Novel Chloroimidazolium-Based Ionic Liquids: Synthesis, Characterisation and Behaviour as Solvents to Control Reaction Outcome

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Novel ionic liquids containing chlorine atoms on the imidazolium cation were synthesised. The physicochemical properties of these ionic liquids were investigated extensively, including glass transition, melting and decomposition temperatures, density, viscosity, miscibility with common solvents and electrochemical window. The behaviour of these ionic liquids as

Introduction

The range of ionic liquids, defined as salts that have a normal melting point below 100 °C,^[1] is vast,^[2] and includes those containing imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium cations and a variety of organic and inorganic anions.^[3] Composed only of charged species, ionic liquids have particular properties, including negligible vapour pressure.^[4] The utility of ionic liquids is increased by the fact that through changing the constituent ions, physical properties such as melting point, viscosity and miscibility with other solvents can be tailored;^[5] thus, ionic liquids can be considered "designer solvents"^{(6]} and it is suggested that "task-specific"⁽⁷⁾ ionic liquids composed of mixtures of multiple cations and multiple anions to give a wider range of solvents,^[8] though such mixtures are rarely well characterised.^[9]

lonic liquids are also potential alternatives to molecular solvents because they can alter reaction outcomes (rate, selectivity, etc.). Through systematic investigation of the effects that ionic liquids have on the outcome of well-described reactions,^[10] we have developed a set of principles for predicting the effects that an ionic liquid might have on reaction outcome. These principles involve considering the extent of charge development in the transition state,^[10b] the nature of the starting materials,^[10a,b,h] the proportion of the ionic liquid in the reaction mixture,^[10a,f-h,j,k,p] and the structure of the constituent ions in the solvent.^[10i-n]

This developing predictive framework suggests that there is the possibility to design an ionic liquid to affect reaction outcome in a given fashion, as well as affecting its physicochemical properties. Systematic variation of the components of an

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solvents was examined through temperature-dependent kinetic analyses on two reactions: a nucleophilic aromatic substitution (S_NAr) reaction and a bimolecular nucleophilic substitution (S_N2) reaction. The properties and effects on reaction outcome of these new ionic liquids were shown to correlate with the change in the nature of the cation.

ionic liquid, particularly the cation,^[11] has been examined extensively (with common modifications including variation of the alkyl chain length(s) on the heteroatom(s) and, if appropriate, the addition of alkyl groups to the heterocyclic ring) in terms of their effect on the physicochemical properties; however, the effect of such changes on reaction control have not been considered extensively. Note that variation of the anion of an ionic liquid often complicates the interpretations of any changes in properties and solvent effects, as the changes to the anion often lead to multiple features (size, coordination ability, etc.) of that ion changing simultaneously; this has been particularly marked in the past for ionic liquids involving the hexafluorophosphate anion.^[10m]

The new ionic liquids targeted here are based on modified imidazolium cations. This cation type was chosen for modification owing to the relative ease of introducing changes, along with the fact that systematic changes to the cation might be expected to have predictable effects on the physicochemical properties of the ionic liquid.^[11] Further, interaction of components of the solution with the cation of an ionic liquid has been shown to be responsible for ionic liquid solvent effects in a range of cases.^[10d,g,h,j,l] The chloro substituent was chosen as an electron-withdrawing group as it was anticipated that it could be introduced relatively easily and its size is comparable to that of a methyl group,^[12] which had been incorporated in similar ionic liquids previously. The bis(trifluoromethanesulfonyl)imide anion ([Tf₂N]⁻) was chosen as it is particularly common in the ionic liquid literature because of the favourable properties it imparts to ionic liquids, including lower viscosity and relatively good electrochemical stability.^[4] lonic liquids containing this anion have also been studied extensively for their effects on reaction outcome.^[10b-j,l,o]

As such, this manuscript describes the synthesis of three new chlorinated ionic liquids (Figure 1): 1-butyl-4-chloro-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([b4Clmim][Tf_2N], 1), 1-butyl-4,5-dichloro-3-methylimidazolium

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Supporting information for this article can be found under http://



Figure 1. Novel chloroimidazolium-based ionic liquids synthesised in this work.

bis(trifluoromethanesulfonyl)imide ([b45Cl₂mim][Tf₂N], **2**) and 1-butyl-2-chloro-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([b2Clmim][Tf₂N], **3**). The physical properties, including glass transition, melting and decomposition temperatures, density, viscosity, miscibility and electrochemical stability of ionic liquids **1–3** are then examined extensively and their utility as solvents is investigated using two well-described organic processes.

Results and Discussion

Synthesis of novel ionic liquids

In the cases for which the appropriate chlorinated imidazoles were commercially available at reasonable cost (namely species **4** and **5**), the chlorinated ionic liquids were prepared using methods analogous to those described in the literature (Scheme 1);^[13] this gave access to the salts [b4Clmim][Tf₂N] **1** and [b45Cl₂mim][Tf₂N] **2**.



Scheme 1. Synthesis of the novel ionic liquids [b4Clmim][Tf₂N] **1** and [b45Cl₂mim][Tf₂N] **2.** i) KOH, CH₃CN, 2 h; ii) CH₃I, 24 h, 88%; iii) CH₃CH₂CH₂CH₂CH₂X, X=I, r.t. 4 weeks, 79%, X=CI, 70 °C, 9 d, 64%; iv) LiTf₂N, H₂O, 24 h, R=H 60%, R=CI 84%.

Note that butylation of chloroimidazole **5** was initially attempted by using the same conditions as for the formation of salt **7**, using *n*-chlorobutane as the alkylating agent. The reaction was found to proceed slowly, presumably because of the greatly reduced nucleophilicity of reagent **6** compared with imidazole **5**. Replacing the electrophile with the *n*-bromobutane also resulted in an impractical reaction rate at room temperature ($\approx 5\%$ conversion in four days); however, increasing the temperature resulted in the formation of a mixture of products consistent with the desired [b45Cl₂mim]⁺ undergoing a reverse Menschutkin reaction to give the 1-butylimidazole, which subsequently reacted further (see Supporting Information for further details). To avoid this unwanted side reaction, we used *n*-iodobutane, and complete consumption of the

starting material **6** was observed through ¹H NMR spectroscopy after four weeks at room temperature, with no indication of the side reactions described above.

As 2-chloroimidazole and its derivatives were not readily available, [b2Clmim][Tf₂N] **3** was prepared from the corresponding non-halogenated salt 1-butyl-3-methylimidazolium chloride ([bmim][Cl], **9**) through deprotonation and reaction with hexachloroethane. After screening of a number of bases, methylmagnesium bromide was found to be an experimentally straightforward choice (Scheme 2). The intermediate mixed salt was not isolated but converted to the desired ionic liquid **3** through anion metathesis; thus, although the mixed salt was not purified, the final compound was prepared successfully.



 $\label{eq:scheme 2. Synthesis of [b2Clmim][Tf_2N] 3. i) CH_3MgBr, THF, 0 ^C; ii) C_2Cl_6, THF, -78 ^C; iii) Li[Tf_2N], H_2O, 24 h, 47 \%.$

The series shown in Figure 1 might be extended with the salt 1-butyl-3-methyl-2,4,5-trichloroimidazolium bis(trifluoromethanesulfonyl)imide ([b245Cl₃mim][Tf₂N]). The corresponding imidazole was not commercially available, and reaction of the ionic liquid [b45Cl₂mim][I] **8** in a fashion analogous to that shown in Scheme 2 was unsuccessful with reaction of the iodide counterion implied (see Supporting Information for further details). This was not investigated further.

Characterisation

It is important to consider the properties of these novel salts 1–3, and particularly, to compare these properties to those of the related ionic liquids shown in Figure 2: the parent ionic



Figure 2. Non-halogenated ionic liquids 10–12 considered in this work for comparison.

liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N], **10**) and the methylated ionic liquids 1butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([bm₂im][Tf₂N], **11**) and 1-butyl-3,4,5-trimethylimidazolium bis-(trifluoromethylsulfonyl)imide ([bm₃im][Tf₂N], **12**). These latter ionic liquids were chosen because of the similarity of the methyl and chloro groups in terms of size. The comparisons allow any effects of chlorination of the cation to be seen, as well as giving some indication of the relative importance of steric and electronic effects.



Ideally, the methyl analogue of ionic liquid **1**, 1-butyl-3,4-dimethylimidazolium bis(trifluoromethanesulfonyl)imide, would also be used. The corresponding 1,5-dimethylimidazole is not readily available commercially, and attempted preparation of this intermediate from 4(5)-methylimidazole (analogous to that shown in Scheme 1) gave an inseparable mixture of regioisomers (see Supporting Information for further details); therefore, the preparation was not pursued further.

Thermophysical properties of ionic liquids 1-3

It is important to understand the thermal properties of an ionic liquid as they demonstrate the temperature range over which the ionic liquid may be used as a solvent. The broader the temperature range, the more useful the ionic liquid becomes.

Each of the ionic liquids **1–3** was analysed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to determine the glass transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d); these data are given in Table 1, with original scans supplied in the Supporting Information.

Table 1. Glass transition, melting and decomposition temperatures of ionic liquids 1–3.					
lonic liquid	Т _д [К]	<i>T</i> _m [K]	<i>T</i> _d [K] ^[b]		
[b4Clmim][Tf ₂ N] 1 [b45Cl ₂ mim][Tf ₂ N] 2 [b2Clmim][Tf ₂ N] 3	$\begin{array}{c} 200.5\pm0.2^{[a]}\\ 211.1\pm0.1^{[b]}\\ 199.0\pm0.2^{[a]} \end{array}$	316 _ ^[c] _ ^[c]	671.9 ± 1.5 619.4 ± 2.3 634.7 ± 1.3		
[a] Uncertainties quoted are the standard deviation of triplicate measure- ments. [b] Uncertainties quoted are the standard deviation of duplicate measurements. [c] No melting transitions could be observed.					

All three of the novel ionic liquids 1-3 vitrified at low temperatures and underwent a glass transition. The order of the glass transition temperatures was ionic liquid [b2Clmim][Tf₂N] $\mathbf{3} < [b4Clmim][Tf_2N] \mathbf{1} < [b45Cl_2mim][Tf_2N] \mathbf{2}$. These data demonstrate that addition of chlorine atoms to the ionic liquid cation increases the glass transition temperature. This can be seen through initial comparison with the non-chlorinated ionic liquid ${\bf 10},$ which has a glass transition temperature of 186 $K^{\rm [14]}_{\rm }$ but also through comparison of the data for species 1-3. Those species with a single chlorine atom added (1 and 2) have comparable glass transition temperatures, whereas the data for ionic liquid 3 show that multiple chlorine atoms on the cation increase the glass transition temperature further. Only glass transitions could be discerned clearly for ionic liguids 2 and 3. Ionic liquid 1 displayed a clear melting point for the initial solid but also demonstrated significant supercooling, such that melting features were not observed on subsequent temperature cycles.

The decomposition temperature was determined using the onset method, that is, the intercept of the extrapolated baseline and the tangent of the first significant decomposition feature. The decomposition temperatures for each of the ionic liquids 1-3 are quite high, which, combined with the glass transition data above, means they may be useful as solvents over a wide range of temperatures. For each of the salts 1-3, the decomposition temperature was slightly lower than that of the non-chlorinated ionic liquid **10**, ($T_d = 712 \text{ K}^{[13a]}$) suggesting that addition of chlorine atoms to the ionic liquid cation facilitates decomposition; this is unsurprising given that a C--Cl bond is weaker than a C-H bond.^[15] The order of the measured decomposition temperatures is $[b45Cl_2mim][Tf_2N]$ 2 < [b2Clmim] $[Tf_2N]$ 3 < $[b4Clmim][Tf_2N]$ 1, which suggests that the greater the number of chlorine atoms on the cation, the lower the thermal stability of the resultant ionic liquid; this, again, is reasonable given the relative C--Cl and C--H bond strengths. Further, the trend shown demonstrates that the position of the chlorine atom is important, with ionic liquid 1 more stable than ionic liquid **3**; the relative reactivity of the chlorine group at each of these positions in different contexts will also be discussed further below.

Density and viscosity of ionic liquids 1-3 and 10-12

The density and viscosity of an ionic liquid are important properties to know to determine the utility of the salt as a solvent. For example, optimal physical properties for an ionic liquid to act as an effective solvent might include a low viscosity to facilitate mixing, and a large density compared with other process fluids to hasten phase separation.^[13a]

Density and viscosity measurements were made for each of the ionic liquids 1–3, 10 and 12 at both 25 °C (for comparison with literature data) and 50 °C (for comparison with ionic liquid 1; the melting point of the chlorinated ionic liquid 1 (41–44 °C) precluded the examination of density and viscosity at the standard temperature of 25 °C as used in the literature). The results of the density and viscosity measurements are shown in Table 2, along with literature data for ionic liquid 11.

For [bmim][Tf₂N] **10**, the density determined was consistent with that reported in the literature.^[16] The addition of the methyl groups to the cation causes a decrease in density, which is observed in both the reported density^[16b,17] of [bm₂im][Tf₂N] **11** and the density determined here for [bm₃im] [Tf₂N] **12**. The differences in density as a result of C2-methylation have been attributed previously to the looser interionic packing in the parent ionic liquid **10** than in the methylated case **11**.^[18]

Addition of chloro substituents to the cation, as in ionic liquids [b4Clmim][Tf₂N] **1** and [b2Clmim][Tf₂N] **3**, causes the density to increase. The position of the chlorine atom does not appear to have a significant effect, as the densities of ionic liquids **1** and **3** are similar (at 50 °C). With two chloro substituents, the density is increased even further, as seen in the case of [b45 L₂mim][Tf₂N] **2**. Hence, the addition of a chlorine atom has the opposite effect to a methyl group, which can be attributed to the introduction of increased dispersion forces owing to incorporation of the chlorine centre.^[11] This effect is enhanced further by the larger atomic weight of the chlorine atom relative to that of carbon and hydrogen.



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Table 2. Densities and viscosities of ionic liquids 10–12 and 1–3.							
lonic liquid	Density [g cm ^{-3}]		Viscosit	y [mPas]			
	25°C	50 °C	25 °C	50 °C			
[bmim][Tf ₂ N] 10	1.4373±0.0018	1.4147 ± 0.0005	50.34±0.82	20.670±0.071			
[bm ₂ im][Tf ₂ N] 11	1.4159 ^[a]	_[b]	93.33 ^[a]	_[b]			
[bm₃im][Tf₂N] 12	1.3892 ± 0.0007	1.3661 ± 0.0005	70.7 ± 1.6	25.54 ± 0.40			
[b4Clmim][Tf ₂ N] 1	_[c]	1.4703 ± 0.0002	_[c]	33.61 ± 0.17			
[b45Cl ₂ mim][Tf ₂ N] 2	1.5467 ± 0.0004	1.5209 ± 0.0005	189.8 ± 2.5	49.76 ± 0.49			
[b2Clmim][Tf ₂ N] 3	1.5005 ± 0.0002	1.4761 ± 0.0005	120.52 ± 0.73	38.40±0.52			
[a] From Katsuta et al. ^[16b] with no errors reported. [b] Not reported. [c] Salt 1 is a solid at this temperature.							

For [bmim][Tf₂N] **10**, the viscosity determined here was also consistent with that reported in the literature.^[16b,17] The presence of methyl groups on the cations of the ionic liquids increases the viscosity, which is observed in both the reported value for [bm₂im][Tf₂N] **11**^[16b] and the viscosity determined here for [bm₃im][Tf₂N] **12**. The viscosity of [bm₂im][Tf₂N] **11** is higher than that of [bm₃im][Tf₂N] **12**, which suggests that the position of the methyl group is important in determining the viscosity; methylation at the C2 position is particularly significant, more so than the number of methyl groups.

The importance of the alkylation site has been studied previously by Bonhôte et al.,^[5] who compared the series of ionic liquids **13–15** (Figure 3). The viscosity of the C2 methylated ionic liquid **14** was 88 MPas (at 20 °C), which is significantly higher than that of the C5 methylated ionic liquid **15** (37 MPas) and ionic liquid **13** (34 MPas) at the same temperature. Subsequent ab initio studies^[19] suggested that the increased viscosity is caused by the high potential energy barriers between ion pair conformations, which limit the movement of ions.



Figure 3. Methylated ionic liquids 13–15 considered previously by Bonhôte et al. $^{\rm [5]}$

Upon chloro substitution of the cation, the viscosity of the ionic liquid increases significantly. For [b2Clmim][Tf₂N] **3**, the viscosity was about twice that of the parent ionic liquid [bmim][Tf₂N] **10** and also greater than that reported for the C2 methylated ionic liquid **11**.^[16b,17] In a similar fashion to the 2-substituted case **3**, the viscosity of ionic liquid [b4Clmim][Tf₂N] **1** is higher than that of [bmim][Tf₂N] **10** at the only common temperature (50 °C). Upon comparison with [b2Clmim][Tf₂N] **3**, the C4 chlorinated ionic liquid **1** was found to have a slightly lower viscosity, demonstrating the importance of the site of substitution. This is consistent with the Bonhôte study discussed above,^[5] in which it was shown that blocking of the C2 position caused a higher viscosity than the equivalent substitution at the C4 position, though it is not clear if the source of the change is the same. Upon addition of multiple chlorine

atoms to the cation, the viscosity increases even further, with ionic liquid $[b45Cl_2mim][Tf_2N]$ 2 having a viscosity almost four times that of the parent ionic liquid 10 and almost double that of the di-methylated ionic liquid 12.

Miscibility of ionic liquids 1–3, 10 and 12 with common solvents

The miscibility of each of the ionic liquids 1–3, 10 and 12 in common solvents was examined; the solvents chosen provided a range of properties, including polarity, hydrogen-donating ability, extent of halogenation and aromaticity. Ionic liquid 1 is solid at room temperature, so rather than its miscibility, its solubility in each of the solvents was examined.

It was found that irrespective of the ionic liquid used (including in the solubility studies of the solid 1), all of the ionic liquids 1-3, 10 and 12 were miscible (or soluble) with most of the solvents considered (for full details, see Supporting Information); immiscibility (or insolubility) was observed only for the solvents that have extreme polarity. All the ionic liquids were partially soluble in both diethyl ether and toluene. This may be because these have similar but low polarities;^[20] however, there is likely to be a contribution in the toluene case from cation-multipole interactions, as used previously to describe the anomalous solubility of benzene in ionic liquids.^[21] (Induced fluctuations in the electrostatics of the solute may enhance the solubility of these species; however, the methodology used in the initial molecular dynamics studies^[21] demonstrated that this was not necessary to explain the observed solubility).

These results demonstrate that the addition of chlorine atoms to the cation does not affect significantly the interaction of an ionic liquid with a range of solvents, suggesting that, on miscibility grounds, the novel ionic liquids **1–3** might be used as solvents, replacing the ionic liquid **10** with little effect.

Electrochemical windows of ionic liquids 1-3 and 10

The electrochemical window measures the relative electrochemical potentials an electrolyte can withstand before the onset of (often unwanted) oxidation and reduction reactions. Chemical stability is often mirrored by electrochemical stability, such that some exceptionally stable ionic liquids have been demonstrated to be superior electrolytes (both neat and in dilute solution) compared with "conventional" electrolytes.

The electrochemical experiments were undertaken using both platinum and glassy carbon (GC) working electrodes. These electrode materials are common in the literature,^[5,22] and sometimes have different electrochemical windows owing to their ability to facilitate (or electrocatalyse) processes to different degrees.^[23] For example, the electrochemical reduction of imidazolium cations is believed to result in an unstable radical (centred on the C2 carbon), which can dimerise^[24] and potentially yield imidazol-2-ylidene carbenes and molecular hydrogen.^[25] Platinum electrodes are known to electrocatalyse this process if the C2 carbon contains a labile proton, such that cation reduction at platinum electrodes occurs at potentials about 0.5 V more positive than at GC electrodes (i.e., platinum electrodes have smaller electrochemical windows than GC electrodes in imidazolium ionic liquids with C2 protons). This difference is reduced significantly by replacing the C2 proton with a methyl group.^[5,22]

The electrochemical windows of each of the ionic liquids 1-3 and 10 were evaluated at both GC and platinum electrodes by performing cyclic voltammetry in approximately 0.1 M solutions of the ionic liquids dissolved in acetonitrile (Figure 4).



Figure 4. Electrochemical window of ionic liquids 1–3 and 10 in 0.1 $\mbox{ m}$ solutions in acetonitrile, recorded at platinum (red) and GC (black) electrodes. Arrows indicate the direction of the scan, and dashed lines indicate the approximate electrochemical window of [bmim][Tf₂N] 10. Scans were recorded under a nitrogen atmosphere at a scan rate of 5 mVs⁻¹.

Acetonitrile is relatively electrochemically stable,^[26] and the use of a dilute solution of ionic liquid allows comparisons that are unbiased by differences in the ionic liquid properties such as melting points, density and viscosity.

The results for the parent salt **10** are consistent with literature reports;^[27] both types of working electrode display large electrochemical windows (\approx 5 V), with the GC case having a larger window than platinum owing to the reduction process described above. Oxidation (of the [Tf₂N]⁻ anion^[28]) is observed at similar potentials.

Upon replacing the C2 hydrogen with a chlorine atom to give the ionic liquid [b2Clmim][Tf₂N] 3, a smaller electrochemical window is observed. No significant change in the oxidation process is seen, but reduction of the cation now occurs at similar potentials for both electrodes. This is reasonable because the C--Cl bond is weaker than both the C--H bond and the C=N bond.^[15] This would account for the electrochemical window remaining the same irrespective of the electrode used, as only electrode materials such as silver are known to electrocatalyse alkyl halide cleavage reactions, but platinum and GC are classed as relatively "inert" (i.e., equally poor electrocatalysts).^[29] The precise reduction products are not known, but are likely to involve either a C2-centred imidazole radical or an imidazol-2-ylidene-based carbene and a chloride anion; electrochemical reduction of the non-chlorinated analogue has been reported to form radicals or carbenes at GC^[24] and platinum^[25] electrodes, respectively.

Regarding the ionic liquid [b4Clmim][Tf₂N] **1**, there is no observable difference in the electrochemical window upon comparison with the parent ionic liquid **10**. As ionic liquid **1** has a C2–H bond that is activated at low potentials by the electrocatalytic platinum electrode, it is reasonable that the reduction process observed is similar to that in the case of the ionic liquid **10**. For the ionic liquid [b45Cl₂mim][Tf₂N] **2**, reduction occurs at the platinum electrode at slightly more positive potentials, either because of the electron-withdrawing effect of the two chlorine atoms, or owing to some electrochemical process involving the chlorine atoms on adjacent carbon centres.

The reduction processes of each of the ionic liquids 1 and 2 at the GC electrode are considerably different from both the parent ionic liquid 10 and the results observed at the platinum electrode. For the mono-chlorinated ionic liquid 1, one reduction process is observed, whereas the di-chlorinated ionic liquid 2 exhibits two processes. Clear hysteresis is also seen, consistent with passivation of the GC electrode through the formation of a dense organic layer that blocks the electrode surface. $^{\scriptscriptstyle [30]}$ This is consistent with direct cleavage of the C–Cl bond resulting in reactive organic radicals that react with the sp²-hybridised GC surface. A similar process has been noted for the reduction of alkylferrocenes with a terminal iodo substituent, for which reduction at -1.7 V versus Ag/AgCl at a GC electrode in acetonitrile resulted in the covalent immobilisation of the alkylferrocene species at the GC surface through C-I cleavage.^[31]

Interestingly, the oxidation features of ionic liquids 1 and 2 also change from those of the parent ionic liquid 10 at both GC and platinum electrodes. Recent computational investiga-



tions have demonstrated that the oxidation potentials of $[Tf_2N]$ -based ionic liquids are limited by the $[Tf_2N]^-$ anion, whereas those of imidazolium-based ionic liquids with $[PF_6]^-$ and $[BF_4]^-$ anions are limited by the relative oxidative (in)stability of the cation.^[28] Hysteresis and passivation were observed for cases 1 and 2 at the GC electrode, consistent with the electrochemistry of the cation rather than the $[Tf_2N]^-$ anion; oxidation was also more facile at the platinum electrode. Although multiple authors have reported anions limiting the reductive electrochemical window of ionic liquids,^[32] the results described here are only the second example after that of the cyclopropenium salts reported by Curnow et al.^[33] of an ionic liquid.

Ultimately, all the ionic liquids 1–3 prepared here have large electrochemical windows (from \approx 4.5 V at platinum before chlorination to \approx 4.0 V after dichlorination), indicating that they are pure, relatively stable and unlikely to undergo unwanted side reactions. Additionally, new electrochemical functionality can be introduced; ionic liquid layers have been formed deliberately on GC to introduce functionality,^[34] and ionic liquids 1 and 2 present the possibility to do this at a GC electrode by potentially direct connection through the imidazolium backbone, through both reduction and oxidation processes, introducing additional versatility to this process.

Kinetic analyses

For investigation of the effects of the novel ionic liquids 1–3 on the outcome of organic processes, they were examined as solvents for two well-described reactions. Chosen because they each proceed to give a single product (so there are no issues with selectivity), are readily monitored and have been investigated previously in ionic liquid media, particularly the parent ionic liquid **10** and the methylated species **11** and **12**, these standard reactions were the nucleophilic aromatic substitution reaction between 1-fluoro-2,4-dinitrobenzene **16** and ethanol (Scheme 3),^[10f,j] and the bimolecular nucleophilic substitution reaction between benzyl bromide **18** and pyridine (Scheme 4).^[10d,g,h,j,m] By comparing the solvent effects observed



Scheme 3. Nucleophilic aromatic substitution reaction of 1-fluoro-2,4-dinitrobenzene 16 to give the ether 17. i) EtOH, NEt₃.



Scheme 4. Menschutkin reaction between benzyl bromide 18 and pyridine to give the salt 19. i) Pyridine.

here with the previous cases (salts **10–12**), we can assess how chlorination of the cation affects ionic liquid solvent effects.

Nucleophilic aromatic substitution (S_NAr)

The reaction between the fluorodinitrobenzene 16 and ethanol (Scheme 3) is a well-known reaction that proceeds through a nucleophilic aromatic substitution mechanism.^[10f] It has been found that the key interaction responsible for ionic liquid solvent effects on this process is that between the fluorodinitrobenzene 16 and the anion of the ionic liquid.^[10f] This interaction is responsible for the enthalpic cost and entropic benefit (the balance of which, in turn, results in an increase in rate constant) on moving from ethanol to the parent ionic liquid 10.^[10f] Upon further study of this rate enhancement, it has been shown that there is a general ionic liquid effect, with the rate enhancement virtually independent of the nature of either the cation or the anion.^[10] It was of interest to determine whether the chlorinated systems 1 and 2 would have the same effect as the ionic liquids used previously (the 2-chloro system 3 was not considered as initial studies showed that it underwent reaction with ethanol under these reaction conditions; for more information, see Supporting Information).

As it is known that there is a general ionic liquid effect for this reaction, it was anticipated that addition of chloro substituents to the imidazolium cation would have little effect on the rate constant. That is, the novel ionic liquids **1** and **2** were expected to behave in a similar fashion to previously examined ionic liquids, including **10–12**.^[10]

It should be noted that no attempt was made to isolate the product **17**, nor determine a yield. This is because any isolated yield would incorporate a component from the extent of conversion (the effect of the ionic liquid on the rate) and a component from the efficacy of isolation (which will be complicated by interactions of aromatic **17** with the solvent^[21]). This is consistent with previous reports.^[10f,i]

The temperature-dependent kinetic analyses in this study were performed in the same manner as previous studies^[10f,i] using ¹⁹F NMR spectroscopy, allowing the construction of an Eyring plot (Figure 5) for the reaction in ethanol and each of the ionic liquids **2** and **3** and the determination of activation parameters in each of the solvent systems (Table 3). Also included to allow direct comparison of solvent effects are data for the non-chlorinated systems **10–12**. The mole fraction of the novel ionic liquids **1–3** used was approximately 0.5, to enable direct comparison with the previous studies.^[10f,i]

The second-order rate constants and activation parameters determined in ethanol were consistent with those reported in the literature.^[10f] As well as enabling determination of the activation parameters, the Eyring plot (Figure 2) can be thought of as a representation of the relative rate constant data, and shows that each of the ionic liquids 1 and 2 results in larger rate constants for the reaction over the range of temperatures used than those observed in the molecular solvent ethanol. Further, the effect of chlorination compared to methylation on the rate constants was minimal (Eyring plots comparing the chlorinated and methylated ionic liquids are presented in Fig-





Figure 5. The bimolecular Eyring plot, from which the activation parameters in Table 3 were determined, for the reaction between the fluorobenzene **16** and ethanol in either ethanol (black) or one of the ionic liquids [b4Clmim] [Tf₂N] **1** (blue) or [b45Cl₂mim][Tf₂N] **2** (red) at $\chi_{\rm lL} \approx 0.5$. Exact mole fractions are outlined in Table 3.

Table 3. Activation parameters for the reaction between the fluoroben- zene 16 and ethanol in either ethanol or one of the ionic liquids 1 , 2 or 10–12 , at $\chi_{IL} \approx 0.5$.					
Solvent	χıl	ΔH^{*} [kJ mol ⁻¹] ^[a]	$\Delta S^{\pm} [J K^{-1} mol^{-1}]^{[a]}$		
ethanol	0	48.7±2.1	-249 ± 7		
[bmim][Tf ₂ N] 10 ^[b]	0.54	49.6 ± 0.5	-229 ± 2		
[bm ₂ im][Tf ₂ N] 11 ^[c]	0.52	49.0 ± 3.9	-223 ± 12		
[bm ₃ im][Tf ₂ N] 12 ^[c]	0.50	51.5 ± 3.2	-211 ± 10		
[b4Clmim][Tf ₂ N] 1	0.53	54.0 ± 1.3	-213 ± 4		
[b45Cl ₂ mim][Tf ₂ N] 2	0.52	51.5 ± 2.1	$-220\pm\!6$		

[a] Uncertainties quoted are from the fit of the linear regression. [b] Data reproduced from Jones et al.^[107] [c] Data reproduced from Tanner et al.^[107]

ures S6 and S7, Supporting Information). This was consistent with the general ionic liquid effect observed previously, and was as expected given the minimal changes seen upon modification of the cation.^[10]

The activation parameters (Table 3) demonstrate that the rate constant enhancement observed in all the ionic liquids relative to that in ethanol is caused by an increase in the entropy of activation, which again is consistent with previous observations, and was as anticipated.^[10f,] From these data it is clear that the chlorinated ionic liquids **1** and **2** behave in a predictable fashion as solvents for this nucleophilic aromatic substitution reaction.

Bimolecular nucleophilic substitution (S_N2)

The Menschutkin reaction (Scheme 4) between benzyl bromide **18** and pyridine proceeds through an $S_N 2$ mechanism.^[35] This reaction has been studied previously in ionic liquids.^[10d,g,h,j,m] It has been found that the key interaction in ionic liquid solutions is that between pyridine and the cation of the ionic liquid.^[10g] This interaction is responsible for the enthalpic cost and entropic benefit (which, in turn, results in an increase in rate constant) upon moving from acetonitrile to the parent ionic liquid **10**.^[10d] The extent of this interaction, and hence the rate enhancement, has been shown to be dependent on the ease of accessing the charged nitrogen centre of the cation.^[10j] Hence, it is of interest here to consider how changing the electronic nature of the substituent affects the interaction, and hence the rate enhancement, so the process was considered in the chlorinated ionic liquids **1–3** (note that in this case the 2-chloro derivative **3** was found to be stable under the reaction conditions and was hence investigated as a solvent). It was anticipated that the electron-withdrawing nature of the substituents on the novel ionic liquids **1–3** would cause an increase in the key interaction identified previously, and hence, in the rate constant for the process, relative to their methylated counterparts.

For the same reasons as in the case above, no attempt was made to isolate the product **19**, nor determine a yield. Once again, this is consistent with previous reports.^[10d,g,h,j,m]

Temperature-dependent kinetic analyses were performed as described previously^[10d,g,]] using ¹H NMR spectroscopy, allowing the construction of an Eyring plot (Figure 6) for the reaction in acetonitrile and each of the ionic liquids **1**–**3**, and the determination of activation parameters in each of the solvent systems (Table 4). The mole fraction of the novel ionic liquids **1**–**3** used



Figure 6. The bimolecular Eyring plot, from which the activation parameters in Table 4 were determined, for the reaction between benzyl bromide **18** and pyridine in either acetontitrile (black) or one of the ionic liquids [b4Clmim][Tf₂N] **1** (blue), [b45Cl₂mim][Tf₂N] **2** (red) or [b2Clmim][Tf₂N] **3** (green), at $\chi_{lL} \approx 0.9$. Exact mole fractions are outlined in Table 4.

Table 4. Activation parameters for the reaction between benzyl bromide 18 and pyridine in either acetonitrile or one of the ionic liquids 1–3 and 10–12, at $\chi_{IL} \approx 0.9$.					
Solvent	χil	$\Delta H^{\pm} [\text{kJ mol}^{-1}]^{[a]}$	$\Delta S^{\pm} [J K^{-1} mol^{-1}]^{[a]}$		
ethanol	0	44.7 ± 0.8	-220 ± 3		
[bmim][Tf ₂ N] 10 ^[b]	0.86	49.9 ± 0.8	-195 ± 3		
[bm ₂ im][Tf ₂ N] 11 ^[c]	0.88	53.5 ± 2.8	-183 ± 10		
[bm ₃ im][Tf ₂ N] 12 ^[c]	0.85	53.5 ± 1.1	-189 ± 4		
[b4Clmim][Tf ₂ N] 1	0.86	54.4 ± 1.4	-180 ± 5		
[b45Cl ₂ mim][Tf ₂ N] 2	0.85	53.7 ± 1.8	-181 ± 6		
[b2Clmim][Tf ₂ N] 3	0.86	53.8±1.0	-183 ± 3		
[a] Uncertainties quoted are from the fit of the linear regression. [b] Data reproduced from Yau et al. ^[10] [c] Data reproduced from Tanner et al. ^[10]					



was about 0.9, enabling direct comparison with previous studies. $^{\scriptscriptstyle [10d,g,j]}$

The second-order rate constants and activation parameters determined in acetonitrile were consistent with those reported previously.^[10]] Performed in each of the ionic liquids [b4Clmim] [Tf₂N] **1**, [b45Cl₂mim][Tf₂N] **2** and [b2Clmim][Tf₂N] **3**, an increase in the rate constant of the Menschutkin reaction was observed over the range of temperatures used compared with the molecular solvent, acetonitrile.

The ionic liquids [b4Clmim][Tf₂N] **1** and [b2Clmim][Tf₂N] **3** exhibited almost identical rate constants over the range of temperatures used, indicating that the position of the chlorine is not important in determining solvent effects on the rate constant. The dichlorinated ionic liquid **2** showed a slightly increased rate of reaction over the range of temperatures compared with the monochlorinated cases **1** and **3**. The origin of all of these rate constant enhancements can be considered by examining the activation parameters (Table 4). The activation parameters for all three ionic liquids **1**–**3** show that the origin of the rate enhancement is an entropic benefit, which overcomes the enthalpic cost. This is consistent with previous observations,^[10]] and suggests that there is ordering of the cation around the starting material **18**.

Once again, it is useful to compare the solvent effects on rate data for chlorinated and non-chlorinated ionic liquids by using an Eyring plot (see Figures S8 and S9, Supporting Information). The rate constant enhancement for ionic liquids 1 and 3 was consistent with that observed for the parent ionic liquid 10 and the methylated ionic liquid 11. The rate constants for the C2-Cl ionic liquid 3, the C2-CH₃ ionic liquid 11 and the parent ionic liquid 10 cases are the same within error, which suggests that the steric and electron-withdrawing nature of the chlorine atom has no effect on the rate constant of the reaction at that position. To a certain extent, this demonstrates a limitation of the predictive tools available, as the chlorinated cases 1 and 3 might be expected to result in a faster rate constant, but they were the same within the uncertainties of measurement across the range of temperatures considered.

The ionic liquid [b45Cl₂mim][Tf₂N] **2** had a very different rate constant profile compared with the previously studied [bm₃im] [Tf₂N] 12, with greater rate constants observed across the range of temperatures used. This demonstrates that changing from two electron-donating methyl substituents to two electron-withdrawing chlorine substituents (of comparable size) on the cation of the ionic liquid alters the solvent effect significantly. The different effects of methylation compared with chlorination are reasonable given the argument presented above: the electron-withdrawing chloro substituents would be expected to increase the interaction of the cation with the nucleophile pyridine. These electronic effects compete with the steric interactions, which were used previously to explain the decrease in rate constants observed on moving between the parent ionic liquid 10 and the dimethylated case 12.^[10]] In the case of the dichloro system 2, the electronic effects counteract the negative steric effects, giving a similar rate constant enhancement to that seen in the parent ionic liquid 10.

Conclusion

The syntheses of three novel imidazolium-based ionic liquids containing chlorine atoms have been described. The thermophysical and physicochemical properties of each of the ionic liquids have been measured and compared with those of the corresponding protiated and methylated systems. The chlorinated ionic liquids have a higher density and viscosity than their non-chlorinated counterparts, along with the same miscibility, whereas the introduction of a chlorine atom reduces the electrochemical window of the system slightly and decreases the temperature at which it decomposes. Interestingly these chlorinated cations demonstrate both reductive and oxidative instability. Importantly, these changes are as expected on the basis of the structural changes made and trends reported in the literature, demonstrating that modification of the cation can be used to alter predictably the properties of an ionic liauid.

The effects of these salts on the outcomes of organic processes were as expected on the basis of the developing understanding of the microscopic interactions that drive ionic liquid solvent effects. The "general ionic liquid effect" seen previously for an S_NAr reaction is replicated, and the balance of introducing substituents with competing steric and electronic effects is demonstrated well in the case of an S_N2 reaction. In addition, a rate constant enhancement is seen, demonstrating the potential utility of these species as solvents for organic processes. The results demonstrate that the cation of an ionic liquid can be modified in a rational fashion, not only to control the properties of the solvent, but also reaction outcomes.

The limitations of the existing understanding of ionic liquid effects are also demonstrated. Quantification of such effects is not possible (though it might be argued that this is limited even for molecular solvents^[36]) and uncertainties in data may limit the ability to determine subtle solvent effects.

Although any replacement of existing solvents with novel ionic liquids must take into account other parameters (including cost, stability and appropriateness of physical properties, relative to both molecular solvents and existing ionic liquids), overall, the key outcome is that the effects of functionalization observed on both ionic liquid properties and how they affect reaction outcome could both be correlated directly to the structure of the cation and its associated interactions with other species. With this understanding, there is the potential to extend this work to the rational design of ionic liquids with appropriate physical and solvent properties for a given application.

Experimental Section

General experimental details; syntheses of ionic liquids 1, 2 and 3; reverse Menschutkin reaction in mixtures containing imidazole 6 and n-bromobutane; deprotonation of salt 8 and reaction with hexachloroethane; alkylation reaction of 4(5)-methylimidazole with *n*-iodobutane; raw DSC plots for ionic liquids 1-3; raw TGA curves of ionic liquids 1-3; complete miscibility data for the salts 1-3, 10 and 12; reaction of ionic liquid 3 in ethanol; Eyring plots compar-



ing the effects of the salts 1 and 2 with the methylated ionic liquids 11 and 12 on the reaction shown in Scheme 3; Eyring plots comparing the effects of the salts 1–3 with the methylated ionic liquids 11 and 12 on the reaction shown in Scheme 4; preparation of the imidazole 6 and the ionic liquids 9, 11 and 12; details of the electrochemical studies; rate data for all of the plots presented in this work; and NMR spectra for all new compounds are provided in the Supporting Information.

Characterisation

Prior to characterisation and kinetic analyses, the ionic liquids were dried under reduced pressure (0.1 mbar) at room temperature for about 4 h, and were found to have < 200 ppm water by using Karl Fischer titration methodology. Ion chromatography was used to determine if there were residual halide anions in the ionic liquids; all were < 0.2 mol%. The glass transition temperatures and melting points were measured on a Mettler Toledo DSC823 with a TS0800GC1 gas controller. The analysis consisted of heating and cooling the sample at a rate of 10° Cmin⁻¹ under a 50 mLmin⁻¹ flow of nitrogen. All measurements were performed in either duplicate or triplicate, with uncertainties reported as the standard deviation. The decomposition temperatures were determined by using a Mettler Toledo TGA/DSC 1 with a GC 200 gas controller. The analysis consisted of heating the sample from 50 °C to 500 °C at a rate of $10\,^{\circ}\text{Cmin}^{-1}$ under a 50 mLmin⁻¹ flow of argon. All measurements were performed in duplicate, with uncertainties reported as the standard deviation. Decomposition temperatures were determined through the onset method using the Mettler Toledo software. The density and viscosity measurements were made on an Anton Paar DMA 4100 M Density Meter and a Lovis 2000 ME Microviscometer, respectively. All measurements were performed in triplicate, and uncertainties are reported as the standard deviation of the triplicate data. Miscibility studies were performed by adding samples of the ionic liquid (1 mL) and the appropriate solvent (1 mL) to a measuring cylinder, inverting several times, and then allowing the mixture to settle; the number of phases and their proportions was then observed. Full details are provided in the Supporting Information. The cyclic voltammetry studies were performed on a µ-Autolab III potentiostat/galvanostat system in a three- electrode setup. The data were handled by using Nova 1.10 software. The experiments were performed using either a glassy carbon (diameter 3 mm) or platinum (diameter 1.4 mm) working electrode, an Ag|Ag⁺ reference electrode and a platinum counter electrode. Potentials were subsequently referenced to the $Fc|Fc^+$ redox couple by adding ferrocene to the solution at the end of the experiment, repeating the scan, estimating $E^{\circ}(Fc|Fc^+)$ from the cyclic voltammogram and referencing the data such that $E^{\circ}(Fc | Fc^{+}) = 0$ V. Further information is given in the Supporting Information.

Kinetic analyses

The ¹H NMR and ¹⁹F NMR kinetic experiments were performed on either a Bruker Advance III 400, Bruker Advance III 500 or a Bruker Advance III 600 spectrometer with a TBI, BBO or BBFO probe. The results were shown to be reproducible between the different spectrometers and probes. Kinetic analyses for the reaction described in Scheme 3 were performed in solutions containing fluorodinitrobenzene **16** (\approx 0.015 molL⁻¹), triethylamine (\approx 0.35 molL⁻¹) and ethanol (\approx 2 molL⁻¹) at a given temperature in the range 304–334 K. For the reaction outlined in Scheme 4, solutions were made up containing benzyl bromide **18** (\approx 0.04 molL⁻¹) and pyridine

 $(\approx 0.5 \text{ mol L}^{-1})$. In all cases the reaction was monitored in situ with the spectrometer set to the desired temperature for the duration of the reaction. All reactions were followed until more than 95% of the starting material (either 16 or 18) was consumed, and all kinetic analyses were performed in triplicate. NMR spectra were processed using the MestReNova 8.1.1 software. The pseudo-firstorder rate constants for the reactions were calculated using either integrations of the signal attributed to the starting material 16 at $\delta \approx -110$ (obtained from the processed ¹⁹F NMR spectra of the reaction in Scheme 3) or integrations of the signal attributed to the benzyl bromide 18 at $\delta \approx$ 4.6 (obtained from the processed ¹H NMR spectra of the reaction in Scheme 4), by fitting the natural logarithm of the integrations to a linear function using the Microsoft Excel 14.4.3 LINEST function. Bimolecular rate constants were obtained from the pseudo-first-order constants by dividing by the initial nucleophile concentration in the reaction mixture. The activation parameters were then determined by fitting the data obtained using the Microsoft Excel 14.4.3 LINEST function to the bimolecular Eyring equation shown in Equation (1).^[10d, 37]

$$\ln\left(\frac{k_2h}{k_BRT^2}\right) = \frac{\Delta S^+}{R} - \frac{\Delta H^+}{RT}$$
(1)

Tables containing the kinetic data for all the systems described can be found in the Supporting Information.

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