# Thermal stability of ionic liquids assessed by potentiometric titration

**Niklas Meine, Flavio Benedito and Roberto Rinaldi***

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**The long-term thermal stability of imidazolium-based ionic liquids is addressed here. We have found that potentiometric titration is a precise, low-cost and quick analytical method to assess the quality changes occurring during the thermal aging of ionic liquids. Using this protocol, we have discovered that imidazolium-based ionic liquids start to decompose, to a small extent, at much lower temperatures than those inferred from thermogravimetric analysis.**

In the last decade, ionic liquids (ILs) have grown in importance for a large number of applications.[1,2] Likewise, the number of commercially available ILs has boomed. With so many options available in the market, these innovative solvents are finding uses in several branches of the chemical industry.[2] In process development, primary criteria for the selection of ILs are not only price, toxicity and recyclability, but also the degradation temperature may play an important role in the final decision.[3] The first serious discussions on the thermal stability of ILs emerged from investigations using thermogravimetric analysis (TGA).[4] In other seminal studies the stability of ILs was inferred from experiments using mass spectrometry,[5,6] FTIR,[6] pyrolysis-gas chromatography coupled to mass spectrometer (GC-MS),[7,8] and UV-Vis measurements.[9] Although a great effort to determine the degradation temperature of several ILs has been devoted, the reported data are rather controversial,[3] and there is no general agreement about the published degradation temperatures for the same ionic liquid. For instance, degradation temperatures ranging from 235 to 450 °C for 1-methyl-3-butylimidazolium bis(tri-fluoromethylsulfonyl)imide are reported.[3]

The debate continues about the best strategies for the determination of the long-term thermal stability of ILs. Here, we show that the potentiometric titration of alkylimidazoles, one of the most important degradation products of alkylimidazolium-based ILs, as revealed by electrospray ionization mass spectrometry (ESI-MS), is a convenient method to monitor the deterioration of the ILs quality occurring upon thermal aging. The most striking result to emerge from this assessment is that imidazolium-based ILs start to decompose already at much lower temperatures than those inferred from TGA studies.

Fig. 1 shows the TG curves of 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, 1-butyl-3-methylimidazolium chloride [BMIM]Cl, 1-butyl-3-methylimidazolium methanesulfonate [BMIM][$CH_3SO_3$] and 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [BMIM][$Tf_2N$]. The TG curves display that [EMIM]Cl and [BMIM]Cl should be stable up to 200 °C under air, while [BMIM][$CH_3SO_3$] seems to be stable up to 300 °C. The decomposition temperatures of [EMIM]Cl, [BMIM]Cl and [BMIM][$CH_3SO_3$], determined from the derivative TG curves, are 278, 291 and 392 °C, respectively. [BMIM][$Tf_2N$] shows the highest thermal stability, as inferred from the negligible weight loss up to 350 °C. [BMIM][$Tf_2N$] decomposes at 461 °C.

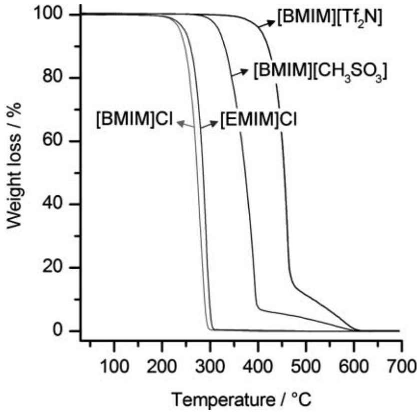

**Fig. 1** TG curves for [BMIM]Cl, [EMIM]Cl, [BMIM][$CH_3SO_3$] and [BMIM][$Tf_2N$]. The ILs were heated to 700 °C at 5 °C $min^{-1}$ under air.

The TG data must be interpreted, however, with caution because some degradation processes, as will be discussed later, do not result in weight loss. Furthermore, dynamic TG analysis is often not sensitive enough to detect sluggish degradation processes, which might be eventually taking place before the decomposition temperature.

To determine whether [BMIM]Cl degrades already at temperatures lower than those indicated by TG analysis, [BMIM]Cl samples were treated at different temperatures between 100 and 200 °C for 24 h. To identify possible degradation products formed in the thermal aging of the IL samples, ESI-MS was used.

Fig. 2 displays the ESI mass spectra of the [BMIM]Cl samples treated at different temperatures. Both spectra from the samples treated at 100 and 120 °C show a main peak at $m/z$ 139, assigned to 1-butyl-3-methylimidazolium species (5, [BMIM]$^+$), and a low intensity peak at $m/z$ 83, attributed to 1-methylimidazolium species (2, [HMIM]$^+$). In the samples heated at 140 or 160 °C, [BMIM]$^+$, [HMIM]$^+$, 1-butyl-imidazolium (4, [HBMIM]$^+$, $m/z$ 125) and 1,3-dibutylimidazolium species (6, [BBIM]$^+$, $m/z$ 181) are detected. In the samples aged above 180 °C, two additional species are found, imidazolium (1, [HHIM]$^+$, $m/z$ 69) and 1,3-dimethylimidazolium (3, [MMIM]$^+$, $m/z$ 97). These results indicate that the degradation of [BMIM]Cl already occurs at 140 °C.

The ESI-MS results show the elimination of the $n$-butyl side-chain and the retroalkylation as preferential pathways of

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*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, Germany. E-mail: rinaldi@mpi-muelheim.mpg.de; Fax: +49 208 306 2995; Tel: +49 208 306 2368*

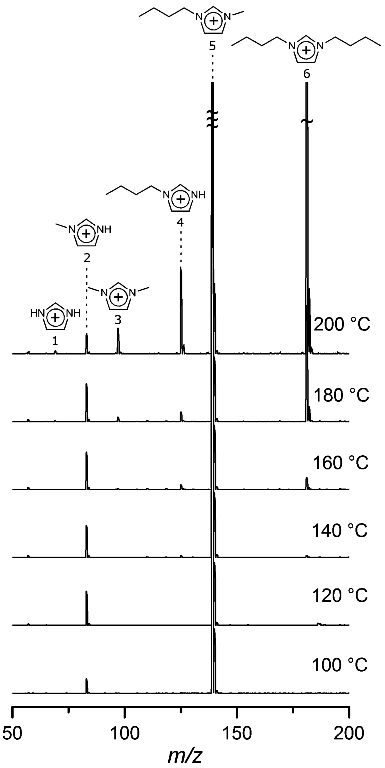

**Fig. 2** Positive-mode ESI mass spectra of BMIMCl samples treated at 100 to 200 °C for 24 h. Note that only 80% of the height of the highest peak in bottom spectrum is shown in the figure.

degradation of [BMIM]Cl below 160 °C. From these processes, $[HMIM]^+$ species and alkylimidazoles are produced, as shown in Fig. 3. Indeed, analyzing the gas-phase by headspace GC-MS revealed the presence of 1-chloromethane, 1-chlorobutane, 1-butene, 1-methylimidazole and 1-butylimidazole, supporting the evidence collected by the ESI-MS experiments.

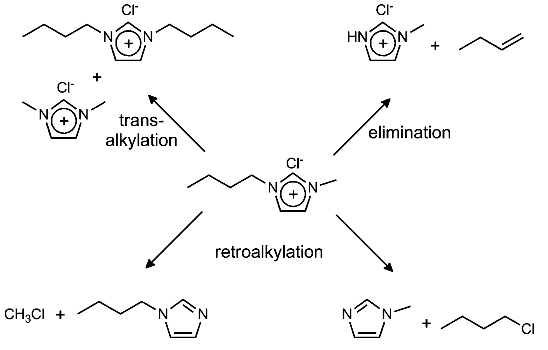

**Fig. 3** Proposed pathways for the thermal degradation of BMIMCl.

Trans-alkylation is another important degradation reaction occurring in the chloride-based ILs above 160 °C. This process is not followed by weight loss. Therefore, trans-alkylation is invisible to TGA. However, it is clear from the ESI-MS (Fig. 2) that $[MMIM]^+$ and [BBIM]Cl species are formed, as indicated in Fig. 3.

Putting the pieces of information together, we realized that the quantification of imidazoles would be a useful strategy to assess the long-term stability of these compounds. To quantify the overall amount of imidazoles, potentiometric acid–base titration was used. The current protocol is much easier than colorimetric[10] or HPLC methods,[11] commonly used to verify the quality of ILs. Using an automated titrator, an aqueous solution of IL sample was first titrated with dilute NaOH solution (0.1000 mol $L^{-1}$). The overall content of imidazoles was then obtained in the back titration with a dilute HCl solution. Both titrations were carried out under argon.

Fig. 4 shows the curves of back titration obtained from the samples of [BMIM]Cl heated at 100 and 200 °C for 24 h.

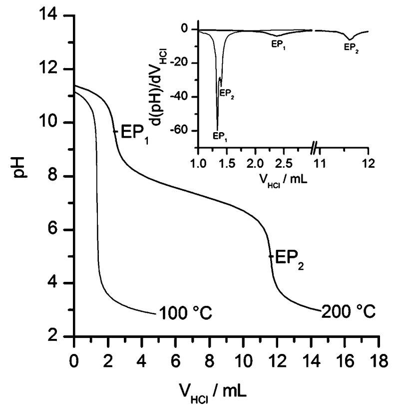

**Fig. 4** Back titration curves obtained from the samples of BMIMCl heated at 100 and 200 °C for 24 h.

At first glance, just a single equivalent point is apparently present in the back titration curve of the [BMIM]Cl sample heated at 100 °C for 24 h, while two equivalent points ($EP_1$ and $EP_2$) are clearly detected in the titration curve of the sample treated at 200 °C for 24 h. The first derivative from the titration curves shows, however, that in both titrations two equivalent points are present. The $EP_1$ is assigned to the neutralization of the excess of NaOH dosed in the direct titration. Analyzing the titration curves, it was possible to determine the $pK_b$ of the analyte that accounts for the $EP_2$. The $pK_b$ value determined is 6.7, which agrees well with those values reported for alkylimidazoles ($pK_b$ 6.9–7.2) under standard conditions.[12] Combining this result with those obtained from ESI-MS experiments indicates clearly that $EP_2$ is associated with the amount of free imidazoles in the samples. The total amount of imidazoles per gram of sample was determined according to eqn (1):

$$\text{imidazoles}\ (\mu\text{mol g}^{-1}) = \frac{M_{\text{HCl}}(V_{\text{EP}_2} - V_{\text{EP}_1})}{m_{\text{sample}}} \times 1000 \qquad (1)$$

where, $M_{\text{HCl}}$ is the HCl solution concentration (mol $L^{-1}$), $V_{\text{EP}_1}$ and $V_{\text{EP}_2}$ (mL) are the volumes of HCl solution dosed at $EP_1$ and $EP_2$, respectively, and $m_{\text{sample}}$ is the sample weight (g).

Table 1 presents the amount of imidazoles found in the [EMIM]Cl and [BMIM]Cl samples treated at different temperatures for 24 h. Heating [EMIM]Cl and [BMIM]Cl at 100 and 120 °C does not increase the imidazole content in the samples. From 140 °C up, the escalating amounts of imidazoles found in the IL samples reveals that [EMIM]Cl and [BMIM]Cl start to degrade. For both ILs, the degradation is not intense between 140 and 160 °C. However, the purity of these ILs markedly drops when treating them above 170 °C for 24 h. Indeed, it is

**Table 1** Degradation of [EMIM]Cl and [BMIM]Cl heated at different temperatures for 24 h, as assessed by the formation of imidazoles

| | [EMIM]Cl | | [BMIM]Cl | |
|---|---|---|---|---|
| $T$/°C | Imidazoles/μmol $g^{-1}$ | Purity[a] (%) | Imidazoles/μmol $g^{-1}$ | Purity[a] (%) |
| As purchased | 16 ± 1 | 99.81 ± 0.01 | 7 ± 1 | 99.92 ± 0.01 |
| 100 | 17 ± 1 | 99.80 ± 0.01 | 8 ± 1 | 99.91 ± 0.01 |
| 120 | 16 ± 1 | 99.81 ± 0.01 | 8 ± 1 | 99.91 ± 0.01 |
| 140 | 34 ± 2 | 99.60 ± 0.02 | 20 ± 1 | 99.76 ± 0.01 |
| 160 | 63 ± 2 | 99.25 ± 0.02 | 39 ± 3 | 99.54 ± 0.04 |
| 170 | 74 ± 2 | 99.12 ± 0.02 | 70 ± 3 | 99.17 ± 0.04 |
| 180 | 121 ± 6 | 98.57 ± 0.07 | 134 ± 1 | 98.42 ± 0.01 |
| 190 | 197 ± 25 | 97.7 ± 0.3 | 377 ± 5 | 95.55 ± 0.06 |
| 200 | 332 ± 4 | 96.06 ± 0.05 | 874 ± 10 | 89.7 ± 0.1 |

[a] The purity of IL was estimated taking into account solely the amount of imidazoles formed and considering imidazoles as HMIMCl.

estimated that *ca.* 4% of [EMIM]Cl and 10% of [BMIM]Cl is already degraded upon heating at 200 °C for 24 h.

The potentiometric titration of free imidazoles is shown to be more sensitive in detection of the degradation of ILs than TGA (Fig. 1). In fact, the degradation processes are much slower than the temperature ramping in the dynamic TG experiments. Accordingly, no weight loss is detected when heating the sample from 30 to 200 °C. Furthermore, both the high boiling point (about 200 °C) and the high solubility of imidazoles in the parent ILs make the evolution of imidazoles from the samples very difficult. This also accounts for the low sensitivity of TGA, even under static condition, to assess the thermal stability of imidazolium-based ILs.

For industrial use, the long-term stability of ILs is an important issue. Fig. 5 presents the amount of imidazoles found in the [BMIM]Cl (99.9%) samples heated at 100 or 140 °C over 10 days. The imidazole content found in the [BMIM]Cl samples aged at 100 °C stayed constant at around 13 μmol $g^{-1}$. This result shows that no degradation occurs upon heating the IL at 100 °C. Treating the samples at 140 °C, however, affects the quality of the IL. Under anhydrous conditions, the imidazoles content increases from 13 ± 1 to 62 ± 1 μmol $g^{-1}$ after heating the samples over 10 days. Water enhances the degradation of [BMIM]Cl. In the IL sample containing 2 wt% water, 78 ± 1 μmol $g^{-1}$ of imidazoles were found, upon aging the IL at 140 °C for 10 days.

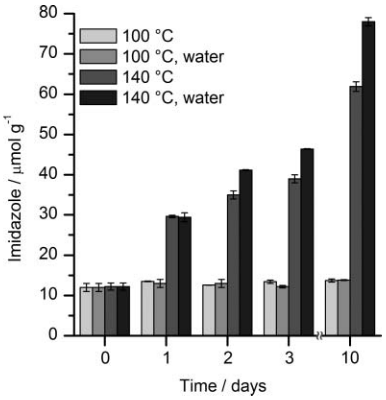

**Fig. 5** Effect of water (2 wt%) on long-term stability of [BMIM]Cl samples heated at 100 and 140 °C.

The long-term stability of ILs containing anions less nucleophilic than $Cl^-$ was also studied. Table 2 shows the amount of imidazoles formed upon heating [BMIM][$PF_6$], [BMIM][$BF_4$], [BMIM][$NTf_2$], [EMIM][$CH_3SO_3$] and [BMIM][$CH_3SO_3$] at different temperatures over 10 days.

Surprisingly, [BMIM][$PF_6$] degrades at 140 °C. The amount of imidazoles formed upon aging [BMIM][$PF_6$] is twice as high as that found for [BMIM]Cl at 140 °C (Fig. 5). This finding contrasts with the thermal stability inferred from the TGA data published elsewhere,[4,13] which indicated that [BMIM] [$PF_6$] would be much more stable than [BMIM]Cl.[4,13] On the other hand, [BMIM][$BF_4$] is totally stable at 140 °C. Work is in progress to understand the factors responsible for the difference of stability found for these ILs.

Table 2 shows that [EMIM][$CH_3SO_3$] and [BMIM][$CH_3SO_3$] degrade, to a small extent, upon aging at 200 °C for 10 days. The analysis of a [BMIM][$CH_3SO_3$] sample using ESI-MS in the positive and negative modes shows that the IL degrade solely to methylimidazole species, as detected in the positive mode spectra. The anion is, however, totally stable upon aging at 250 °C, as revealed by the negative mode spectra. For both [EMIM][$CH_3SO_3$] and [BMIM][$CH_3SO_3$], the amount of imidazoles grows steadily upon heating at above 200 °C. Therefore, the concentration of imidazoles may build up in a continuous process using these IL at above 200 °C.

Interestingly, [BMIM][$NTf_2$] resists to degradation even after aging for 10 days at 250 °C, as seen in Table 2. The imidazole content increases just a little after heating the IL for 24 h. However, the amount of imidazoles remained practically constant over the next 9 days of aging at 250 °C. This clearly shows that [BMIM][$NTf_2$] has a unique thermal stability compared with the other ILs studied here.

## Conclusions

Titrating imidazoles is a precise, low-cost and quick analytical method to assess the thermal stability and the quality of alkylimidazolium ILs. This protocol has revealed the degradation of IL, to a small extent, at much lower temperatures than those inferred from TGA. Although thermogravimetric analysis is useful to rank the ILs according to their onset decomposition temperature, this technique fails to provide a clear view about the long-term stability of ILs. Indeed, potentiometric titration

**Table 2** Formation of imidazoles in [BMIM][$PF_6$], [BMIM][$BF_4$], [EMIM][$CH_3SO_3$], [BMIM][$CH_3SO_3$] and [BMIM][$NTf_2$] samples upon heating at different temperatures

| | | Imidazoles/µmol $g^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| IL | $T$/°C | Initial | 1 d | 2 d | 3 d | 10 d |
| [BMIM][$PF_6$] | 140 | 2 ± 1 | 62 ± 1 | 73 ± 1 | 68 ± 2 | 115 ± 16 |
| [BMIM][$BF_4$] | 140 | 1 ± 1 | 6 ± 1 | 13 ± 2 | 12 ± 1 | 8 ± 2 |
| [EMIM][$CH_3SO_3$] | 140 | 8 ± 1 | 4 ± 1 | 5 ± 1 | 6 ± 1 | 5 ± 1 |
| | 200 | 8 ± 1 | 27 ± 3 | 36 ± 3 | 40 ± 1 | 87 ± 8 |
| | 250 | 8 ± 1 | 285 ± 2 | 524 ± 2 | 654 ± 1 | 1259 ± 11 |
| [BMIM][$CH_3SO_3$] | 140 | 18 ± 1 | 18 ± 2 | 22 ± 2 | 19 ± 1 | 21 ± 1 |
| | 200 | 18 ± 1 | 33 ± 2 | 53 ± 1 | 55 ± 1 | 119 ± 2 |
| | 250 | 18 ± 1 | 412 ± 1 | 723 ± 1 | 911 ± 2 | 1839 ± 15 |
| [BMIM][$NTf_2$] | 140 | 12 ± 2 | 10 ± 2 | 10 ± 4 | 7 ± 1 | 15 ± 1 |
| | 200 | 12 ± 2 | 20 ± 1 | 22 ± 1 | 27 ± 1 | 34 ± 7 |
| | 250 | 12 ± 2 | 33 ± 3 | 28 ± 1 | 35 ± 4 | 36 ± 2 |

of imidazoles reveals that [EMIM]Cl and [BMIM]Cl start to degrade when heated above 120 °C. The stability of ILs is not only influenced by their composition, *i.e.* anion type and alkyl substituent at the imidazolium ring, but also by water. The presence of small amounts of water (2 wt%) leads to increased degradation of [BMIM]Cl at 140 °C. Surprisingly, [BMIM][$PF_6$] is less stable than [BMIM]Cl at 140 °C. On the other hand, [BMIM][$BF_4$], [EMIM][$CH_3SO_3$], [BMIM][$CH_3SO_3$] and [BMIM][$Tf_2N$] are totally stable at 140 °C for 10 days. Furthermore, [BMIM][$NTf_2$] shows superior stability compared with the ILs studied here. This IL showed good stability at 200 and 250 °C upon heating for 10 days. Finally, the thermal stability of ILs depends heavily on the nucleophilic character of both IL anion and solute. Taken together, these results suggest that the long-term stability of ILs is a complex problem with obvious and serious implications for their use as solvent media of chemical reactions.

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