Chloroalkylsulfonate ionic liquids by ring opening of sultones with organic chloride salts†

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An efficient route to prepare ionic liquids with chloroalkylsulfonate anions is presented; the synthesis proceeds in a one-step ring-opening reaction of sultones with an organic chloride salt and provides a very attractive access to new anion functionalised ionic liquids.

Functionalised and task specific ionic liquids have attracted growing interest in recent years due to the possibility to incorporate additional properties into traditional ionic liquid structures.[1] Both cation[2] and anion[3] functionalised ionic liquids have been described and there exists even a small number of dual-functionalised ionic liquid systems.[4]

Regarding the synthesis of anion functionalised ionic liquids most reported procedures include at least one anion metathesis step. While lactate[5] and camphorsulfonate[6] ionic liquids are directly obtained from commercial alkali salts or acids, more complicated anion structures[1,7] are usually prepared in multi-step syntheses as alkali or ammonium salts followed by the anion metathesis. Unfortunately, anion metathesis is always a very problematic step concerning the resulting ionic liquid quality in particular if highly water-soluble ionic liquids are prepared. In the latter case, the hydrophilic nature of the ionic liquid prevents washing steps with water to eliminate traces of the initial anion (from the alkylation step).

In this paper we describe for the first time an alternative reaction to synthesise ionic liquids with functionalised anions, namely the ring opening reaction of a sultone by the nucleophilic chloride anion of an ionic liquid. The reactions of 1,4-butane sultone with 1,3-dialkylimidazolium chlorides and tetraethylammonium chloride are displayed in Scheme 1.

The reaction builds on the known ability of sultones to react in a ring-opening reaction with various nucleophiles.[8] In the past, the ring-opening reaction of sultones with amines has also been applied to obtain ammonium ions even in the context of ionic liquid synthesis.[9]

In the system described here, where the chloride ion of an organic salt is the nucleophile, the reaction proceeds smoothly
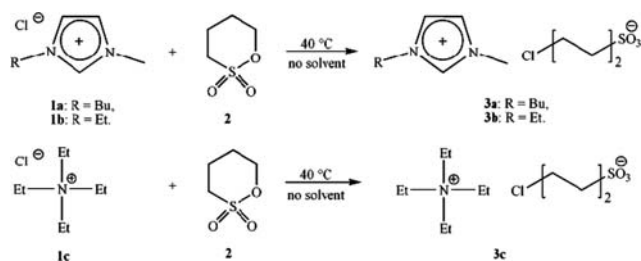
Scheme 1 Reaction of 1,3-dialkylimidazolium chlorides and tetraethylammonium chloride with 1,4-butane sultone to form the corresponding chlorobutylsulfonate ionic liquids.

to full conversion under mild conditions in 24 h if both reactants are used stoichiometrically.‡ By titration with AgNO$_3$ it could be confirmed that the chloroalkylsulfonate salts obtained in this way are essentially free of chloride impurities (<200 ppm Cl$^-$) which is of great advantage compared to the traditional metathesis routes.

For our kinetic studies (see Fig. 1) we applied an excess of the sultone (20 eq.) to realize pseudo-first order conditions. The excess of sultone was removed by distillation or extraction (recovered sultone could be reused) and the anion functionalised ionic liquid was isolated in quantitative yield. The absence of 1,4-butane sultone in the isolated product was confirmed by elemental analysis.

The activation energy of the ring opening reaction was found to be 79 kJ mol^{-1} (for detailed results see ESI†). Interestingly, similar experiments reacting [BMIM]Cl with 1,3-propane sultone revealed a much higher reaction rate for the five-membered sultone compared to the six-membered sultone. Under the same reaction conditions as illustrated in
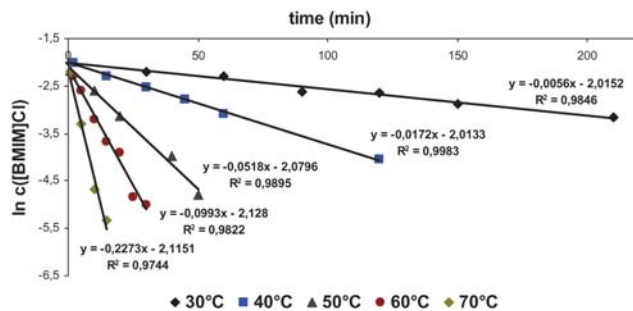

Fig. 1 Synthesis of 1-butyl-3-methylimidazolium ([BMIM]) 4-chlorobutylsulfonate at different temperatures ([BMIM]Cl : 1,4-butane sultone = 1 : 20, solvent: nitroethane).

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† Electronic supplementary information (ESI) available: (1) Kinetics: Reaction of [BMIM]Cl with 1,4-butane sultone. (2) DSC measurements of ILs 3a–c. (3) TGA analyses of ILs 3a–c. (4) NMR analyses after treating 3a for 4 h at 210 °C in an open system. (5) XPS analysis at 330 K. (6) Instruments. See DOI: 10.1039/b805444d

Fig. 1, the 1,3-propane sultone reached full conversion in less than 10 min at 30 °C (for comparison: the reaction with 1,4-butane sultone showed only 12% conversion after 10 min at 30 °C). These results reflect the relative stabilities of the five- and six-membered sultone rings.

All chloroalkylsulfonates prepared in this study were obtained as colorless liquids if the chloride salt starting material was colorless, too. All products were remarkably water soluble and hydrolysis stable at the temperature conditions applied in this study (up to 60 °C). For further investigation of their physico-chemical properties, all chloroalkylsulfonate ionic liquids were dried overnight at 50 °C in high vacuum (1×10^{-3} mbar). After this treatment, water contents were still surprisingly high for the imidazolium based chloroalkylsulfonates indicating their strong ability to interact with water. Table 1 shows the viscosities of selected chloroalkylsulfonates. Ionic liquids **3a–c** were found to behave like Newtonian fluids.

Ionic liquids **3a–c** are liquids at room temperature. Their glass transition points have been determined by DSC (see ESI† for details). The fact that even **3c** forms a liquid at room temperature is remarkable since other tetraethylammonium salts—even those with anions that are known to form low-melting ionic liquids—show much higher melting points. For example, [NEt$_4$][NTf$_2$] was found to melt at 109 °C,[10] the melting point of [NEt$_4$][CF$_3$SO$_3$] has been determined to be 160–162 °C. This comparison demonstrates the ability of the chloroalkylsulfonate anion to lead to low melting salts, at least for symmetrical ammonium cations.

In order to make sure that the ionic liquids under investigation were of high purity we decided to use also an IL surface sensitive analytical technique. In our laboratories we recently established X-ray photoelectron spectroscopy (AR-XPS) as a suitable method to determine impurities down to an extremely low level if those impurities show at least some surface activity in the ionic liquid system.[11] Consequently, we characterised the chemical composition and the electronic structure of the freshly prepared ionic liquid [BMIM][ClC$_4$H$_8$SO$_3$] by angle-resolved XPS under ultra high vacuum (UHV) conditions. Since the inelastic mean free path of photoelectrons of organic compounds is $\sim$3 nm,[11] measurements at 0° (normal emission) probe the surface near region (information depth, ID: 7–9 nm) whereas measurements at 70° only probe the topmost layers (ID: 2–3 nm). The XPS data in Fig. 2 show the expected signals of C, N, O, S and Cl, with no sign of other elements, ruling out surface contaminations of *e.g.*, Si-containing impurities, which were observed for other ionic liquids in the past (probably from grease and sealings).[12] For all IL-related core levels, no significant changes of intensity with emission angle were observed, which is an indication for a homogeneous distribution of the elements within the near surface region. It
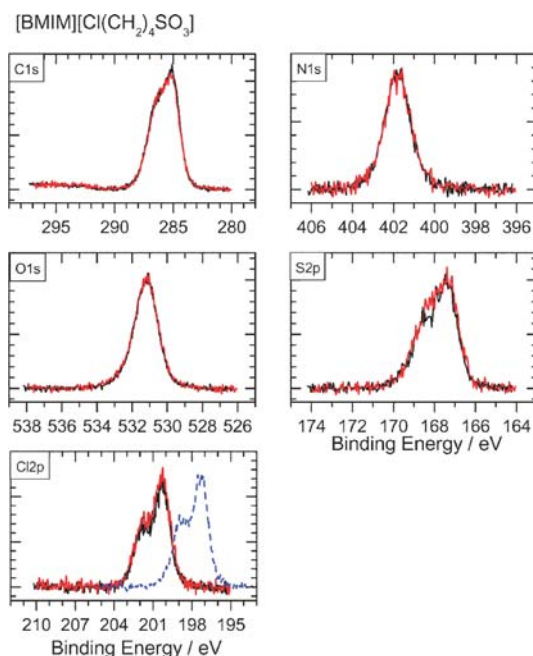

[BMIM][Cl(CH$_2$)$_4$SO$_3$]

Fig. 2 AR-XP spectra of **3a** ([BMIM][ClC$_4$H$_8$SO$_3$]) in the C 1s, N 1s, O 1s, S 2p and Cl 2p regions. The spectra were collected at emission angles of 0° (black, bulk sensitive) and 70° (red, surface sensitive). In the Cl region, a chloride spectrum of [EMIM]Cl (blue) is added for comparison.

also rules out pronounced preferential vertical orientation of IL molecules at the surface, as was described for [BMIM][BF$_4$] by AR-XPS.[13] The quantitative evaluation of the XPS signals in both geometries yields a composition of C : N : O : S : Cl = 12.1 : 2.0 : 3.0 : 1.0 : 0.9 which is in good agreement with the expected stoichiometry of 12 : 2 : 3 : 1 : 1. Finally, no signals related to residual chloride ions from the synthesis reaction could be observed, confirming a complete conversion of the chloride IL.

For comparison, the Cl 2p spectrum of [EMIM]Cl is added in Fig. 2 (left bottom), showing the chloride signal to be shifted to lower binding energies by about 3 eV in comparison to the Cl-sulfonate signal. As expected, the Cl binding energy position of the chloroalkylsulfonate (200.3 eV, Cl 2p$_{3/2}$) is in the range of neutral Cl-alkyl species (*e.g.*, poly(vinyl chloride) 200.0–200.6 eV).[14]

As the thermal stability is crucial for the use of an ionic liquid, thermal gravimetric analyses (TGA) were carried out for **3a–c**. The TGA measurements were performed in the range 20–450 °C with a gradient of 10 K min^{-1} (see ESI† for details). **3a–c** showed similar weight losses in the TGA experiment with on-set temperatures of 214.9 °C (**3a**), 214.2 °C (**3b**) and 210.1 °C (**3c**), respectively. Interestingly, all three ionic liquids

Table 1 Viscosities of selected chloroalkylsulfonates ionic liquids

Ionic liquid	Water content/ppm	$T_g{}^a$/°C	Viscosity (20 °C)/mPa s
[EMIM][ClC$_4$H$_8$SO$_3$] (**3b**)	1462	−65.7	648
[BMIM][ClC$_4$H$_8$SO$_3$] (**3a**)	1969	−63.9	800
[NEt$_4$][ClC$_4$H$_8$SO$_3$] (**3c**)	340	−46.5	5250

^{a} T_g = glass transition point.

reached a plateau after a first decomposition step of which the weight loss corresponds to the loss of 1,4-butane sultone. After evaporation of the 1,4-butane sultone the remaining chloride ionic liquid decomposed at slightly higher temperatures under the conditions of these TGA measurements (decomposition temperatures: **3a** = 294.4 °C; **3b** = 307.4 °C; **3c** = 269.7 °C). This decomposition pathway was also confirmed by keeping **3a** for 4 h at 210 °C collecting the volatile components. After this treatment the volatile fraction contained significant amounts of 1,4-butane sultone and the remaining liquid consisted of mainly [BMIM]Cl (according to ^{1}H NMR analysis, for details see ESI†). The retro-reaction affording the chloride ionic liquid was also confirmed by a special XPS experiment at 330 K. Under the UHV conditions of the XPS experiment (removal of the volatile sultone!) this temperature is obviously high enough to detect after several hours the appearance of a chloride signal next to the Cl-signal from the chloroalkylsulfonate ion (for details see ESI†) unambiguously proving the formation of chloride anions in the surface near volume of the ionic liquid.

In conclusion, we have reported a very convenient one-step synthesis to anion functionalised ionic liquids starting from commercial chloride ionic liquids. The resulting chloroalkylsulfonates exhibit a number of interesting physico-chemical properties but their thermal stability is limited by the retro-reaction to a practical application range below 150 °C. Nevertheless, we expect the here reported reaction to be of high practical relevance as the obtained chloroalkylsulfonates may act as starting materials for further anion functionalisation. The ring opening reaction of sultones with other organic salts carrying nucleophilic anions is also a very interesting topic and currently under investigation in our laboratories.

Notes and references

‡ The imidazolium chlorides were obtained from Merck. 1,3-propane sultone, 1,4-butane sultone and tetraethylammonium chloride were purchased from Aldrich (please note that 1,3-propane sultone has been described as a potent carcinogen[15]). For details concerning the analytical equipment used for product characterization see ESI.†
Synthesis of chlorobutylsulfonate ionic liquids: To the chloride salt an equimolar amount of 1,4-butane sultone was added in small portions using standard Schlenk techniques. The reaction mixture was stirred for 24 h at 40 °C. In the case of the kinetic experiments a threefold volume of water was added. The excess sultone was extracted with dichloromethane and the water phase was dried under reduced pressure.
3a 1-Butyl-3-methylimidazolium 4-chlorobutylsulfonate: NMR data: δ_H (400 MHz, CDCl$_3$, Me$_4$Si) 0.72 (t, 3H, CH$_2$CH_3, J = 7.37 Hz), 1.12 (m, 2H, CH$_3$CH_2), 1.60–1.67 (m, 2H, CH_2CH$_2$N), 1.67–1.78 (m, 4H, CH$_2$CH$_2$), 2.62 (t, 2H, ClCH$_2$, J = 7.53 Hz), 3.33 (t, 2H, SCH$_2$, J = 6.09 Hz), 3.81 (s, 3H, NCH$_3$), 4.04 (t, 2H, NCH$_2$, J = 7.37 Hz), 7.29 (s, 1H, NCHCH), 7.41 (s, 1H, NCHCH) and 9.56 (s, 1H, NCHN); δ_C (100 MHz, CDCl$_3$, Me$_4$Si) 13.05 (CH$_2$CH$_3$), 19.02 (CH$_3$CH$_2$), 22.61 (ClCH$_2$CH$_2$), 31.28 (CH$_2$CH$_2$), 31.72 (SCH$_2$CH$_2$), 35.93 (CH$_3$N), 44.55 (ClCH$_2$), 49.11 (CH$_2$N), 50.68 (SCH$_2$), 121.9 (NCHCH), 123.5 (NCHCH) and 137.3 (NCHN). Elemental analysis. Found: C, 45.5; H, 7.6; N, 9.9; S, 10.1%; M, cation, 139; anion, 171. C$_{12}$H$_{23}$ClN$_2$O$_3$S

requires C, 46.4; H, 7.5; N, 9.0; S, 10.3%; M, cation, 139; anion 171.
3b 1-Ethyl-3-methylimidazolium 4-chlorobutylsulfonate: NMR: δ_H (400 MHz, d$_6$-DMSO, Me$_4$Si) 1.37 (t, 3H, CH$_2$CH_3, J = 7.20 Hz), 1.61–1.77 (m, 4H, CH$_2$CH$_2$), 2.43 (t, 2H, ClCH$_2$, J = 7.31 Hz), 3.56 (t, 2H, SCH$_2$, J = 6.38 Hz), 3.83 (s, 3H, NCH$_3$), 4.17 (q, 2H, NCH$_2$, J = 7.20 Hz), 7.74 (s, 1H, NCHCHN), 7.83 (s, 1H, NCHCHN) and 9.32 (s, 1H, NCHN); δ_C (100 MHz, d$_6$-DMSO, Me$_4$Si) 15.69 (CH$_3$CH$_2$), 23.18 (ClCH$_2$CH$_2$), 31.79 (SCH$_2$CH$_2$), 36.14 (CH$_3$N), 44.57 (ClCH$_2$), 45.92 (CH$_2$N), 51.08 (SCH$_2$), 122.5 (NCHCH), 124.1 (NCHCH) and 137.1 (NCHN). Elemental analysis. Found: C, 40.8; H, 7.0; N, 10.4; S, 10.8%; M, cation, 111; anion, 171. C$_{10}$H$_{19}$ClN$_2$O$_3$S requires C, 42.5; H, 6.8; N, 9.9; S, 11.3%; M, cation, 111; anion, 171.
3c Tetraethylammonium 4-chlorobutylsulfonate: NMR: δ_H (400 MHz, CDCl$_3$, Me$_4$Si) 1.18 (t, 12H, CH$_2$CH_3), 1.73–1.80 (m, 4H, CH$_2$CH$_2$), 2.62 (t, 2H, ClCH$_2$), 3.23 (q, 8H, NCH$_2$) and 3.39 (t, 2H, SCH$_2$); δ_C (100 MHz, CDCl$_3$, Me$_4$Si) 7.44 (CH$_3$CH$_2$N), 22.85 (ClCH$_2$CH$_2$), 31.53 (SCH$_2$CH$_2$), 44.85 (ClCH$_2$), 50.70 (CH$_2$N) and 52.26 (SCH$_2$). Elemental analysis. Found: C, 46.0; H, 9.6; N, 5.1; S, 10.1%; M, cation, 130; anion, 171. C$_{12}$H$_{28}$ClNO$_3$S requires C, 47.7; H, 9.4; N, 4.6; S, 10.6%; M, cation, 130; anion, 171.

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