Vol 439|16 February 2006|**doi:10.1038/nature04451**

nature

LETTERS

The distillation and volatility of ionic liquids

Martyn J. Earle[1], José M.S.S. Esperança[2], Manuela A. Gilea[1], José N. Canongia Lopes[2], Luís P.N. Rebelo[2], Joseph W. Magee[3], Kenneth R. Seddon[1] & Jason A. Widegren[3]

It is widely believed that a defining characteristic of ionic liquids (or low-temperature molten salts) is that they exert no measurable vapour pressure, and hence cannot be distilled[1,2]. Here we demonstrate that this is unfounded, and that many ionic liquids can be distilled at low pressure without decomposition. Ionic liquids represent matter solely composed of ions, and so are perceived as non-volatile substances. During the last decade, interest in the field of ionic liquids has burgeoned[3], producing a wealth of intellectual and technological challenges and opportunities for the production of new chemical and extractive processes[4–6], fuel cells and batteries[7], and new composite materials[8,9]. Much of this potential is underpinned by their presumed involatility. This characteristic, however, can severely restrict the attainability of high purity levels for ionic liquids (when they contain poorly volatile components) in recycling schemes, as well as excluding their use in gas-phase processes. We anticipate that our demonstration that some selected families of commonly used aprotic ionic liquids can be distilled at 200–300 °C and low pressure, with concomitant recovery of significant amounts of pure substance, will permit these currently excluded applications to be realized.

The belief that ionic liquids are not volatile can probably be traced back to a report on first-generation ionic liquids[10] by Øye and co-workers[11], that the Franklin acidic $[C_2mim]Cl - AlCl_3$ system (in which $[C_2mim]^+$ is 1-ethyl-3-methylimidazolium) does not exhibit a measurable vapour pressure, even at raised temperatures, whereas the analogous $NaCl$-$AlCl_3$ system exhibited a significant vapour pressure of Al_2Cl_6 (refs 11, 12). However, for $[C_2mim]Cl - AlCl_3$ systems with a greater than 2:1 excess of $AlCl_3$, a detectable vapour pressure of Al_2Cl_6 was observed above 191 °C. Again, this is not a vapour of ions, and is generated by dissociating the ionic liquid[13]. With the discovery of second-generation and third-generation ionic liquids, and the explosion of newly discovered systems, this lack of volatility seems to have been assumed rather than tested.

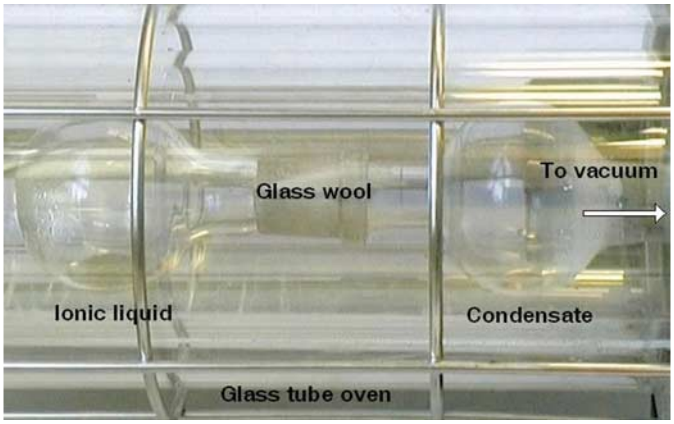


Figure 1 | Labelled photograph of the Kugelrohr oven and distillation apparatus. The central glassware rapidly rotates.

Of course, it is known that ionic liquids can be thermally decomposed, leading to transalkylation (alkyl scrambling) in the condensate. For example, $[C_2mim]Cl$ thermally decomposes when heated to 190 °C in vacuum: the volatile decomposition products (1-methylimidazole, 1-ethylimidazole, chloromethane, chloroethane, ethene and hydrogen chloride) can be recondensed to create a new ternary ionic liquid system: $[C_1mim]Cl - [C_2mim]Cl - [C_2eim]Cl$, in which $[C_1mim]^+$ is 1,3-dimethylimidazolium and $[C_2eim]^+$ is 1,3-diethylimidazolium[14]. Similarly, ionic liquids with protonated cations, $[BH]X$ (for example, $[Hmim]Cl$), will dissociate on heating to produce the molecular base, B, and the molecular acid, HX, which can be recondensed to regenerate $[BH]X$[15,16]. However, in neither scenario did the ionic liquid exert a vapour pressure—the vapour consisted of uncharged molecular components, not the ionic liquid itself.

We show here that a range of pure, aprotic, ionic liquids can be vaporized under vacuum at 200–300 °C and then recondensed at lower temperatures. Some selected families of ionic liquids show no signs of degradation either in the distillate or the residue. We also demonstrate significant enrichment in distillations of mixtures of ionic liquids. Multiple-ion cluster transfer into the gas phase is most probably the underlying mechanism by which these compounds first evaporate, then maintain their stability in the low-density phase, and, finally, recondense as a pure ionic liquid at lower temperatures[17].

Two types of apparatus were used for these experiments: a Kugelrohr apparatus (Fig. 1) and a sublimation apparatus (see Supplementary Information). Survey experiments were performed at 300 °C and 0.1 to 5 mbar in the Kugelrohr apparatus (1 mbar = 100 Pa). These temperatures and pressures are below the predicted boiling points[18] of the ionic liquids, but it was possible to vaporize the ionic liquids and then condense them on colder parts of the Kugelrohr apparatus. Typically, times for the distillation were 4 to 6 h. A photograph of the apparatus is given in Fig. 1. In this apparatus, there is a possibility of splashing as a result of bubbles bursting in the ionic liquid, and to prevent this from affecting the

Table 1 | Distillation rates at 300 °C and 0.1 mbar

Second-generation ionic liquid	Distillation rate ($g\,h^{-1}$)
$[C_2mim][NTf_2]$	0.120
$[C_{10}mim][NTf_2]$	0.070
$[C_{16}mim][NTf_2]$	0.024

Results obtained in the Kugelrohr apparatus.

---

[1]The QUILL Centre, The Queen's University of Belfast, Stranmillis Road, Belfast BT9 5AG, UK. [2]Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal. [3]Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305, USA.

results glass wool was placed between the oven flask and the collection flask.

To demonstrate the distillation of pure ionic liquids, 1.0 g samples of $[C_2mim][NTf_2]$ and $[C_{10}mim][NTf_2]$ (in which $[C_{10}mim]^+$ is 1-decyl-3-methylimidazolium, and $[NTf_2]^-$ is bis{(trifluoromethyl)-sulphonyl}amide, also known as bistriflamide, $[N(SO_2CF_3)_2]^-$) were heated for five hours at 300 °C and 0.1 mbar. This process was filmed and two time-lapse (speeded up 100 and 150 times) video files are available in the Supplementary Information to demonstrate the process in action. $[C_{16}mim][NTf_2]$ (in which $[C_{16}mim]^+$ is 1-hexadecyl-3-methylimidazolium) was treated similarly. The condensate was collected and analysed by ^1H, ^{19}F and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. These three ionic liquids are stable to prolonged heating at the distillation temperature and could be distilled, although the distillation rate varied according to the chemical structure (Table 1). The NMR spectra of these three compounds showed that no detectable decomposition had occurred during the distillations.

Distillations of a range of other ionic liquids were performed at 300 °C in the Kugelrohr apparatus (Table 2). Generally, the bistriflamide ionic liquids distilled without significant decomposition, and only salts containing the larger tetraalkylammonium ($[NC_{w\,x\,y\,z}]^+$), tetraalkylphosphonium ($[PC_{w\,x\,y\,z}]^+$), or cholinium ($[C_{x\,y\,z}N(C_2H_4OH)]^+$) cations showed signs of decomposition. For the triflate ($[OTf]^-$) salts, only $[C_2dbu][OTf]$ (in which $[C_ndbu]^+$ is 1-alkyl-1,8-diazabicyclo[5.4.0]undec-7-enium) distilled without significant decomposition. The vapour pressures for triflate salts seemed lower than for similar bistriflamide salts, as shown by their low distillation rates ($<0.01\ g\,h^{-1}$). Examples of tosylate ($[OTs]^-$, $[Me\text{-}4\text{-}C_6H_4SO_3]^-$) and hexafluorophosphate ($[PF_6]^-$) ionic liquids distilled very slowly, with little decomposition (the $[PF_6]^-$ salt must be free of acidic or basic impurities for a clean distillation). Ionic liquids with other anions (for example, halides, sulphates, or carboxylates) decomposed on distillation. The principal mechanism of decomposition was by dealkylation or transalkylation of the cation[14]. This is aided by a nucleophilic anion. The triflate anion has low nucleophilicity, and hence forms relatively thermally stable ionic liquids. The bistriflamide anion has an extremely low nucleophilicity, and hence forms very thermally stable ionic liquids; this also leads to a very low probability of transfer of a proton from the cation to the anion.

To probe the effects of temperature and pressure on the distillation of ionic liquids, three experiments were performed with $[C_6mim][NTf_2]$ in a small glass sublimation apparatus (Table 3). No precautions for splashing were needed in this apparatus because it is mechanically still and bubble formation was not observed at the temperatures and pressures of these experiments. For each experiment, $[C_6mim][NTf_2]$ was heated from room temperature to 200 or 250 °C, then held at the maximum temperature for 1–2 h. The temperature at which condensation was first observed on the cold finger condenser (or on the walls of the apparatus) was noted. At the end of the experiment, the relative rate of distillation was determined from the amount of $[C_6mim][NTf_2]$ that had condensed on the cold finger. Additionally, the purities of the distillate and of the undistilled residue were checked by ^1H and ^{19}F NMR spectroscopy. The distillation at atmospheric pressure (in dry air) and 250 °C failed in that the distillation was very slow, and much of what 'distilled' consisted of decomposition products. On the other hand, the distillation at 200 °C and ≤ 0.001 mbar proceeded much faster, despite being 50 °C lower in temperature, and subsequent NMR analysis showed that the distillate was pure $[C_6mim][NTf_2]$. The pressure–temperature effects on the distillations are intimately related to the vapour pressure of the ionic liquids. A manuscript reporting the determination of the vapour pressure of $[C_{12}mim][NTf_2]$ by a direct static method is under preparation, and a recent paper[19] describing the use of an indirect (Knudsen) method for vapour pressure determination of $[C_4mim][NTf_2]$ has also appeared.

Table 2 | Effects of distillation at 300 °C in the Kugelrohr apparatus

Ionic liquid	Conditions	Fraction of residue decomposed (%)	Fraction of distillate decomposed (%)
$[C_4mim][NTf_2]$	8 h, 6 mbar	2	2
$[C_4dmim][NTf_2]$	4 h, 6 mbar	1	1
$[C_8dbu][NTf_2]$	4 h, 6 mbar	3	3
$[NC_{2\,2\,2\,6}][NTf_2]$	4 h, 6 mbar	1	50
$[NC_{2\,2\,2\,2}][NTf_2]$	4 h, 6 mbar	1	2
$[C_4mpyrr][NTf_2]$	4 h, 6 mbar	1	1
$[PC_{6\,6\,6\,14}][NTf_2]$	4 h, 6 mbar	1	65
$[PC_{4\,4\,4\,16}][NTf_2]$	4 h, 6 mbar	1	60
$[C_{6\,1\,1}N(C_2H_4OH)][NTf_2]$	4 h, 6 mbar	15	85
$[C_2mim][OTf]$	4 h, 7 mbar	4	12
$[C_6mim][OTf]$	4 h, 6 mbar	1	50
$[C_2dbu][OTf]$	4 h, 8 mbar	1	1
$[C_4mim][PF_6]$	4 h, 6 mbar	1	1
$[C_4mim][FAP]$	18 h, 8 mbar	99	50
$[P(s\text{-}C_4)_3C_1][OTs]$	4 h, 6 mbar	5	5
$[C_2mim][OSO_3C_2H_5]$	5 h, 7 mbar	99	99
$[PC_{6\,6\,6\,14}][decanoate]$	6 h, 7 mbar	98	95

$[C_nmpyrr]^+$ is 1-alkyl-1-methylpyrrolidinium; $[FAP]^-$ is trifluorotriperfluoroethylphosphate. A fraction of 1% represents the limit of our detection, and is thus an upper bound.

Thus, reduced pressure allowed the distillation to occur more rapidly, at a lower temperature, and without observable decomposition. The unrecognized importance of low pressure to the success of such distillations may have contributed to the myth that ionic liquids cannot be distilled—for example, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) studies (which register the thermal decomposition of ionic liquids) have all been reported at atmospheric pressures.

Thus we have presented experimental data to demonstrate that several ionic liquids can be vaporized and recondensed without significant decomposition. We now consider the mechanism of mass transfer. Below, we rule out the three conceivable alternative mechanisms of mass transfer that could explain our results without involving the vaporization of the ionic liquids as ionic species.

We have eliminated the possibility of physical transfer (either by 'spraying', 'splashing' or 'creeping') by investigating the distillation of equimolar binary mixtures of ionic liquids (see Table 4). The observed difference in the compositions of the distillate and residue in such experiments cannot be explained by a physical transfer mechanism. For all of these distillations, the composition of the distillate is enriched in one component (or in two ions for the case in which all four ions in the mixture are different) compared to the residue, which is the hallmark of separative distillation.

It could also be proposed that the ionic liquids were not being transferred into the gas phase as ionic species, but were being volatilized as neutral molecular species by a proton transfer mechanism (for example, the BASIL process[20] involves protonating 1-methylimidazole to an ionic liquid, [Hmim]Cl, which dissociates on heating). Examination of Table 2 reveals that ionic liquids derived from tetraalkylammonium cations, *N*,*N*-pyrrolidinium cations, and 1-alkyl-1,8-diazabicyclo[5.4.0]undec-7-enium cations can be distilled without significant decomposition. For these cation types, there is no feasible mechanism to transfer a proton to the anion; in other words, the only possible mechanism for volatilization of these

Table 3 | Pressure effects on the distillation of $[C_6mim][NTf_2]$

p (mbar)	t_{max} (°C)	t at which distillation was first observed (°C)	Distillation rate ($mg\,h^{-1}$)	Purity of the distillate (%)
830	250 ± 5	250 ± 5	<1	~ 50
0.07	200 ± 5	170 ± 5	3	>99
≤ 0.001	200 ± 5	155 ± 5	15	>99

Results obtained in the sublimation apparatus.

Table 4 | **Distillation of approximately equimolar mixtures of ionic liquids**

Ionic liquid A	Ionic liquid B	Composition ratios of the residue (A:B)	Composition ratios of the distillate (A:B)	Fraction of distillate decomposed (%)
$[C_2mim][NTf_2]$†‡	$[C_{16}mim][NTf_2]$	24:76	76:24	<1
$[C_2mim][NTf_2]$§	$[C_6mim][NTf_2]$	51:49	59:41	<1
$[C_4mpyrr][NTf_2]$‡	$[NC_{2\,2\,2\,2}][NTf_2]$	47:53	53:47	<1
$[C_4mim][NTf_2]$§	$[C_4mim][PF_6]$	52:48	98:2	<1
$[C_2mim][OTf]$‡	$[NC_{2\,2\,2\,2}][NTf_2]$	*	*	<1

† A mass balance of greater than 99% was observed when 40% of the mixture had distilled. Fractional distillation led to a distillate which was 97:3 (A:B).

‡ This mixture was distilled in the Kugelrohr apparatus at 300 °C and 0.05 mbar for 6–8 h.

§ This mixture was distilled in the sublimation apparatus at 190–200 °C and ≤0.001 mbar for 1–3 h.

* The undistilled residue contained 56% $[C_2mim]^+$, 44% $[NC_{2\,2\,2\,2}]^+$, 47% $[OTf]^-$ and 53% $[NTf_2]^-$; the distillate contained 30% $[C_2mim]^+$, 70% $[NC_{2\,2\,2\,2}]^+$, 57% $[OTf]^-$, and 43% $[NTf_2]^-$.

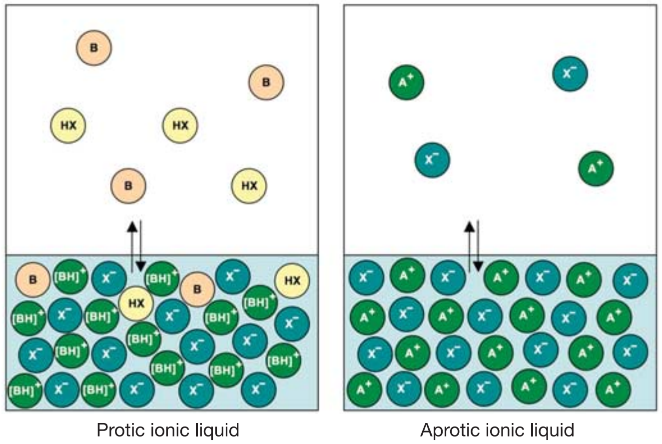
ionic liquids is as intact ions, either alone or aggregated. This is represented schematically in Fig. 2.

In the case of tetraalkylphosphonium-based ionic liquids, the majority decomposed before distillation could occur. However, in the case of tris(*sec*-butyl)methylphosphonium tosylate, distillation without significant decomposition was observed, and again there is no possible mechanism which can be envisaged involving proton transfer. Finally, the possibility of dissociative alkyl transfer was eliminated, as there was no evidence for alkyl scrambling in any experiment (such as when $[C_2mim]Cl$ is distilled)[14].

In the cases of 1-alkyl-3-methylimidazolium salts, the majority distilled without decomposition. However, here a proton transfer mechanism must be considered, as the possibility of transferring the 2-H proton from the cation to the anion, creating a carbene and a free acid, is feasible. Nonetheless, a study of the decomposition of $[C_2mim][NTf_2]$ by pyrolysis mass spectrometry found no evidence for the formation of $HNTf_2$ at 300 °C (ref. 21). We further note that when we replace the 2-H proton on the cation with a 2-methyl group, the new ionic liquid $[C_4dmim][NTf_2]$ (in which $[C_4dmim]^+$ is 1-butyl-2,3-dimethylimidazolium) is both volatile and less decomposed than $[C_4mim][NTf_2]$ (see Table 2). If a proton transfer mechanism were dominant, the 2-methylated ionic liquid would have had its volatility suppressed with a much greater level of decomposition. Indeed, examination of Table 4 reveals that in a mixture of tetraethylammonium bistriflamide and 1-ethyl-3-methylimidazolium triflate, a tetraethylammonium ionic liquid vaporizes preferentially to an imidazolium ionic liquid, making a proton transfer mechanism appear highly improbable.

Thus, if we examine all the reported cases, we can completely discount direct physical transfer of liquids, and also eliminate the possibility of dissociative mechanisms (either alkyl or proton transfer) for all ionic liquids except those based around the 1-alkyl-3-methylimidazolium cation, and even in that case proton transfer must be considered to be highly unlikely. For these latter ionic liquids, we believe that there is no significant contribution from dissociation of the cation to form carbenes, but at this stage it cannot be entirely eliminated.

These distillations, accompanied by the recovery of substantial amounts of commonly employed ionic liquids, corroborate recent theoretical predictions[18] that some selected families of ionic liquids could boil at a temperature sufficiently low to avoid decomposition. These observations lay to rest a paralysing and invalid assumption that has dominated and restricted the field of ionic liquids since its origins, and should open up new ways for exploiting their properties. At the very least, a new method for purifying ionic liquids now exists, and we can imagine other applications (such as isolation of highly soluble products by high-temperature crystallization). However, near ambient temperature the vapour pressure of ionic liquids remains negligible, so we have, in effect, the best of both worlds.



Protic ionic liquid

Aprotic ionic liquid

Figure 2 | **Schematic representation of the differences between protic and aprotic ionic liquids, in both the liquid and the gaseous phases.** For the protic ionic liquids, a dynamic equilibrium exists between the ionic and dissociated forms: $[BH]^+X^-(l) \leftrightarrows B(l) + HX(l) \leftrightarrows B(g) + HX(g)$. Green circles represent cations, blue circles represent anions, other coloured circles represent neutral molecules; *l*, liquid phase; *g*, gaseous phase. For the gaseous phase over the aprotic ionic liquid, the representation is purely schematic and has no implication for the actual degree of aggregation.

Received 26 August; accepted 21 November 2005.

1. Seddon, K. R. Room-temperature ionic liquids—neoteric solvents for clean catalysis. *Kinet. Catal.* **37,** 693–697 (1996).
2. Seddon, K. R. in *Molten Salt Forum: Proceedings of 5th International Conference on Molten Salt Chemistry and Technology* (ed. Wendt, H.) 53–62 (Trans Tech Publications, Zürich, 1998).
3. ISI Essential Science Indicators *Special Topics: Ionic Liquids* ⟨http://www.esi-topics.com/ionic-liquids/index.html⟩ (ISI, 2004).
4. Rogers, R. D. & Seddon, K. R. (eds) *Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities—Transformations and Processes* (American Chemical Society, Washington DC, 2005).
5. Rogers, R. D. & Seddon, K. R. (eds) *Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities—Properties and Structure* (American Chemical Society, Washington DC, 2005).
6. Atkins, M. P. *et al. Ionic Liquids: A Map for Industrial Innovation: Q001 (January 2004)* (QUILL, Belfast, 2004).
7. Ohno, H. (ed.) *Electrochemical Aspects of Ionic Liquids* (Wiley-Interscience, Hoboken, 2005).
8. Rogers, R. D. & Seddon, K. R. (eds) *Ionic Liquids: Industrial Applications for Green Chemistry* (American Chemical Society, Washington DC, 2002).
9. Rogers, R. D., Seddon, K. R. & Volkov, S. (eds) *Green Industrial Applications of Ionic Liquids* (Kluwer, Dordrecht, 2002).
10. Wasserscheid, P. & Welton, T. (eds) *Ionic Liquids in Synthesis* (Wiley-VCH, Weinheim, 2003).
11. Dymek, C. J. Jr, Hussey, C. L., Wilkes, J. S. & Øye, H. A. in *Joint (Sixth) International Symposium on Molten Salts* (eds Mamantov, G. *et al.*) 93–104 (The Electrochemical Society, Pennington, New Jersey, 1987).
12. Øye, H. A. & Wahnsiedler, W. E. in *The Fourth International Symposium on Molten Salts* (eds Blander, M., Newman, D. S., Saboungi, M. L., Mamantov, G. & Johnson, K.) 58–73 (The Electrochemical Society, Pennington, New Jersey, 1984).
13. Øye, H. A., Jagtoyen, M., Oksefjell, T. & Wilkes, J. S. Vapour pressure and thermodynamics of the system 1-methyl-3-ethylimidazolium chloride-aluminium chloride. *Mater. Sci. Forum* **73–75,** 183–190 (1991).

14. Jeapes, A. J. *et al.* Process for recycling ionic liquids. World Patent *WO* **01/** 15175 (2001).
15. Yoshizawa, M., Xu, W. & Angell, C. A. Ionic liquids by proton transfer: Vapor pressure, conductivity, and the relevance of ΔpK_a from aqueous solutions. *J. Am. Chem. Soc.* **125,** 15411–15419 (2003).
16. Kreher, U. P., Rosamilia, A. E., Raston, C. L., Scott, J. L. & Strauss, C. R. Self-associated, "distillable" ionic media. *Molecules* **9,** 387–393 (2004).
17. Abdul-Sada, A. K., Elaiwi, A. E., Greenway, A. M. & Seddon, K. R. Evidence for the clustering of substituted imidazolium salts *via* hydrogen bonding under the conditions of fast atom bombardment mass spectrometry. *Eur. Mass Spectrom.* **3,** 245–247 (1997).
18. Rebelo, L. P. N., Canongia Lopes, J. N., Esperança, J. M. S. S. & Filipe, E. On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem. B* **109,** 6040–6043 (2005).
19. Paulechka, Y. U., Zaitsau, Dz. H., Kabo, G. J. & Strechan, A. A. Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide. *Thermochim. Acta* **439,** 158–160 (2005).
20. Maase, M. *et al.* Method for the separation of acids from chemical reaction mixtures by means of ionic fluids. World Patent WO 03/062171 (2003).
21. Baranyai, K. J., Deacon, G. B., MacFarlane, D. R., Pringle, J. M. & Scott, J. L. Thermal degradation of ionic liquids at elevated temperatures. *Aust. J. Chem.* **57,** 145–147 (2004).

Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements This work was supported by a grant from FC&T, Portugal (to J.M.S.S.E. and L.P.N.R.). The Belfast team wishes to thank the industrial members of QUILL for support and Al Robertson (Cytec) for supplying the phosphonium ionic liquids. For J.W.M. and J.A.W. this work represents an official contribution of the National Institute of Standards and Technology and is not subject to copyright in the USA.

Author Information Reprints and permissions information is available at npg.nature.com/reprintsandpermissions. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to L.P.N.R. (luis.rebelo@itqb.unl.pt).