (Figure 2).

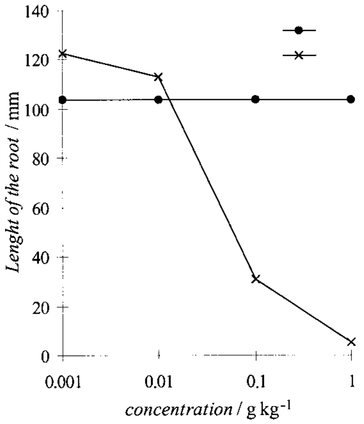


Figure 2. Length of barley roots according to concentration of the obtained $[BF_4]$; ●: trace analysis, ×: $[(C_nOm)_2im][BF_4]$.

Conclusion

Reaction of imidazole with $ROCH_2Cl$ in DMF produced 1,3-dialkoxymethylimidazolium chlorides in high yields. These are useful synthetic precursors to symmetrical imidazolium-based ILs. The new $[(C_nOm)_2im][X]$ RTILs described herein were found to be stable to air and water, to be denser than water, and to have relatively low viscosities. Their properties proved to be dependent on the nature of the anion and on the bulkiness of the cation. The strong effect of the anion was particularly evident on their melting points, solubilities, and antielectrostatic properties. The estimated antielectrostatic properties and antimicrobial activities promise a broad spectrum of application for these ILs. They can be neutralized by oxygenation using $KMnO_4$ in aqueous solution.

Experimental Section

Elemental analyses were performed at the Adam Mickiewicz University, Poznań. ^{1}H NMR spectra were recorded on a Varian XL 300 spectrometer at 300 MHz with tetramethylsilane as the standard; ^{13}C NMR spectra were recorded on the same instrument at 75 MHz. A Mettler Toledo DA 110 M scale was used for the mass/density measurements. Simultaneous TG/DTA experiments were performed using a MOM (Hungary) Derivatograph-PC. Thermal degradation temperatures were determined using a Büchi model B-545 automatic apparatus. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC calibrated with a 99.9999 mol% purity indium sample.

Chloromethyl alkyl ethers were prepared by passing HCl through a mixture of formaldehyde and the appropriate alcohol.

Preparation of $[(C_nOm)_2im][Cl]$: The reaction flask was charged with freshly distilled DMF (30 mL), imidazole (9.5 g, 0.14 mol, 1 equiv), and chloromethyl alkyl ether (0.28 mol, 2 equiv). The solution was stirred at 30 °C for 4 h, and then cooled to room temperature. For chlorides with substituents containing 3–9 carbon atoms, DMF was expelled from the reaction mixture under reduced pressure and the products were repeatedly washed with warm hexane (3 × 14 mL). On the other hand, for chlorides with an alkoxy group with 10–12 carbon atoms, ethyl acetate (30 mL) was added to the reaction mixture. The product, which precipitated in the form of a white sediment, was recrystallized from an EtOAc/EtOH mixture (10:1, *v*/*v*). The final product was obtained as a hygroscopic compound and drying required rotary evaporation at ca. 50°C/8 mmHg for 8 h.

[(C$_7$Om)$_2$im][Cl]: ^{1}H NMR (CDCl$_3$): δ = 10.85 (s, 1H; CH), 7.75 (d, *J* = 1.4 Hz, 2H; 2×CH), 5.84 (s, 4H; 2×CH$_2$), 3.61 (t, *J* = 6.5 Hz, 4H; 2×CH$_2$), 1.57 (q, *J* = 6.8 Hz, 4H; 2×CH$_2$), 1.26 (m, 16H; 8×CH$_2$), 0.87 (t, *J* = 6.7 Hz, 6H; 2×CH$_3$); ^{13}C NMR (CDCl$_3$): δ = 137.4, 121.4, 79.1, 70.5, 31.3, 28.9, 28.6, 25.5, 22.2, 13.7; elemental analysis calcd (%) for $C_{19}H_{37}N_2O_2Cl$ (360.97): C 63.22, H 10.33, N 7.76; found: C 63.01, H 10.57, N 7.48.

Procedure for ion exchange: A saturated aqueous solution of NaBF$_4$ or KPF$_6$ or LiNTf$_2$ was added to a stoichiometric amount of a saturated hot aqueous solution of a prepared [(C$_n$Om)$_2$im][Cl]. The reaction mixture was stirred at room temperature for 2 h affording a heterogeneous mixture. After separation of the phases, the aqueous phase was decanted and the obtained salt was washed with water until chloride ions were no longer detected using AgNO$_3$. The prepared salt was dried for 10 h at 80°C in vacuum (8 mmHg). *For salts soluble in water:* The water was removed from the reaction mixture under reduced pressure. Ethyl acetate was added to the remaining suspension and the organic phase was washed with water. The volatile materials were removed under reduced pressure.

[(C$_6$Om)$_2$im][BF$_4$]: ^{1}H NMR (CDCl$_3$, 25°C): δ = 9.12 (s, 1H; CH), 7.48 (d, *J* = 1.6 Hz, 2H; 2×CH), 5.91 (s, 4H; 2×CH$_2$), 3.56 (t, *J* = 6.5 Hz, 4H; 2×CH$_2$), 1.51 (q, *J* = 6.8 Hz, 4H; 2×CH$_2$), 1.27 (m, 12H; 6×CH$_2$), 0.87 (t, *J* = 6.7 Hz, 6H; 2×CH$_3$); ^{13}C NMR (CDCl$_3$): δ = 135.7, 121.6, 79.5, 70.7, 31.4, 29.1, 25.4, 22.4, 13.9; elemental analysis calcd (%) for $C_{17}H_{33}N_2O_2BF_4$ (384.26): C 53.09, H 8.66, N 7.29; found: C 52.81, H 8.97, N 7.08.

[(C$_7$Om)$_2$im][PF$_6$]: ^{1}H NMR (CDCl$_3$, 25°C): δ = 8.79 (s, 1H; CH), 7.48 (d, *J* = 1.4 Hz, 2H; 2×CH), 5.54 (s, 4H; 2×CH$_2$), 3.54 (t, *J* = 6.5 Hz, 4H; 2×CH$_2$), 1.57 (q, *J* = 6.9 Hz, 4H; 2×CH), 1.27 (m, 16H; 8×CH$_2$), 0.87 (t, *J* = 6.7 Hz, 6H; 2×CH$_3$); ^{13}C NMR (CDCl$_3$): δ = 137.4, 121.5, 79.7, 70.9, 31.6, 29.1, 28.9, 25.6, 22.5, 13.9; elemental analysis calcd (%) for $C_{19}H_{37}N_2O_2PF_6$ (470.25): C 48.48, H 7.99, N 5.96; found: C 48.11, H 7.57, N 5.88.

[(C$_7$Om)$_2$im][NTf$_2$]: ^{1}H NMR (CDCl$_3$, 25°C): δ = 9.04 (s, 1H; CH), 7.53 (d, *J* = 1.4 Hz, 2H; 2×CH), 5.57 (s, 4H; 2×CH$_2$), 3.53 (t, *J* = 6.6 Hz, 4H; 2×CH$_2$), 1.58 (q, *J* = 6.9 Hz, 4H; 2×CH$_2$), 1.26 (m, 16H; 8×CH$_2$), 0.87 (t, *J* = 6.6 Hz, 6H; 2×CH$_3$); ^{13}C NMR (CDCl$_3$): δ = 135.2, 126.0, 121.8, 121.7, 117.5, 113.3, 79.6, 70.9, 31.7, 29.1, 28.9, 25.7, 22.6, 14.0; elemental analysis calcd (%) for $C_{21}H_{37}N_3O_6F_6$ (541.26): C 46.56, H 6.89, N 7.76; found: C 46.71, H 6.57, N 7.58.

Preparation of 1-alkoxymethylimidazoles: ROCH$_2$Cl (0.05 mol) was slowly added to a stirred anhydrous solution of triethylamine (5.06 g, 0.05 mol) in toluene (50 mL), and stirring was continued at 80°C for 15 min. Imidazole (3.4 g, 0.05 mol) was then added. After 30 min, the mixture was refluxed. After cooling to room temperature, the triethylamine hydrochloride produced was filtered off and the toluene was evaporated. The product was purified by vacuum distillation.

Antielectrostatic properties: The antielectrostatic effect was measured on a polypropylene film, which was free from lubricants and antioxidants. From this 0.25 mm film, 12.5 mm diameter disks were cut out. The PP disks were washed with acetone and then dried by placing them in an air-conditioned room. The disks were then immersed in 0.5% solutions of studied chlorides in chloroform for 60 s. After removal from the solution, each disk was hung up so that the chloroform could evaporate spontaneously. The surfaces of the disks were then rubbed with a cotton pad to ensure complete coverage with the precipitated material. The disks were stored for 24 h in an air-conditioned room at 20 ± 2°C with a relative humidity of 60 ± 5%. Finally, the surface resistance and half-charge decay times were measured. The measuring apparatus has been described previously.[16] The relative error in the determination of these two quantities did not exceed 7%.

Antimicrobial activity: Eleven standard strains were used: rods were represented by *Pseudomonas aeruginosa* ATCC 15442, *Escherichia coli* NCTC 8196, *Klebsiella pneumoniae* ATCC 4352, and *Proteus vulgaris* NCTC 4635; cocci by *Staphylococcus aureus* ATCC 6538, *Staphylococcus aureus MRSA* ATCC 43300, *Staphylococcus epidermidis* ATCC 12228, *Micrococcus luteus* ATCC 9341, and *Enterococcus hirae* ATCC 10541, and fungi by *Candida albicans* ATCC 10231 and *Rhodotorula rubra* (Demml 1889, Lodder 1934). Standard strains were supplied by the National Collection of Type Cultures (NCTC), London, and the American Type Culture Collection (ATCC). The *R. rubra* was obtained from the collection of the Department of Pharmaceutical Bacteriology, University of Medical Sciences, Poznań, Poland. Antimicrobial activity was determined by the tube dilution method, as described previously.[31]

QSAR analysis

Structural parameters: The theoretically calculated logarithms of 1-octanol/water partition coefficient parameters (*C*log*P*) were chosen as structural parameters for the obtained [(C$_n$Om)$_2$im][Cl] ILs. For these chlorides, the parameters (*C*log*P*) were calculated by means of the KOWIN v.1.66 program (Syracuse Research Corporation, NY, United States) from EPI Suite software package, v.3.10 (U.S. Environmental Protection Agency), based on the Meylan–Howard method.

Statistics: The statistical analysis was carried out using Statistica v.6 software (StatSoft, Inc., Tulsa, OK, United States).

Determination of permanganate index: A sample of 3 mmol of the IL was heated in boiling water with KMnO$_4$ and H$_2$SO$_4$ for 10 min. The estimations were performed in accordance with the norm (EN ISO 8467:1995).

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