CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701427

Trialkylammoniododecaborates: Anions for Ionic Liquids with Potassium, Lithium and Protons as Cations

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Abstract: Herein we report a new class of low-melting ionic liquids (IL) that consist of *N*,*N*,*N*-trialkylammonioundecahydrododecaborates(1−) as the anion and a range of cations. The cations include the common cations of conventional ILs such as tetraalkylammonium, *N*-alkylpyridinium, and *N*-methyl-*N*′-alkylimidazolium. In addition, their salts with lithium, potassium, and proton cations also exist as ILs. Pulse radiolysis studies indicate that the anions do not react with solvated electrons.

Keywords: boranes · boron · conducting materials · ionic liquids · lithium · pulse radiolysis

Introduction

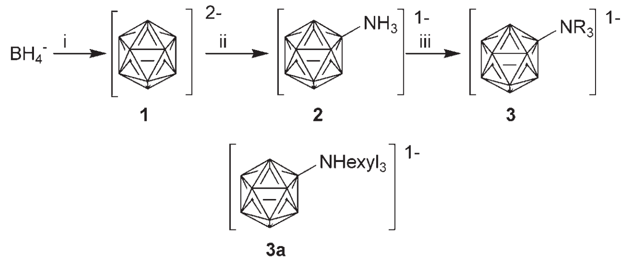
Ionic liquids (ILs), that is, salts with melting points below 100 °C, have been known for several decades. Lately, they have attracted considerable attention as they have become more accessible. Their properties differ from those of molecular solvents. They have very low vapor pressures and are incombustible. Their use relies on, among other properties, their high electric conductivity and their ability to solubilize various kinds of materials, and they have potential in many different applications, for example, as solvents in reactions and extractions and in electrochemical applications (for reviews, see ref. [1]).

Most ILs consist of a simple anion (tetrafluoroborate, hexafluorophosphate, chloride, bis-(trifluormethylsulfonyl)amide) combined with a number of different classes of cations. The cations (mostly tetraalkylammonium, tetraalkylphosphonium, *N*-alkylpyridinium, and *N*-methyl-*N*′-alkylimidazolium) can be varied to influence the properties of the ILs. Rarely can the properties of ILs be systematically changed by changing the anion structure, perfluoroalkyltrifluoroborates[2] and boric acid esters[3] are some of the few examples.

We have found that *N*,*N*,*N*-trialkylammonioundecahydrododecaborate(1−) derivatives represent a new type of anions for use as ILs. They can form ILs with the classes of cations presently used. In addition, for the first time, these anions have allowed potassium-containing ILs to be obtained, as well as noncorrosive and hydrolysis-resistant ILs with Li^+ and unsolvated H^+ cations.

Results and Discussion

The dodecaborate cluster $B_{12}H_{12}^{2-}$ (**1**) can easily be obtained from $NaBH_4$ by using I_2 as an oxidizing agent (Scheme 1).[4]



Scheme 1. Synthesis of the IL anions. i) I_2/diglyme; ii) $H_2NO{-}SO_3H/H_2O$; iii) RBr, CH_3CN, KOH.

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$B_{12}H_{11}NH_3^-$ (**2**) was first described by Hertler und Raasch, who prepared it from **1** with hydroxylamine-*O*-sulfonic acid.[5] The nitrogen atom can be alkylated with alkyl halides in the presence of base, which leads to trialkylated products with unbranched alkyl halides.[6] Isoalkyl and benzyl halides react to give disubstituted products.

The reaction of **2** with alkyl bromides to give $B_{12}H_{11}NR_3^-$ (**3**) proceeds smoothly in acetonitrile at room temperature with KOH as base. Trialkylation is found for linear alkyl halides and for halides in which there is branching after the β-carbon atom. Attempts to speed up the reaction by heating resulted in byproducts, especially bromine-substituted clusters.

The exchange of K^+ for organic cations can be achieved in water for chain lengths up to hexyl as these salts are readily soluble in water. By adding the desired cation as the chloride, the cluster is precipitated. For longer alkyl chains, for which water solubility is poor, the K^+ salt can be dissolved in a mixture of ethyl acetate and methanol; addition of an equimolar amount of the chloride salt of the cation leads to the precipitation of KCl. The IL is then obtained by removal of the solvent (the last traces can be removed by prolonged heating in vacuo).

The compounds gave ^1H and ^{13}C NMR and ESI mass spectra in accordance with the proposed structures. We had found previously that ESI-MS is also capable of detecting small amounts of ionic impurities.[7] When alkylation is performed at higher temperatures, partial halogenation of the cluster is found which further corroborates the purity of the substances obtained under mild conditions. ^{11}B NMR spectra agree with the structure of the cluster; impurities are, however, difficult to detect because of the inherent broadness of the signals. Elemental analysis was carried out for several compounds. The results are reported in Table 1. As observed by others before,[8] different results were obtained for identical compounds in different laboratories, and a correct composition was analyzed for only one compound in one laboratory.

Many of the further investigations were carried out with *N*,*N*,*N*-trihexylammonioundecahydrododecaborate (**3a**).

The liquids obtained have a syrupy consistency. Viscosity decreases with increasing temperature, as expected. Variable-temperature viscosity measurements were performed on two of the ionic liquids. For the *N*-methyl-*N*′-ethylimidazolium (emim$^+$) salt of **3a**, the viscosity at 75.3 °C was measured to be 12607 cP, which decreased to 2635 cP at 94.5 °C. For the methyltrioctylammonium ($MeOc_3N^+$) salt of **3a**, the measured viscosity ranged from 11584 cP at 54.4 °C to 774 cP at 94.3 °C. Both data sets fit well to an Arrhenius dependence (Figure 1), with activation energies for viscous flow equal to 87 ± 1 kJ mol^{-1} for the emim$^+$ salt and 68 ± 1 kJ mol^{-1} for the $MeOc_3N^+$ salt.

The melting points obtained in a conventional capillary are shown in Table 2. Owing to the rather high viscosity, melting points are not easy to determine by this method. Melting points measured in a capillary agreed nevertheless quite well with data obtained by differential scanning calorimetry (DSC) (Table 3). Upon cooling to −100 °C, supercooled liquids are obtained that show glass transitions and only minor endothermic transitions upon reheating. For the salts of **3a**, the melting enthalpies ranged between 2 kJ mol^{-} (*N*-hexylpyridinium as the counterion) and 46 kJ mol^{-1} (*N*-methyl-*N*′-ethylimidazolium as the counterion). For comparison, for *N*-methyl-*N*′-alkylimidazolium chlorides, melting enthalpies of between 0.233 kJ mol^{-1} (octyl, m.p. 12 °C) and 30.93 kJ mol^{-1} (decyl, m.p. 38 °C) have been found.[9]

Table 1. Elemental analysis data of different salts of trihexylammonioundecahydrododecaborate.

Cation and formula	Composition [%]		
	calcd	Lab 1	Lab 2
methyltrioctylammonium salt, $C_{43}H_{104}N_2B_{12}$			
H	13.46	13.701, 13.553	14.27, 14.53
B	16.65		
C	66.29	69.89, 70.05	64.89, 64.92
N	3.60	3.28, 3.38	3.53, 3.42
N-ethyl-*N*′-methylimidazolium salt, $C_{24}H_{61}N_3B_{12}$			
H	11.79	11.483	11.89
B	24.87		15.81
C	55.28	51.44	55.41
N	8.06	4.27	7.36
K salt, $C_{18}H_{50}NKB_{12}$			
H	11.21	11.568, 11.611	
B	28.87		
C	48.10	50.82, 50.26	
N	3.13	3.81, 3.68	
K	8.70		
tetrabutylammonium salt, $C_{34}H_{86}N_2B_{12}$			
H	13.28	13.543, 13.524	
B	19.87		
C	62.56	65.27, 65.31	
N	4.29	4.63, 4.59	

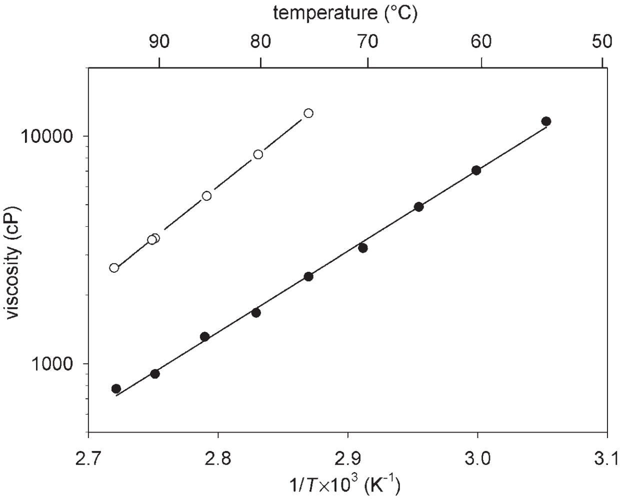

Figure 1. Viscosity of the *N*-ethyl-*N*′-methylimidazolium (open circles) and methyltrioctylammonium (closed circles) salts of trihexylammonioundecahydrododecaborate (**3a**) as a function of T^{-1}.

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Table 2. Melting points of *N,N,N*-trialkylammonioundecahydrododecaborate salts measured in a capillary.

$B_{12}H_{11}NR_3^-$ R=	Melting point [°C] N(Me)$_4$	N(Bu)$_4$	*N*-hexylpyridinium	*N*-methyl-*N'*-butylimidazolium	K	Li	H
H	>250	188–190					
CH_3			128–129				
C_2H_5	314 (decomp)[a]	194[a]	130–132	128–130	370 (decomp)[b]		
C_3H_7	256–258	172–174	126–128	143–145	>250		
C_4H_9	222–225	175–176	40–50	115–116	190 (decomp)		
i-C_5H_{11}		112–114	<25	87–90	128–134		
C_6H_{13}	183–186	75–78	47–50	95–97	65	65	80
$C_{12}H_{25}$	60	40–45	<25	25	40		
$C_3H_6CH{=}CH_2$		50–60					

[a] See ref. [6]. [b] See ref. [10].

Table 3. Melting points, melting enthalpies and weight loss upon heating of *N,N,N*-trihexylammonioundecahydrododecaborate (**3a**) salts.

Cation	M.p. in capillary [°C]	M.p. by DSC [°C]	Melting enthalpy [J g^{-1}]	Weight loss at 300°C [%]
N(Bu)$_4$	75–78	87	36	29
N-hexylpyridinium	47–50	59	2	11
N-methyl-*N'*-ethylimidazolium	57–58	60	46	32
K	65	79	28	4
methyltrioctylammonium	<25	<−44[a]	[b]	21
methyldiethylpropylammonium	45–50	34[c]	23	5

[a] The mid-point of the glass transition is −44°C. [b] Not applicable. [c] The onset of a broad transition with a maximum at 69°C. An additional sharper transition is observed at 129°C, $\Delta H = 21$ J g^{-1}.

The thermal stability of this new class of ILs is good (Figure 2). All ILs could be heated to around 200°C to remove the last traces of solvents. Thermogravimetric analysis (TGA) of the salts of **3a** show a weight loss of between 4 (potassium salt) and 31% (methyltrioctylammonium salt) at 300°C. The weight loss observed at around 100°C in some of the salts might be caused by the loss of water as the substances are hygroscopic and could not be introduced into the TG apparatus without exposure to the ambient atmosphere.

The conductivity of the neat ILs (either as the liquid or supercooled liquid) follows Arrhenius behaviour (Figure 3). The conductivities are fairly low which can be attributed to the generally high viscosities of these ILs.

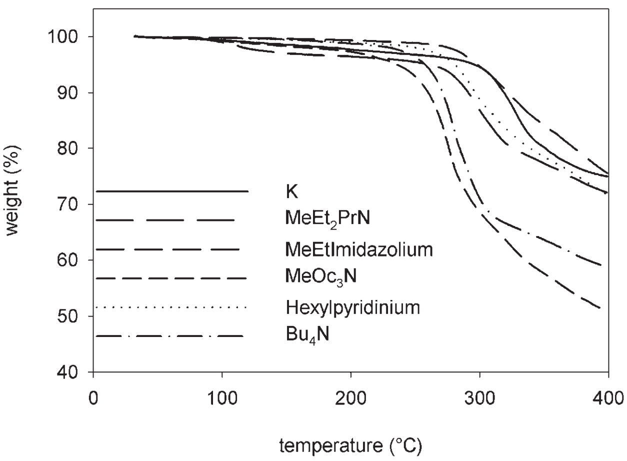

Figure 2. TGA analysis of trihexylammoniododecaborates with different cations.

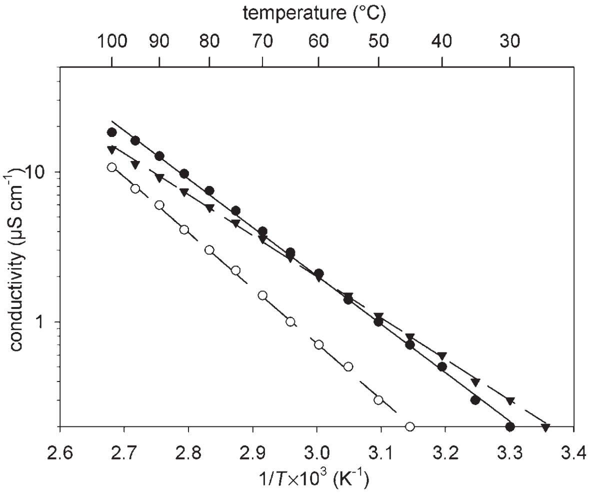

Figure 3. Arrhenius plot of the conductivity of the neat ionic liquids of trihexylammonioundecahydrododecaborate (**3a**) with *N*-hexylpyridinium (closed circles), methyltrioctylammonium (triangles) and tetrabutylammonium (open circles) as counterions. The lines shown are linear regression curves.

As electrolytes in acetonitrile solutions, the conductivities of the potassium and lithium salts of **3a** peak at around 8 mS cm^{-1} in a 0.5 M solution (Figure 4). The molar conductivities extrapolated to very low concentrations are around 80–100 mS cm^{-1} M^{-1}, only slightly less than that of *N*-butyl-*N*-methylimidazolium hexafluorophosphate. The maximum conductivity is less than that of $LiPF_6$ (maximum conductivity 41.5 mS cm^{-1} at 1.5 M) and KPF_6 (26 mS cm^{-1} at 1 M) in the same solvent.[11]

The proton salt of **3a** can be prepared by ion-exchange. The proton salt of **1** was previously described by Muetterties et al.[12] It was obtained, however, only as the H_3O^+ salt. We could remove the water by prolonged heating at 200°C, without decomposition. A solution of the salt in deuteriobenzene did not show any NMR-visible sign of protonation of benzene; the latter was observed by Reed et al. with the proton salt of the hexachlorocarborane anion, $CB_{11}H_6Cl_6^-$.[13]

The chemical stability of the cluster is great. Reducing agents such as Pt/H_2 and NaH give no reaction.[14] The clus-

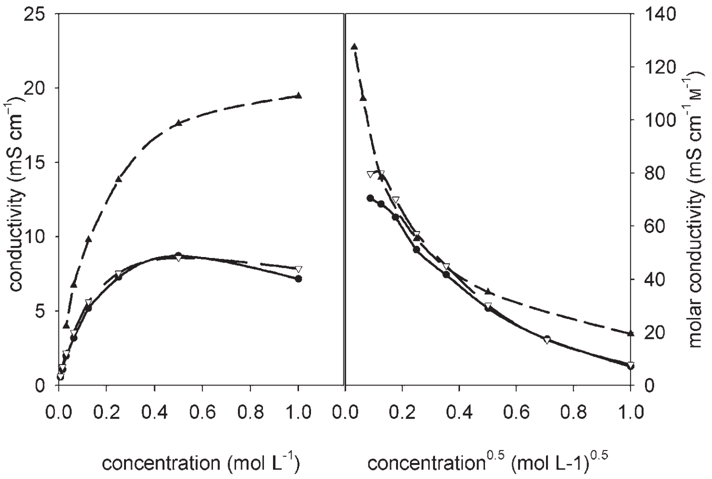

Figure 4. Conductivity (left) and molar conductivity (right) of lithium (solid line with circles) and potassium (long dashed line with open triangles) salts of trihexylammonioborate in acetonitrile. For comparison, the conductivity of *N*-butyl-*N*-methylimidazolium hexafluorophosphate (short dashed line with closed triangles) in the same solvent is shown.

ter is stable against strong acids (only hydrogen-exchange is observed), as corroborated by the isolation of the proton salt.[15] Oxidation agents such as H_2O_2 lead to hydroxylation of the intact cluster.[16] Electrochemical oxidation of the unsubstituted cluster to an hydrogen-bridged dimer occurs at +1.85 V, with no reduction down to −2.8 V.[17] It is expected that the ammonio-substituted cluster, which bears an electron-withdrawing substituent, requires higher potentials for oxidation. The ILs described here, therefore, have a number of potential uses.

One such potential use of borated ionic liquids is the processing of spent nuclear fuel. Ionic liquids are under serious scrutiny as potential alternative solvents for the separation of radioactive elements for reuse or disposal because their properties can potentially improve process safety and efficiency.[18] The isotope ^{10}B, present in 20% natural abundance, has a very high thermal neutron-capture cross-section. Calculations[19] have shown that ionic liquids with sufficiently high natural boron concentrations can be used as nuclear-processing media as they are inherently safe with regards criticality accidents. Although the ionic liquids described herein have relatively high viscosities and may not be suitable as neat solvents, their high boron content permits them to be diluted by other ionic liquids while still affording a high degree of protection. A significant issue that needs to be addressed is whether ionic liquids have sufficient stability towards the effects of the ionizing radiation emitted by radioactive fuel components to permit their use in nuclear processing. Radiation stability investigations have already been carried out on some ionic liquids.[20] A preliminary pulse radiolysis experiment was performed to assess the radiation stability of the anion **3a** as the emim$^+$ and $MeOc_3N^+$ salts. Three dilutions of each salt (15–50 mM) were made in the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($Pyrr_{14}$ NTf_2) in which the solvated electron is known to have a broad absorption band peaking at 1100 nm.[21] The observed rates of decay of the solvated electron were compared with that the value observed in neat $Pyrr_{14}$ NTf_2, and a second-order rate constant of $(1.84 \pm 0.06) \times 10^8\,M^{-1}s^{-1}$ was obtained for the reaction of the electron with emim **3a**. The reaction in question is actually the scavenging of the electron by the emim$^+$ cation; a similar rate constant was obtained for the reaction of bmim$^+$ with the electron in a less viscous ionic liquid.[22] In contrast, the $MeOc_3N^+$ cation does not scavenge electrons. When the $MeOc_3N^+$ **3a** salt was diluted in $Pyrr_{14}$ NTf_2, there was no evidence for the reaction of electrons with either the cation or the anion. This indicates that the anion **3a** is stable towards reduction under radiolytic conditions, although the electrochemical results suggest that it is possible that the anion can be radiolytically oxidized.

Large, weakly coordinating anions have been prepared on the basis of carborane[23] and dodecaborate[13] clusters. Carborane-containing ILs were first described by Reed[24] and Zhu[25] and their co-workers; $CB_{11}H_{12}^-$ with *N*-pentylpyridinium as the cation was reported to have a m.p. of 19 °C and the 1-propyl-$CB_{11}H_{11}$ anion with *N*-methyl-*N′*-ethylimidazolium as the cation to have a m.p. of 45 °C. Wesemann and co-workers reported stannaborate salts that melt.[26] The anions described herein, based on the dodecaborate cluster, have advantages over the monocarbon carboranes and stannaborates as they are prepared much more easily in 100 g quantities without special equipment or expensive chemicals and because they allow a much greater variation of side-chains, including unsymmetrically substituted ammonio derivatives.

Conclusions

A new class of ionic liquids has been described in which the anion is a trialkylammonio derivative of the dodecaborate(2−) cluster. The anions can be prepared in large quantities even with conventional laboratory equipment. The cations can be chosen quite freely, and even potassium, lithium, and unsolvated proton cations yield low-melting solids.

The high chemical and physical stability of these ILs makes them attractive in, for example, electrochemical and high-temperature applications. Further investigations should clarify whether unsymmetrical substitution of the nitrogen atom can reduce the viscosity of the ILs and thereby increase their potential applications. From a fundamental point of view, it will be of interest to study whether these anions have a coordination power as low as the carboranes described by Reed.[27]

Experimental Section

DSC spectra were recorded on a TA Instruments 2920 MDSC instrument, Version 2.5 F, Module DSC Standard and TGA spectra on a TA

Instruments 2950 TGA HR apparatus, Version 6.0E, Module TGA 1000 C. The heating rate was 5 K$\,$min^{-1} in both types of measurements.

Viscosities were measured by using a Cambridge Applied Systems ViscoLab 4000 reciprocating piston viscometer equipped with a flow-through jacket for temperature control. The flow-through jacket was connected to a refrigerated circulating bath. To avoid the absorption of atmospheric moisture by the samples, the viscometer head was located in a nitrogen-purged acrylic box with hand access ports. In addition to the gas purge, two small Dewars of liquid nitrogen were placed in the box to further reduce the humidity through nitrogen boil-off and water vapor condensation.

Conductivity measurements were performed with an inoLab pH Cond Level 1 instrument from WTW by using an MI-900 micro-conductivity cell from Microelectrodes. Samples were thermostatted in an oil bath.

The purity of the compounds was assessed by ESI mass spectrometry and ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as it is known that the elemental analysis of dodecaborate-containing compounds is not reliable.[8] This was confirmed by analysis of selected compounds in two different laboratories (Schwarzkopf, Inc., New York, and Elemental Analysis Service, University of Chemnitz (Germany); see Table 1 for the results).

Electron pulse radiolysis transient-absorption experiments were carried out at the BNL Laser-Electron Accelerator Facility.[21] Salts of anion **3a** were diluted to 15–50 mM in Pyrr$_{14}$ NTf$_2$ and purged of oxygen by bubbling with argon. The disappearance of the solvated electron was monitored by measuring its absorbance at 900 nm using a silicon photodiode detector. This wavelength was selected because the detector response is better at this wavelength than at the peak of 1100 nm and also the absorption band is broad enough to provide a good signal.

General procedure for the preparation of *N,N,N*-trialkylammonioundecahydro-*closo*-dodecaborate(1−) potassium salts: Ammonioundecahydro-*closo*-dodecaborate potassium salt (196.6 mg, 1 mmol) was dissolved in dry CH_3CN (15–20 mL) at room temp. Solid powdered KOH (840 mg, 15 mmol) was added to this solution, followed by the dropwise addition of the corresponding alkyl bromide. The mixture was stirred at room temperature for 24 h and the solid (KBr and excess KOH) was filtered off. The solvent was removed by rotary evaporation and the residue was recrystallized from Et_2O (chain length: 1–6 carbon atoms) or purified by chromatography on SiO_2 (eluent: Et_2O/EtOAc, 2:1). Yield: 80–90%.

Exchange of potassium for organic cations (tetramethylammonium, tetrabutylammonium, *N*-methyl-*N*′-butylimidazolium, *N*-hexylpyridinium, *N*-methyl-*N*′-ethylimidazolium, methyldiethylpropylammonium): For alkyl chains of 1–6 carbon atoms the exchange was performed in water. The potassium salt was dissolved in water and an equimolar amount of the organic cation as the bromide was added. The solution was extracted with EtOAc and the organic phase was dried. The residue was purified by chromatography on SiO_2 (eluent: Et_2O/EtOAc, 2:1). Yield: 90–95%.

For longer chains, the potassium salt was dissolved in EtOAc and a solution of the cation bromide (1 equiv) was added. The KBr that precipitated was removed by filtration, the solvent was evaporated, and the residue was purified by chromatography on SiO_2 (eluent: Et_2O/EtOAc, 2:1). Yield: 90–95%.

Exchange of potassium for lithium or protons: The solution of the salt in water was passed over an ion-exchanger in the H^+ form. For the H^+ salt, the solvent was evaporated. For the Li^+ salt, titration with LiOH and subsequent evaporation of the solvent yielded the desired product. The H^+ salts could also be obtained by dissolving the potassium salts in acetonitrile and by treating them with HCl gas. After removal of the KCl precipitate, the solvent was evaporated. Salts other than H^+ could be obtained by titration with the appropriate hydroxide.

3, R = $\mathbf{CH_3}$: ^{1}H NMR (200 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: *N*-hexylpyridinium): $\delta = 0.12$–2.42 (m, 11 H; BH), 0.89 (t, *J*(H,H) = 6.60 Hz, 3 H; CH_3), 1.33 (m, 6 H; CH_2), 1.67–1.82 (m, 2 H, CH_2), 2.84 (s, 9 H; N-CH_3), 4.50 (t, *J*(H,H) = 7.58 Hz, 2 H; N-CH_2), 8.02 (t, *J*(H,H) = 6.85 Hz, 2 H; Ar), 8.50 (t, *J*(H,H) = 7.83, 1 H; Ar), 8.67 ppm (d, *J*(H,H) = 5.87 Hz, 2 H; Ar); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: potassium): $\delta = 57.3$ ppm (N-$(CH_3)_3$); MS (ESI, negative): *m*/*z*: 200 [A]$^-$.

3, R = $\mathbf{C_2H_5}$: ^{1}H NMR (200 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: *N*-hexylpyridinium): $\delta = 0.1$–2.70 (m, 11 H; BH), 0.89 (t, *J*(H,H) = 6.60 Hz, 3 H; CH_3), 1.28 (t, *J*(H,H) = 7.09 Hz, 9 H; CH_3CH_2), 1.33 (m, 6 H; CH_2), 1.54–1.82 (m, 2 H; CH_2), 3.24 (q, *J*(H,H) = 7.17 Hz, 6 H; N-CH_2CH_3), 4.50 (t, *J*(H,H) = 7.58 Hz, 2 H; N-CH_2), 8.02 (t, *J*(H,H) = 6.85 Hz, 2 H; Ar), 8.49 (t, *J*(H,H) = 7.83, 1 H; Ar), 8.67 ppm (d, *J*(H,H) = 5.38 Hz, 2 H; Ar); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: potassium): $\delta =$ 10.47 (CH_3), 54.94 ppm (N-CH_2); MS (ESI, negative): *m*/*z*: 242 [A]$^-$.

3, R = $\mathbf{C_3H_7}$: ^{1}H NMR (200 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: tetramethylammonium): $\delta = 0.10$–2.60 (m, 11 H; BH), 0.84 (t, *J*(H,H) = 7.33 Hz, 9 H; CH_3), 1.72–1.86 (m, 6 H; $CH_3\mathit{CH}_2CH_2$), 2.98–3.06 (m, 6 H; N-CH_2), 3.07 ppm (s, 12 H; CH_3-N); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: potassium): $\delta = 11.45$ (CH_3), 18.67 (CH_2), 63.67 ppm (N-CH_2); MS (ESI, negative): *m*/*z*: 284 [A]$^-$.

3, R = $\mathbf{C_4H_9}$: ^{1}H NMR (200 MHz, [D$_1$]chloroform, 25 °C, TMS, cation: *N*-hexylpyridinium): $\delta = -0.10$–2.40 (m, 11 H; BH), 0.86–0.98 (m, 12 H; CH_3), 1.27–1.36 (m, 12 H; CH_2), 1.68–1.90 (m, 6 H; CH_2), 1.98–2.06 (m, 2 H; CH_2), 3.12–3.20 (m, 6 H; CH_2-N), 4.68 (t, *J*(H,H) = 7.58 Hz, 2 H; N-CH_2), 8.05 (t, *J*(H,H) = 7.09 Hz, 2 H; Ar), 8.51 (t, *J*(H,H) = 7.83, 1 H; Ar), 8.96 ppm (d, *J*(H,H) = 5.87 Hz, 2 H; Ar); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: potassium): $\delta = 14.51$ (CH_3), 21.22 (CH_2), 27.31 (CH_2), 62.18 ppm (N-CH_2); MS (ESI, negative): *m*/*z*: 326 [A]$^-$.

3, R = *i*-$\mathbf{C_5H_{11}}$: ^{1}H NMR (200 MHz, [D$_1$]chloroform, 25 °C, TMS, cation: *N*-butyl-*N*′-methylimidazolium): $\delta = -0.11$–2.56 (m, 11 H; BH), 0.91–0.99 (m, 21 H; CH_3), 1.37 (q, *J*(H,H) = 7.50 Hz, 2 H; CH_2), 1.67–1.80 (m, 8 H; CH_2), 1.84–1.92 (m, 3 H; $CH(CH_3)_2$), 3.15–3.22 (m, 6 H; N-CH_2), 3.99 (s, 3 H; CH_3-N), 4.22 (t, *J*(H,H) = 7.58 Hz, 2 H; N-CH_2), 7.33 (d, *J*(H,H) = 9.29 Hz, 2 H; imidazolium), 8.97 ppm (s, 1 H; imidazolium); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: potassium): $\delta = 23.19$ (CH_3), 28.24 (CH_2), 33.49 (CH), 61.54 ppm (N-CH_2); MS (ESI, negative): *m*/*z*: 368 [A]$^-$.

3, R = $\mathbf{C_6H_{13}}$: ^{1}H NMR (200 MHz, [D$_1$]chloroform, 25 °C, TMS, cation: tetramethylammonium): $\delta = 0.10$–2.50 (m, 11 H; BH), 0.89 (t, *J*(H,H) = 6.36 Hz, 9 H; CH_3), 1.28 (s, 18 H; CH_2), 1.74–1.82 (m, 6 H; CH_2), 3.03–3.11 (m, 6 H; N-CH_2), 3.07 ppm (s, 12 H; N-CH_3); ^{13}C NMR (50 MHz, [D$_6$]benzene, 25 °C, TMS, cation: potassium): $\delta = 14.32$ (CH_3), 23.05 (CH_2), 24.62 (CH_2), 26.87 (CH_2), 31.89 (CH_2), 61.76 ppm (N-CH_2); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: tetrabutylammonium): $\delta = 14.22$, 14.71 (CH_3), 20.72, 23.72, 24.76, 25.29, 27.65, 32.62, 32.68 (CH_2), 59.71, 59.77, 59.83 (CH_2-N), 62.38 ppm (CH_2-N); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: *N*-hexylpyridinium): $\delta =$ 14.65, 14.73 (CH_3), 23.49, 23.72, 25.29, 26.70, 27.65, 32.31, 32.68 (CH_2), 62.41, 63.28 (N-CH_2), 129.82, 145.85, 147.11 ppm (Ar); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: *N*-ethyl-*N*′-methylimidazolium): $\delta = 14.68$ (CH_3), 15.91 (CH_3CH_2), 23.69, 25.26, 27.62, 32.65 (CH_2), 37.25 (N-CH_3), 46.24 (N-CH_2CH_3), 62.38 (N-CH_2), 123.33, 125.02 ppm (imidazolium); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: ethyldimethylammonium): $\delta = 8.92$ ($\mathit{CH}_3CH_2CH_2$-N), 11.14 (CH_3CH_2-N), 14.71 (CH_3), 17.09 ($CH_3\mathit{CH}_2CH_2N$), 23.66, 25.24, 27.59, 32.62 (CH_2), 51.32, 51.40, 51.49 (N-CH_3), 61.14 (N-CH_2CH_3), 62.35, 62.58 (N-CH_2), 66.23, 66.28 ppm (N-$\mathit{CH}_2CH_2CH_3$); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: methyltrioctylammonium): $\delta = 14.76$ (CH_3), 23.19, 23.75, 25.32, 27.29, 27.71, 30.09, 30.49, 30.63, 32.65, 32.70, 32.87, 33.07 (CH_2), 49.52 (CH_3N), 62.41, 62.94 ppm (CH_2-N); MS (ESI, negative): *m*/*z*: 410 [A]$^-$.

3, R = $\mathbf{C_{12}H_{25}}$: ^{1}H NMR (200 MHz, [D$_1$]chloroform, 25 °C, TMS, cation: potassium): $\delta = 0.20$–2.30 (m, 11 H; BH), 0.89 (t, *J*(H,H) = 6.45 Hz, 9 H; CH_3), 1.27 (s, 54 H; CH_2), 1.64–1.92 (m, 6 H; CH_2), 3.02–3.18 ppm (m, 6 H; N-CH_2); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS; cation: potassium): $\delta = 14.82$ (CH_3), 23.80, 27.82, 30.35, 30.49, 30.54, 30.65, 30.77, 33.04 (CH_2), 62.32 ppm (N-CH_2); MS (ESI, negative): *m*/*z*: 662 [A]$^-$.

3, R = $\mathbf{CH_2CH_2CH_2CH{=}CH_2}$: ^{1}H NMR (200 MHz, [D$_3$]acetonitrile, 25 °C, TMS, cation: tetramethylammonium): $\delta = 0.10$–2.30 (m, 11 H; BH), 0.72–0.91 (m, 6 H; CH_2), 1.93–2.05 (m, 6 H; CH_2), 2.97–3.07 (m, 6 H; N-CH_2), 3.09 (s, 12 H; N-CH_3), 4.95–5.08 (m, 6 H, $CH_2{=}CH$), 5.73–5.86 ppm (m, 3 H, $CH{=}CH_2$); ^{13}C NMR (50 MHz, [D$_3$]acetonitrile, 25 °C, TMS; cation: tetramethylammonium): $\delta = 24.65$ (CH_2), 32.00 (CH_2), 56.68 ($(CH_3)_4N$),

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61,99 (N-CH_2), 116.14 ($CH{=}CH_2$), 139.11 ppm ($CH{=}CH_2$); MS (ESI, negative): m/z: 362 $[A]^-$; MS (ESI, positive): m/z: 74 $[cat]^+$.

Acknowledgements

Financial support from the Ministry for Construction, Environment and Transport in Bremen (Germany) within the support program "Applied Environmental Research", Grant FV162, is gratefully acknowledged. E.J. acknowledges support from the Otto Benecke Foundation. We are grateful to Prof. Spange, Technical University Chemnitz, for allowing us to perform elemental analysis in the Department of Chemistry. The work performed at Brookhaven National Laboratory was carried out with the U.S. Department of Energy under contract DE-AC02-98CH10886 and was supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. J.F.W. thanks Ms. Jasmine Hatcher for assistance with the viscosity and radiolysis experiments.

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Received: September 11, 2007
Revised: October 26, 2007
Published online: December 7, 2007

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