Exothermic and thermal runaway behaviour of some ionic liquids at elevated temperatures†

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The exothermic behaviour and intrinsic safety of a number of ionic liquids being considered for battery and solar cell applications have been investigated at elevated temperatures by analysing data from accelerated rate calorimetric (ARC) studies.

Ionic liquids have been the subject of intense study in recent years because of their attractive properties for a variety of applications. To a large extent it is the thermal, chemical and electrochemical stability of selected ILs that are the features of interest. Where this is the case they offer the potential of very stable, non-flammable and non-volatile reaction solvents,[1,2] electro-deposition solvents,[3] extractants[4] and battery or solar cell electrolytes.[5] However, though more detailed analyses of breakdown behaviour have begun to appear in recent years,[6] a full understanding of the high temperature behaviour of most ionic liquids is not yet available. In any application where even a moderate quantity of ionic liquid may become exposed to elevated temperatures, this information is vital from a safety standpoint. For example, the use of ionic liquids in large battery packs for electric vehicles, where elevated temperatures may occur under extreme service or collision/ accident conditions, requires an understanding of their behaviour under these conditions.[7,8] As we will show, a wide range of behaviours is exhibited by the ionic liquids that are being considered for such applications; some are encouragingly stable, while others are not.

Explosions due to thermal runaway are also one of the major safety issues faced by chemical industries.[9] In an exothermic reaction, if the heat generation in the system exceeds the heat removal capacity, thermal runaway can occur, leading to secondary reactions and/or potentially to an explosion.[10] Knowledge of the thermokinetics of exothermic reactions assists in mitigating such disastrous events and provides a means for designing inbuilt safety systems.[11] Hence the main objective of the present study was to investigate the safety of a number of commonly used ionic liquids and generate thermo-kinetic data for them. The output of this study will be of direct relevance to the use of these ionic liquids in any application where the onset temperature for exothermic processes is even a remote possibility. The ionic liquids chosen for this study are a series of methylimidazolium and methylpyrrolidinium salts of anions including bis(trifluoromethanesulfonyl)amide, BF_4, $B(CN)_4$, bis(fluorosulfonyl)amide and tricyanomethanide.

The accelerated rate calorimetry (ARC) technique is a relatively simple and direct way to study the thermal behaviour of a compound or a mixture of compounds. It has been used to identify potentially dangerous exothermic behaviour[7,8,12–14] and also to show that certain ionic liquids can be used as moderators to control exothermic behaviour in polymerisation reactions.[15] The process involves heating the sample in an adiabatic calorimeter in small temperature steps and evaluating, at each step, the tendency of the sample to attain isothermal conditions, or, if an exothermic process is present, to self-heat. Knowledge of the thermal inertia (ϕ) of the calorimeter bomb and the sample itself allows calculation of the enthalpy of reaction. Further details can be found in the ESI†.

The ionic liquids tested in this study were as follows: 1-ethyl-3-methylimidazolium tricyanomethanide ([C$_2$mim][TCM]) was synthesised as per the literature procedure,[16] while 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide ([C$_2$mim][FSI]‡) and *N*-ethyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)amide ([C$_3$mpyr][FSI]) were purchased from Dai-chi Kogyo Seikayu. 1-ethyl-3-methylimidazolium-tetracyanoborate ([C$_2$mim][B(CN)$_4$]) and 1-ethyl-3-methyl imidazolium tetrafluoroborate ([C$_2$mim][BF$_4$]) were purchased from MERCK. The ionic liquids were intentionally used as received, in order to test them under practical conditions. The synthesis of 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([C$_2$mim][NTf$_2$]), *N*-ethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([C$_2$mpyr][NTf$_2$]) and *N*-butyl-*N*-methylpyrrolidinium iodide ([C$_4$mpyr][I]) followed literature procedures.[17] The preparation of diethylphosphate ionic liquids followed the literature methods.[18] The synthesis of 1-ethyl-3-methylimidazolium diethylphosphate ([C$_2$mim][DEP]) involved dropwise addition of triethylphosphate (46 g, 0.252 mol) to a flask containing 21 g of *N*-methylimidazole at 140 °C under nitrogen and stirring. The liquid was stirred overnight at the same temperature, then cooled and dried *in vacuo* for 24 h. The product was liquid at room temperature. (Crude yield 90%) MS (ESI): ES + *m/z*: 111.09 (C$_6$H$_{11}$N$_2$$^+$), ES− *m/z*: 153.03 ((C$_2H_5$O)PO$_2$$^-$). In a similar manner *N*-ethyl *N*-methylpyrrolidinium diethylphosphate ([C$_2$mpyr][DEP]) was prepared by a slow addition of triethylphosphate (17 g, 0.094 mol) into a flask containing *N*-methylpyrrolidine (8 g, 0.094 mol) at 160 °C under nitrogen and stirring. The liquid was stirred overnight at the same temperature, then cooled and dried under vacuum overnight. A liquid was formed at room temperature. (Crude yield 92%) ES + *m/z*: 114.13 (C$_7$H$_{16}$N$^+$), ES− *m/z*: 153.03 ((C$_2$H$_5$O)PO$_2$$^-$).

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† Electronic supplementary information (ESI) available: The instrumental techniques, adiabatic thermo-kinetics and the time-to-temperature plots for each IL. See DOI: 10.1039/b911568d

A summary of ARC data for the various ionic liquids studied is presented in Table 1. The table lists the temperatures of onset, T_o and completion, T_f of exothermic activity, as well as the deduced enthalpy of reaction of the exothermic process for each ionic liquid. The types of thermal phenomena observed in this study are exemplified by the ARC data for [C_2mim][B(CN)$_4$], as shown in Fig. 1 and Fig. S1, ESI†. The ARC results show the onset of exothermic activity at 315 °C. The sample then continues to heat itself up, at increasing rate, with a maximum self-heat rate of 1.25 °C min^{-1} being reached at 364 °C (Fig. 1). The time–temperature profile (Fig. S1, ESI†) shows that the time for the sample to self-heat from 315 to 364 °C is about 100 minutes. The maximum pressure rise observed during this time was about 8 bar. The adiabatic temperature rise, T_{ad}, was thus 48.9 °C and if ϕ corrections are applied (as per eqn (3) in the ESI†) the actual temperature rise, T_{ab}, would have been 158 °C. However, this ionic liquid is not classified here as dangerous because the exothermic activity occurs at reasonably high temperature (above 300 °C) and the rate of self-heating was also not found to be large (not more than 1.25 °C min^{-1}).

On the other hand, completely inert behaviour was observed for imidazolium ionic liquids of the BF$_4$, DEP and NTf$_2$ anions. The enhanced stability of the NTf$_2$ anion has been observed previously[19] and we believe a similar thermal stability exists for BF$_4$ and DEP anions. The ARC results of these ionic liquids show no exothermic activity and/or pressure generation at any temperature up to 400 °C. This seems to indicate the thermal stability of these anions and also, by implication, of the imidazolium cations involved. The TGA results of these ionic liquids (not shown here) also substantiate this observation by showing no considerable weight loss up to 400 °C. Hence these ionic liquids can be considered for high temperature applications.

If we now consider the FSI anion, a completely different behaviour is observed. The ARC results for [C_2mim][FSI], Fig. 2, show an onset of exothermic activity at 165 °C and the self-heat rate gradually increases, reaching a sharp maximum around 300 °C. The exothermic activity continues up to 412 °C. In the time-to-temperature (Fig. S2, ESI†) profile it was observed that the temperature jumps sharply from 165 °C to 325 °C and then again from 325 to 425 °C, the second jump being not quite so rapid. During these temperature jumps the maximum pressure rise (Fig. 2) was observed to be 65 bars.
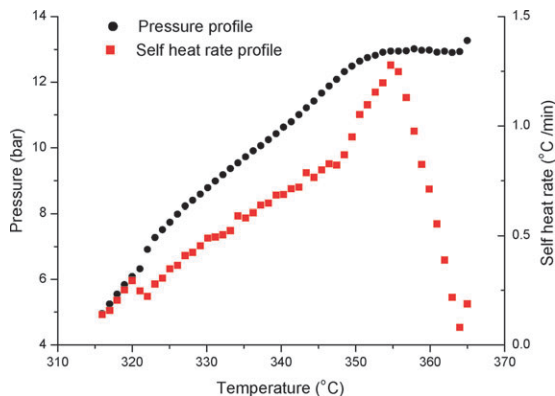
Table 1 Summary of accelerated rate calorimeter data for various ionic liquids (sample mass = 1.0 g)

Ionic liquid	T_o/°C	T_f/°C	ΔT_{ad}/°C	ΔT_{ab}/°C	ΔH_r/J g^{-1} ±5%
[C_2mim][B(CN)$_4$]	316	365	49	158	−330
[C_2mim][BF$_4$] No exotherm	—	—	—	—	—
[C_2mim][DEP] No exotherm	—	—	—	—	—
[C_2mim)][FSI]	165	412	247	534	−1120
[C_2mim][TCM]	230	282	51	164	−340
[C_2mim][NTf$_2$] No exotherm	—	—	—	—	—
[C_2mpyr][DEP]	290	353	62	193	−400
[C_3mpyr][FSI]	210	406	196	614	−1290
[C_4mpyr][I]	305	311	5.0	30	−63
[C_2mpyr][NTf$_2$]	385	413	27	165	−350

The adiabatic temperature rise was calculated to be 246 °C and, with the ϕ corrections taken into consideration, the temperature rise would be 534 °C. This shows that in the event of this ionic liquid being exposed to temperatures in excess of only 165 °C, catastrophic temperature and pressure rises could result. In a sealed container, such as a battery pack, this would probably cause rupture of the container unless a vent is included. The likely cause of this behaviour is the rupture at elevated temperatures of the F–S bond liberating heat and the pressure rise in the system could be due to the liberation of SO$_2$. The results indicate the potential danger of the decomposition of the anion releasing large amounts of energy and the vapour phase reaction products potentially causing an explosion. Hence we believe that this ionic liquid cannot be immediately considered as safe for high temperature applications, or any situation where a high temperature may be experienced.

A slightly different behaviour was observed when the FSI anion was replaced by the TCM anion. In this case (Fig. 3), the onset of exothermic activity occurs at a slightly higher temperature (230 °C) and completes at 281 °C, with an adiabatic temperature rise of about 51 °C. This ionic liquid can be considered more stable since the self-heat rate was considerably lower and the time-to-temperature profile (Fig. S3, ESI†) longer. The pressure increases were also not as large.

Attention has also been focussed on the effect of cation on the FSI and DEP anion based ionic liquids. In both cases, the imidazolium and pyrrolidinium ionic liquids were investigated. The ARC results show (Table 1) that the exothermic activity of pyrrolidinium based ionic liquids (for the DEP anion) was
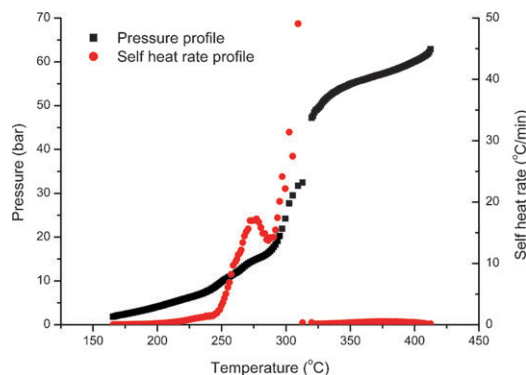

Fig. 1 Self-heat rate and pressure profiles for [C_2mim][B(CN)$_4$].

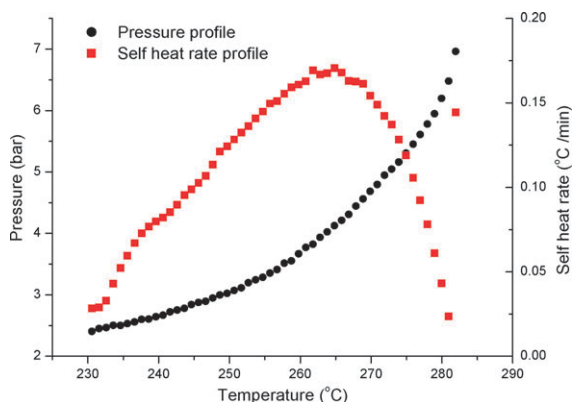**Fig. 2** Self-heat rate and pressure profiles for [C_2mim][FSI].

Fig. 3 Self-heat rate and pressure profiles for [C$_2$mim][TCM].

found to be greater compared to the imidazolium ionic liquids where there was no exothermic activity at all. This could be due to the higher stability of the imidazolium ring as compared to the pyrrolidinium ring. FSI is less stable also in the pyrrolidinium based ionic liquid.

To summarise, adiabatic calorimetric studies of imidazolium ionic liquids exhibited no exothermic activity (no self-heating phenomena) for the [BF$_4$], [NTf$_2$] and [DEP] anions and they can be considered as relatively safe for use as solvents in high temperature applications. On the other hand, the ionic liquids that contain [FSI], [TCM] and B(CN)$_4$ anions exhibited exothermic, self-heating behaviour accompanied by pressure increases. In the cases studied the imidazolium cation exhibited greater thermal stability than the pyrrolidinium cation.

Notes and references

‡ In the authors' opinion this anion is most properly named as an amide (*cf*. dicyanamide). However it is frequently referred to in the literature and supplied commercially as "FSI" (where the "I" indicates imide) and we have retained this abbreviation to avoid confusion.

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