Applications of ionic liquids in the chemical industry

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In contrast to a recently expressed, and widely cited, view that "Ionic liquids are starting to leave academic labs and find their way into a wide variety of industrial applications", we demonstrate in this *critical review* that there have been parallel and collaborative exchanges between academic research and industrial developments since the materials were first reported in 1914 (148 references)

"*If you want to find something new, look for something new!*"
Yves Chauvin, Nobel Address, 2005.[1]

In a recent front page article in *Chemical and Engineering News* entitled 'Out Of The Ivory Tower', it was[2] argued that "Ionic liquids are starting to leave academic labs and find their way into a wide variety of industrial applications". By following the history of ionic liquids, the major developments in the area, and the development of industrial processes, we will demonstrate that this view is misleading. In fact, we map the parallel developments between academic research and industrial developments since the materials were first reported in 1914.

1 History doesn't repeat itself; historians merely repeat each other

1.1 In the beginning

The field of ionic liquids began in 1914 (see Fig. 1) with an observation by Paul Walden (see Fig. 2),[3] who reported the

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physical properties of ethylammonium nitrate ($[EtNH_3][NO_3]$; mp 13–14 °C), which was formed by the neutralisation of ethylamine with concentrated nitric acid.[4] It is extremely instructive to revisit this paper, as the thinking behind the work, and some of the issues of association are as relevant today as they were in 1914. He wrote: "In the following, I will disclose my investigations on the electric conductivity and, derived from the capillarity constant, the molecular size of some organic ammonium salts. Anhydrous salts were chosen, which melt at relatively low temperatures, approximately up to 100 °C. These low melting points limited the degree of thermolysis of both the solvent and the dissolved salts in the molten salt. Therefore, they allowed for the reproducibility of the observation of melts of anhydrous mineral salts at *low temperatures* previously only feasible at *high temperatures*. They offered the possibility to conduct all measurements by means of the methods and apparatus employed at usual temperatures. The conditions in these low-melting salts approximated thus those experimental conditions applied to investigate conventional aqueous and non-aqueous solvents in detail, which are anticipated by the osmotic theory of van't Hoff and the theory of electrolytic dissociation of Arrhenius." And then later, "The general

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Kenneth Seddon was born in Liverpool in 1950, and graduated from Liverpool University with a first class BSc(Hons) and a PhD, whence he moved to a research Fellowship at St Catherine's

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College, Oxford, and later to a Lectureship in Experimental Chemistry at the University of Sussex. In 1993, he was appointed to the Chair in Inorganic Chemistry at the Queen's University of Belfast, where he is also a co-director of QUILL (Queen's University Ionic Liquids Laboratories), an industrial–academic consortium which was awarded the 2006 Queen's Anniversary Prize for Higher and Further Education. He is a Professor Catedrático Visitante at ITQB (New University of Lisbon), holds an honorary chair at the DICP in Dalian, China (where he directs a research group at CHILL – modelled on QUILL), and is Adjunct Director of the Centre for Green Manufacturing at the University of Alabama. He has published over 300 papers and patents, co-authored four books, and co-edited eight books.

picture of these organic salts at low temperatures (below, or around 100 °C) thus corresponds to the experiences made with inorganic (single, non-complexing) molten salts at much higher temperatures (approximately between 300 and 600 °C). In either case, if the salt molecules are associated, and if this (approximate) degree of association increases from $x = 6$–9, a complete dissociation of the simple ions of the molten salt of course does not exist; although an electrolytic dissociation appears to be existent, but it affects certainly the presence of complex ions besides the non-complexing ions (as a result of a step-wise cleavage of the associated salt molecules). The degree of dissociation thus affects both types of ions and will reach different values for each particular salts (*i.e.* subject to the nature of the cation and anion), depending on the composition and type of binary salt." Discussions and arguments about the state of association/dissociation are still current in 2007.[5]

However, despite Walden's clear exposition, and his discovery of a new class of liquids, this paper did not prompt any significant interest at the time. Today, however, this is widely acknowledged as the start of the field of ionic liquids, and it has left an important legacy. The current definition for ionic liquids is derived from here: ionic liquids are most commonly defined as materials that are composed of cations and anions which melt at or below 100 °C. This temperature does not have any chemical or physical significance, but has persisted until the present day; it is only now that it is being queried.

Извѣстія Императорской Академіи Наукъ. — 1914.

(Bulletin de l'Académie Impériale des Sciences de St.-Pétersbourg).

Ueber die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzenen Salze.

(Mit 3 Figuren).

Von P. Walden.

Im Nachstehenden will ich meine Untersuchungen über die elektrische Leitfähigkeit und die aus den Kapillaritätskonstanten abgeleiteten Molekulargrösse einiger organischen Ammoniumsalze mitteilen. Gewählt wurden *wasserfreie* Salze, welche bei relativ *niedrigen Temperaturen*, etwa bis zu 100° C. schmelzen. Diese niedrigen Schmelztemperaturen engten die Möglichkeit einer *Wärmespaltung* sowohl des Solvens, als auch des gelösten Salzes in der Salzschmelze ein; sie eröffneten daher die *Reproduzierbarkeit* der bisher nur bei *hohen* Temperaturen, in den *Schmelzen* der wasserfreien *Mineralsalze* gemachten Beobachtungen bei *niedrigen Temperaturen*; sie boten die Möglichkeit dar, mit Hilfe der für gewöhnliche Temperaturen gebräuchlichen Methoden und Apparate alle Messungen durchzuführen. Die Verhältnisse in *diesen* niedrig schmelzenden Salzen näherten sich daher den Versuchsbedingungen, wie sie für die gewöhnlichen wässrigen und nichtwässrigen Lösungsmittel eingehend erforscht worden sind und durch die osmotische Theorie van't Hoffs und die elektrolytische Dissoziationstheorie von Arrhenius beherrscht werden.

Das allgemeine Bild dieser *organischen Salze* bei *niedrigen Temperaturen* (unter, bezw. um 100° C.) entspricht also den Erfahrungen an *anorganischen* (einfachen) *geschmolzenen Salzen bei weit höheren* Temperaturen (etwa zwischen 300—600° C.). Wenn die Salzmolekeln in dem einen, wie in dem andern Fall *assoziiert* sind, und dieser (approximative) Assoziationsgrad bis auf $x = 6 - 9$ ansteigt, so kann von einer *vollkommenen* Dissoziation des geschmolzenen Salzes in die *einfachen Jonen* natürlich *keine Rede sein*; eine elektrolytische Dissoziation ist augenscheinlich vorhanden, sie betrifft aber sicherlich das Vorhandensein von komplexen Jonen neben einfachen (infolge einer stufenweisen Aufspaltung der assoziierten Salzmolekeln). Der Dissoziationsgrad betrifft also beide Arten von Jonen und wird, je nach der Zusammensetzung und dem Typus des binären Salzes (d. h. je nach der Natur des Kations und Anions), verschiedene Werte für die einzelnen Salze annehmen. —

Fig. 1 Extracts from the first paper describing an ionic liquid.[4]

Fig. 2 Paul Walden, the discoverer of ionic liquids (and the Walden inversion).[3]

1.2 The industrial revolution

After two decades of silence, ionic liquids (in the guise of "liquefied quaternary ammonium salts") appear in a patent from 1934 (see Fig. 3), which claimed that when halide salts of nitrogen-containing bases (such as 1-benzylpyridinium chloride, 1-ethylpyridinium chloride, *etc.*) were mixed with cellulose at the temperatures above 100 °C, the cellulose dissolved, and solutions of a different viscosity were formed.[6] These new solutions, that contained the cellulose in a very reactive form, were suitable for various chemical reactions, *i.e.* etherification and esterification. The cellulose derivatives, if not precipitated directly, could be separated from the solutions using suitable precipitating agents and used for producing threads, films and artificial masses. This patent is a herald of what scientists are trying to achieve nowadays using cellulose, which will be described later (see Section 3.1.4).

1.3 The shape of things to come

After another fallow phase in their history, ionic liquids re-emerged in the period just after World War II. In the patent literature in 1948,[7] and later in the open literature,[8] the application of mixtures of aluminium(III) chloride and 1-ethylpyridinium bromide to the electrodeposition of aluminium was described. The phase diagram of AlCl$_3$ and 1-ethylpyridinium bromide system is shown in Fig. 4, and demonstrates that there is a narrow window of composition between 63 and 68 mole per cent of aluminium(III) chloride where the system is liquid at or below room temperature. This is an important discovery, but the selected system based on mixed bromide and chloride salts meant that the solvent was chemically complicated and hence difficult to investigate. This

Patented Jan. 9, 1934

1,943.176

UNITED STATES PATENT OFFICE

1,943,176

CELLULOSE SOLUTION

Charles Graenacher, Basel, Switzerland, assignor to Society of Chemical Industry in Basle, Basel, Switzerland

No Drawing. Application September 16, 1931, Serial No. 563,218, and in Switzerland September 27, 1930

21 Claims. (Cl. 260—100)

This invention relates to new cellulose solutions and the application thereof for making various products chemically or mechanically, and to these products themselves.

5   The invention is based on the observation that the liquefied quaternary ammonium salts for themselves or in presence of suitable liquids have the surprising property of dissolving cellulose with the formation of solutions of more or less 10 viscosity. Such liquids are above all anhydrous nitrogen-containing bases, such as anhydrous ammonia, or organic bases which do not decompose the quaternary ammonium salts, such as alkylamines (for example mono-, di- or tri-15 methylamine), aniline, monomethylaniline, dimethylaniline, pyridine, picoline, lutidine, technical pyridine bases, mixtures of these compounds, etc.

necessary, with suitable anhydrous diluents or other suitable additions. As such additions may be named, for example, substances having a reducing action, as, for instance, para-formaldehyde, glucose, lactose and the like; other suitable additions are substances, such as starch, dextrin and the like.

The following examples illustrate the invention, the parts being by weight:—

Example 1

200 parts of anhydrous benzyl-pyridinium chloride are melted in a stirring vessel and heated to 110–115° C. At this temperature 10 parts of cellulose (preferably in the form of regenerated cellulose) are stirred in and the mixture is kept at the same temperature, with continuous stirring, until a homogeneous mixture is produced.

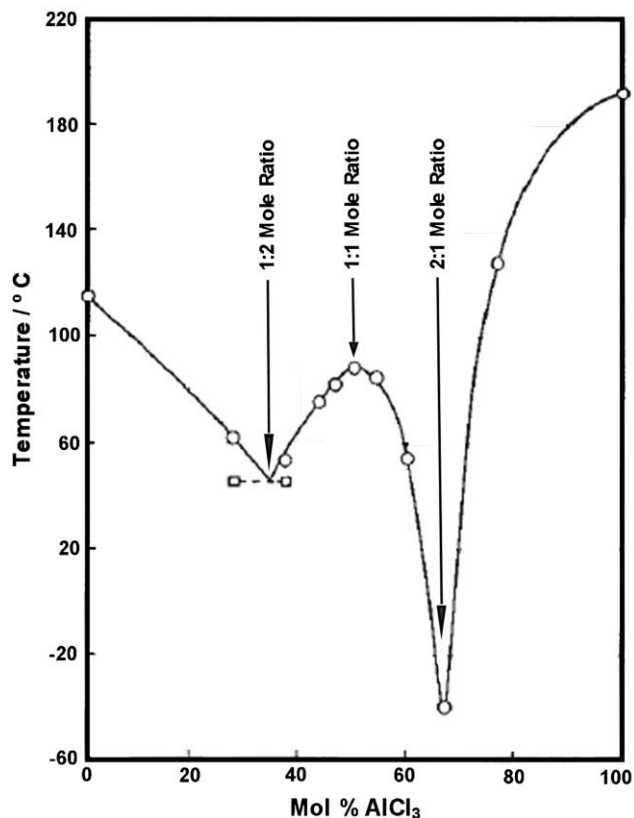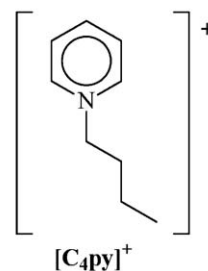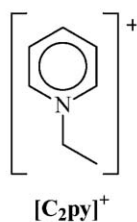Fig. 3 The first patent relating to an industrial application of ionic liquids.[6]

$[C_2py]^+$

$[C_4py]^+$

Fig. 4   Phase diagram for the $[C_2py]Br$–$AlCl_3$.[8]

Fig. 5   Two partial phase diagrams for $[C_4py]Cl$–$AlCl_3$.[11]

problem was eliminated after another 25 years, when the Osteryoung group in 1975,[9] aided by Bernard Gilbert,[10] studied in detail the chemical and physical properties of ionic liquids made from 1-butylpyridinium chloride and aluminium(III) chloride, the $[C_4py]Cl$–$AlCl_3$ system.† The phase diagram of $AlCl_3$ and 1-butylpyridinium chloride, surprisingly given its importance, is poorly determined in the literature, and the published partial diagrams are shown in Fig. 5.[11] The room temperature (20 °C) liquid range occurs between about 60 and 67% mole per cent of aluminium(III) chloride. But whilst being investigated for their fundamental properties, applications of these ionic liquids were also being studied[12] and patented[13] by the United States Air Force, who were (*inter alia*) interested in developing ionic liquids as battery electrolytes.[14,15]

1.4 Let there be light

Whilst the work of Osteryoung's group (see Section 1.3) was a real breakthrough in the field, the system they had developed, $[C_4py]Cl$–$AlCl_3$, had serious limitations. It was liquid at room temperature, but only over a very narrow compositional range, and the cation was very easily reduced (a real constraint for work on battery applications and electrodeposition). In an elegant and inspired study,[16] unfortunately never fully published in the open literature, Wilkes and Hussey used MNDO (MNDO = Modified Neglect of Differential Overlap) semi-empirical molecular orbital calculations to predict the LUMO energies for about sixty heterocyclic cations, and then correlated these with extant reduction potentials.[14] The result was a prediction that 1,3-dialkylimidazolium cations, known since 1884,[17] would be substantially more stable to reduction than the 1-alkylpyridinium cations. This led to the synthesis of the now archetypal ionic liquid system, $[C_2mim]Cl$–$AlCl_3$,[18]‡ and its subsequent characterisation.[19–23] The phase diagram of this system[21] is illustrated in Fig. 6.

From Fig. 6, it is immediately clear that the liquid range of this system is much wider that for the Hurley and Wier (Fig. 4) or Osteryoung (Fig. 5) systems: it is a low viscosity liquid at room temperature from $X(AlCl_3) = 0.33$ to $X(AlCl_3) = 0.67$ {where $X(AlCl_3)$ is the mole fraction of the notional

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† $[C_npy]^+$ stands for the 1-alkylpyridinium cation, where the index *n* represents the number of carbon atoms in the linear alkyl chain.
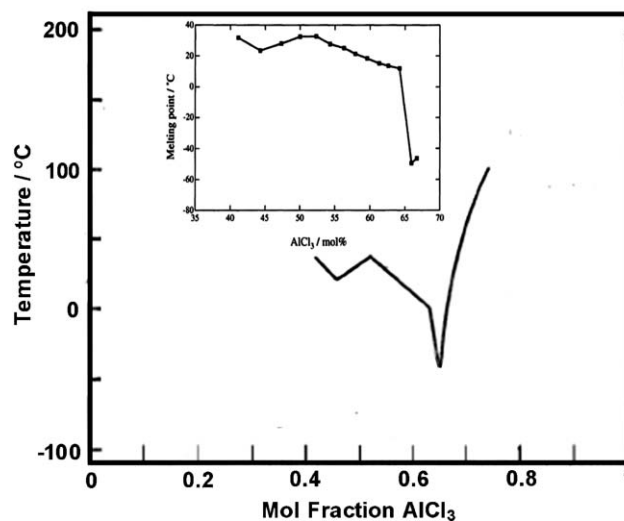
‡ $[C_nmim]^+$ stands for the 1-alkyl-3-methylimidazolium cation, where the index *n* represents the number of carbon atoms in the linear alkyl chain.
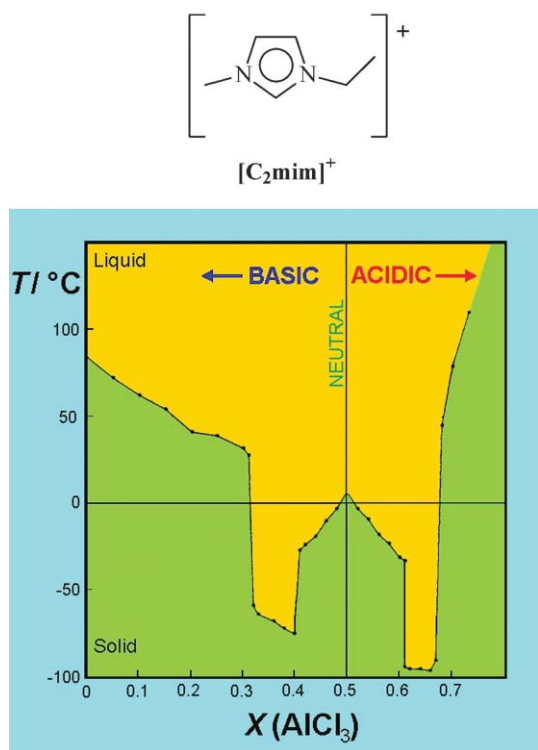
$[C_2mim]^+$

Fig. 6 The phase diagram for the $[C_2mim]Cl$–$AlCl_3$ system.[21]

aluminium(III) chloride content, although it should be clearly noted that there is no uncomplexed aluminium(III) chloride present}.

The most distinctive feature of the chloroaluminate(III) systems (which have been reviewed in detail elsewhere)[24,25] is that, depending on the apparent mole fraction of aluminium(III) chloride, the ionic liquid is acidic $\{X(AlCl_3) > 0.5\}$, basic $\{X(AlCl_3) < 0.5\}$, or neutral $\{X(AlCl_3) = 0.5\}$, referring to the Franklin acidity and basicity,[26] although frequently assumed to refer to the Lewis acidity and basicity. The composition of the system is strongly dependent on $X(AlCl_3)$, as the primary equilibrium of eqn (1) ($K \sim 10^{-16.3}$ – and note how close this is to the auto-ionisation constant for water)[23] dominates (see Fig. 7).

$$2[AlCl_4]^- \rightleftharpoons [Al_2Cl_7]^- + Cl^- \qquad (1)$$
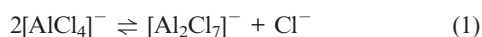
For very acidic systems $\{X(AlCl_3) = 0.67$–$0.75\}$, a further equilibrium, eqn (2), governs the anion concentration:

$$2[Al_2Cl_7]^- \rightleftharpoons [Al_3Cl_{10}]^- + [AlCl_4]^- \qquad (2)$$
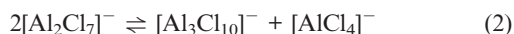
The $[Al_3Cl_{10}]^-$ anion has been observed by mass spectrometry,[27] and detected potentiometrically.[19,28]

A major drawback of all chloroaluminate(III) ionic liquids was their moisture sensitivity. Any trace of moisture decomposes these ionic liquids (although the hydrolysed aluminium species can be reconverted to the chloroaluminate(III) species by treatment with phosgene).[29] This is a major disadvantage for industrial application, as moisture must be excluded from all the reagents and equipment involved in all operations. Similarly, all laboratory preparations must be carried out in an
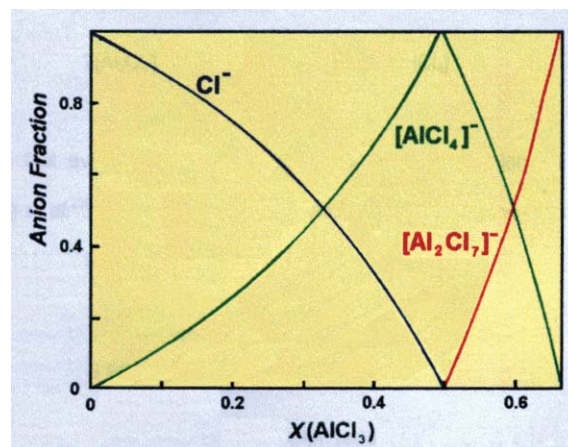

Fig. 7 The concentration of anions in the $[C_2mim]Cl$–$AlCl_3$ system as a function of composition, $X(AlCl_3)$.

inert-atmosphere box, or by employing standard Schlenk techniques.

Thus, the predictions of Wilkes and Hussey[16] were fully realised in the experiments, and the $[C_2mim]Cl$–$AlCl_3$ ionic liquid system also proved to be much less viscous than the $[C_4py]Cl$–$AlCl_3$ system, and had a much wider electrochemical window. This was the first genuine example of an ionic liquid system that was liquid at room-temperature: it opened up a field for electrochemistry specialists, and laid the foundations for the explosion of interest that was to follow.

1.5 Let there be air and water

In 1992, Wilkes and Zaworotko[30] reported, under the title of "Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids", the preparation and characterisation of a new range of ionic liquids that still contained the 1-ethyl-3-methylimidazolium cation, but now also contained a range of alternative anions, $[C_2mim]X$ (X = $[CH_3CO_2]$, $[NO_3]$ or $[BF_4]$).[30] These new salts could be prepared and used on the bench, rather than in an inert-atmosphere box. Since 1992, a wide range of ionic liquids has been developed incorporating many different anions: including hexafluorophosphate, ethanoate, trifluoroethanoate, sulfate, hydrogensulfate, alkylsulfate, nitrate, biscyanamide $[N(CN)_2]^-$, trifluoromethanesulfonate $[CF_3SO_3]^-$, bis{(trifluoromethyl)-sulfonyl}amide $[N(CF_3SO_2)_2]^-$, and tris{(trifluoromethyl)-sulfonyl}methanide $[C(CF_3SO_2)_3]^-$. This is thus another landmark paper, and justifiably widely cited. However, on an independent line, we should not forget that the first ionic liquid, $[EtNH_3][NO_3]$ (see Section 1.1), was a nitrate, and that in the same year as the Wilkes and Zaworotko paper appeared, and predating it, Cooper and O'Sullivan reported the syntheses of $[C_2mim][CF_3SO_3]$ and $[C_2mim][CH_3SO_3]$ under the title "New, stable, ambient-temperature molten salts", but only in a conference proceedings volume.[31]

At that time, it was not fully appreciated how much these ionic liquids absorbed water from the atmosphere. They still need to be handled in dry atmosphere, even though they do not react with water. In the presence of moisture, hexafluorophosphate ionic liquids are the least acceptable media for electrochemistry, as they release HF. Therefore, ionic liquids
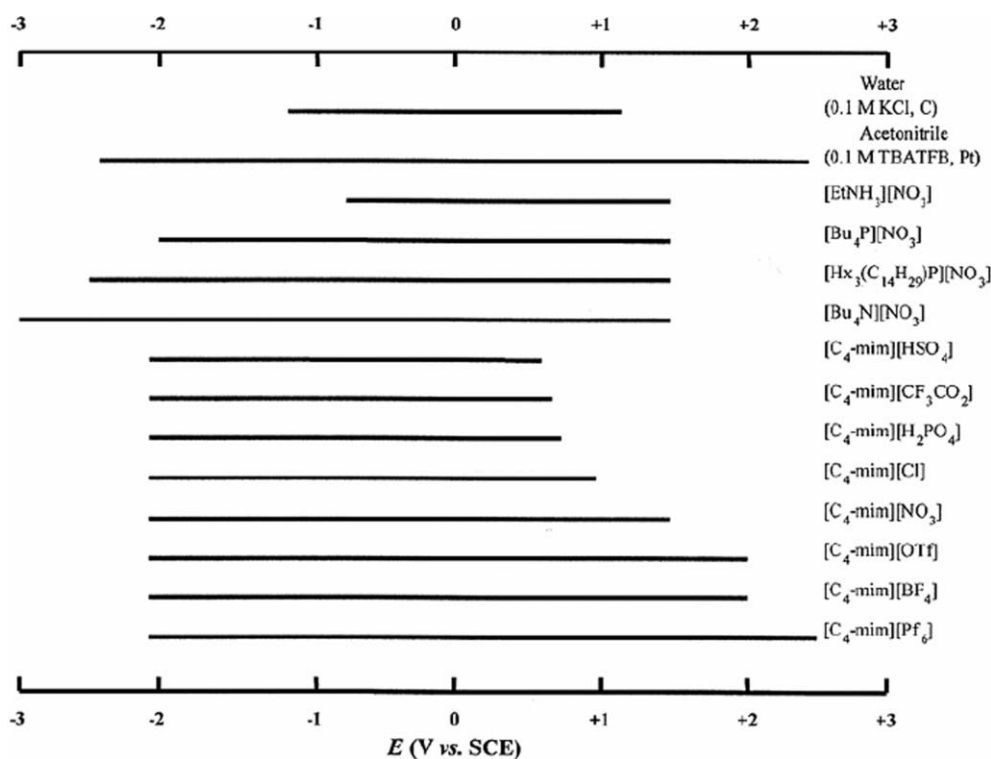
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Fig. 8 The electrochemical windows for some typical ionic liquids.[34]

based on more hydrophobic anions such as trifluoromethane-sulfonate $[CF_3SO_3]^-$ (triflate; $[OTf]^-$), bis{(trifluoromethyl)-sulfonyl}amide $[N(CF_3SO_2)_2]^-$ (bistriflamide, $[NTf_2]^-$), and tris{(trifluoromethyl)sulfonyl}methanide $[C(CF_3SO_2)_3]^-$ ($[CTf_3]^-$), have been developed by Grätzel and coworkers.[32,33] These ionic liquids have received extensive attention not only because of their low reactivity with water, but also because of their large electrochemical windows: the electrochemical window for water is 1.23 V, and for ionic liquids could be 5–6 V (see Fig. 8).

Over the years that followed, new classes of cations, based on phosphonium and pyrrolidinium were developed. It soon became clear that over one million simple ionic liquids could be synthesised.[35,36]

1.6 Design and conquer

"*A common mistake people make when trying to design something completely foolproof is to underestimate the ingenuity of complete fools.*"

Douglas Noel Adams, *Mostly Harmless, 1992*

The melting points of the Group 1 chlorides are given in Table 1. As can be seen, these are significantly above room temperature, and far too high to be used as a medium for organic chemistry. However, the eutectic compositions of mixed systems do melt at significantly lower temperatures than either component. Applying the understanding of lattice energies gained from the Kapustinskii equation,[37] the effect of increasing the size of the anion can be seen in Table 2. The melting points of these simple tetrachloroaluminate(III) salts are in the range of the boiling points of high-boiling organic solvents. However, as this represents the lowest temperature at which these systems are liquids, and not the highest (as for organic solvents), it is necessary to bring the melting point down even further. This can be done by increasing the size of the cations: replacing the simple inorganic cations with organic cations depresses the melting point to temperatures at or below room temperature. Moreover, the asymmetry of the cation has been long recognised[38] as an important factor in lowering the melting points: asymmetrical, "ugly" cations have a bigger effect than symmetrical "beautiful" cations. For example, salts of the "ugly" 1-butyl-3-methylimidazolium cation (which has only C_1 symmetry, its only element of symmetry being the identity operator) melt at lower temperatures (by about 100 °C)

Table 1 Melting points of the Group 1 chlorides

System	mol%	mp/°C
LiCl	100	610
NaCl	100	803
KCl	100	772
CsCl	100	646
LiCl–CsCl	60–40	355
NaCl–KCl	50–50	658
CsCl–KCl	35–65	610

Table 2 Melting points of Group 1 chloroaluminates(III)

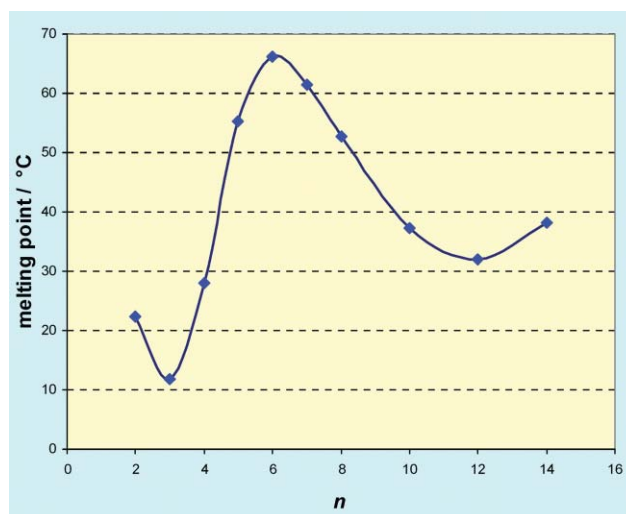| System	mol%	mp/°C
AlCl₃	100	192
LiCl–AlCl₃	50–50	144
NaCl–AlCl₃	50–50	151
KCl–AlCl₃	50–50	256
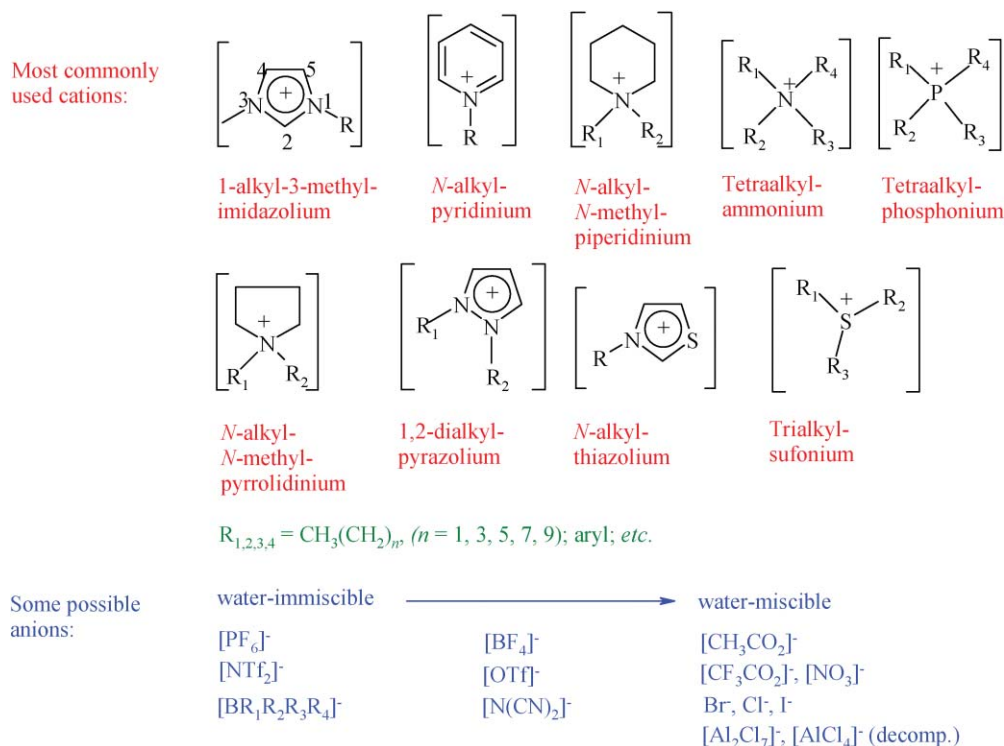
Fig. 9 Some commonly used ionic liquid systems.[36] The abbreviation $[C_n mpyr]^+$ represents the 1-alkyl-1-methylpyrrolidinium cation, where the index n represents the number of carbon atoms in the linear alkyl chain. $[P_{wxyz}]^+$, $[N_{wxyz}]^+$ and $[S_{xyz}]^+$ are normally used to represent tetraalkylphosphonium, tetraalkylammonium and trialkylsulfonium cations, respectively, where the indices w, x, y and z indicate the length of the corresponding linear alkyl chains.

than the analogous salts of the "prettier" 1-butylpyridinium cation (which has C_{2v} symmetry). Moreover, conformational differences in the cations can frustrate crystallisation, leading to glass formation and/or polymorphism.[39] The effect of symmetry in melting points is also reflected in the higher melting points reported for 1,3-dimethylimidazolium and 1,3-diethylimidazolium salts in comparison with the more unsymmetrical 1-ethyl-3-methylimidazolium or 1-butyl-3-methylimidazolium cation analogues.[40] MacFarlane et al.[41] also reported that salts derived from the ammonium or pyrrolidinium cations (see Fig. 9) were solid at room temperature when the cation substituents formed a highly symmetrical species, whereas lower symmetry forms produced liquids at room temperature (see Table 3), often displaying glass-forming behaviour. Finally, the phosphonium ionic liquids also display this phenomenon. In the series $[P_{666n}][PF_6]$, the melting points (see Fig. 10) maximise at the salt with the symmetrical (T_d) cation, $[P_{6666}][PF_6]$, and drop away as one of the chains gets either longer or shorter, with concomitant symmetry lowering to C_{3v}.

Table 3 Melting points and glass transition temperatures/°C of selected ammonium and pyrrolidinium bis{(trifluoromethyl)sulfonyl}amide salts[41]

Structure	T_g/°C	T_m/°C
$[N_{1111}][N(SO_2CF_3)_2]$		133
$[N_{1124}][N(SO_2CF_3)_2]$	−92	−8
$[C_1 mpyr][N(SO_2CF_3)_2]$		132
$[C_4 mpyr][N(SO_2CF_3)_2]$	−87	−18

Most common ionic liquids are formed through the combination of an organic heterocyclic cation, such as dialkylimidazolium, and an inorganic or organic anion, such as nitrate or methanesulfonate. Typical cations and anions of ionic liquids, and their common abbreviations, are shown in Fig. 9. However, it should be remembered that, in principle, any singly charged cation or anion could be used, and ionic liquids based on doubly charged species have been reported too.
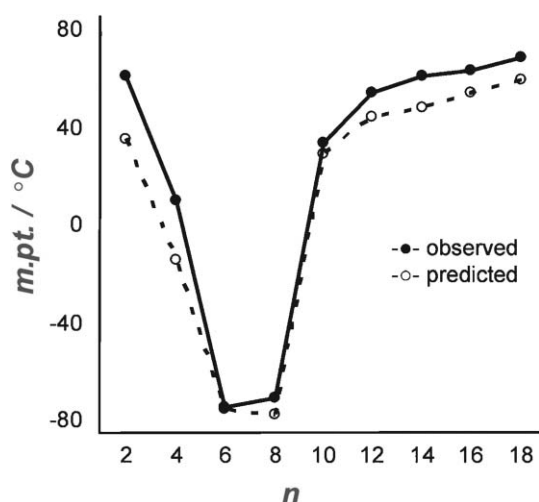

Fig. 10 The melting points of $[P_{666n}][PF_6]$ as a function of n.[42]

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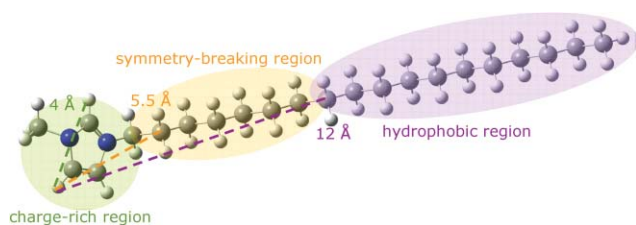*Chem. Soc. Rev.*, 2008, **37**, 123–150 | 129

So, a spate of qualitative and semi-qualitative observations led to the conclusion that, to design ionic liquids, the use of an ugly cation with a single positive charge was a good criterion. This was recently supported by a computational study of anion and cation effects on the melting points of imidazolium salts, using a QSPR approach.[43] Not only was the experimental melting point curve for the series [$C_n$mim][PF_6] remarkably well reproduced (see Fig. 11), but the predictions were rationalised in terms of the cationic structure (see Fig. 12). This quantified and rationalised the empirical observations, and confirmed that the empirical design criteria had a sound theoretical grounding. So, as scientists, we must recognise the wisdom and perspective of artist John Constable:

"*I never saw an ugly thing in my life: for let the form of an object be what it may - light, shade, and perspective will always make it beautiful.*"
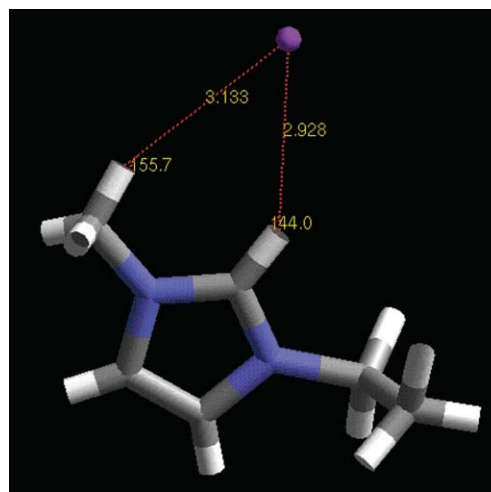
Another factor which influences melting point is the presence or absence of strong hydrogen bonds in the lattice. The presence of hydrogen bonding in the structures of 1-alkyl-3-methylimidazolium salt was first reported in 1986 (see Fig. 13),[44] but despite the lack of recognition of the existence of CH⋯X$^-$ hydrogen bonds in those days,[22] it soon became accepted as a real phenomenon.[45] Hence, halide salts tend to

Fig. 13 Hydrogen bonding in the structure of [C_2mim]I (distances in Å).[44]

have much higher melting points than, say, their tetrafluoroborate[46] or hexafluorophosphate[47] analogues.

1.7 Venimus, vidimus, vicimus (or, more aptly, ήρθαμε, εβλέίδαμε, κατακτήσαμε)

By the mid 1990s, the basic understanding of the ionic liquids concept was well known in a narrow scientific community, mostly electrochemists, but this area of esoteric curiosity was of little interest, or too specialised, for synthetic industrial applications. However there was a suggestion that ionic liquids could be used for green chemistry and industrial chemistry:[38,40]

"*The reactions we have observed represent the tip of an iceberg – all the indications are that room-temperature ionic liquids are the basis of a new industrial technology. They are truly designer solvents: either the cation or the anion can be changed, if not at will, then certainly with considerable ease, in order to optimise such phenomena as the relative solubilities of the reactants and products, the reaction kinetics, the liquid range of the solvent, the cost of the solvent, the intrinsic catalytic behaviour of the media, and air-stability of the system. For the first time, it is possible to design a solvent to optimise a reaction (with control over both yield and selectivity), rather than to let the solvent dictate the course of the reaction. [...] This, quite literally, revolutionises the methodology of synthetic organic chemistry: it will never be the same again!*"[40]

At that time, this suggestion must have seemed ludicrous. Only twenty papers per year were being published. There was no public hint of industrial applications. Nevertheless, behind the scenes, several industries (*viz.* BP, BNFL, Unilever) were filing patents related directly to potential uses of ionic liquids for large scale green industrial processes.[48–50] By the late 1990s, with the publication of these patents on the use of ionic liquids as solvents for organic synthesis (both catalytic and non-catalytic) and the formation of an industrial academic consortium QUILL[51] in Belfast involving sixteen companies, which aimed to develop generic ionic liquid technologies for industrial applications, there rose an increasing interest for green chemistry. In 2000, the dawn of the new millennium, at a crucial meeting in Crete, an Advanced Research Workshop

Fig. 11 Predicted and observed melting points for a series of 1-alkyl-3-methylimidazolium hexafluorophosphate, [$C_n$mim][PF_6], ionic liquids with increasing carbon chain length on the cation.[43]

Fig. 12 An optimised structure of a 1-methyl-3-octadecylimidazolium cation showing the structural regions that are important for determining the melting point. From left: at 4 Å the charge-rich region localised on the imidazolium ring; at 5.5 Å the symmetry-breaking region that decreases the melting point; from 12 Å onwards the hydrophobic region that increases the melting point due to van der Waals interactions.[43]
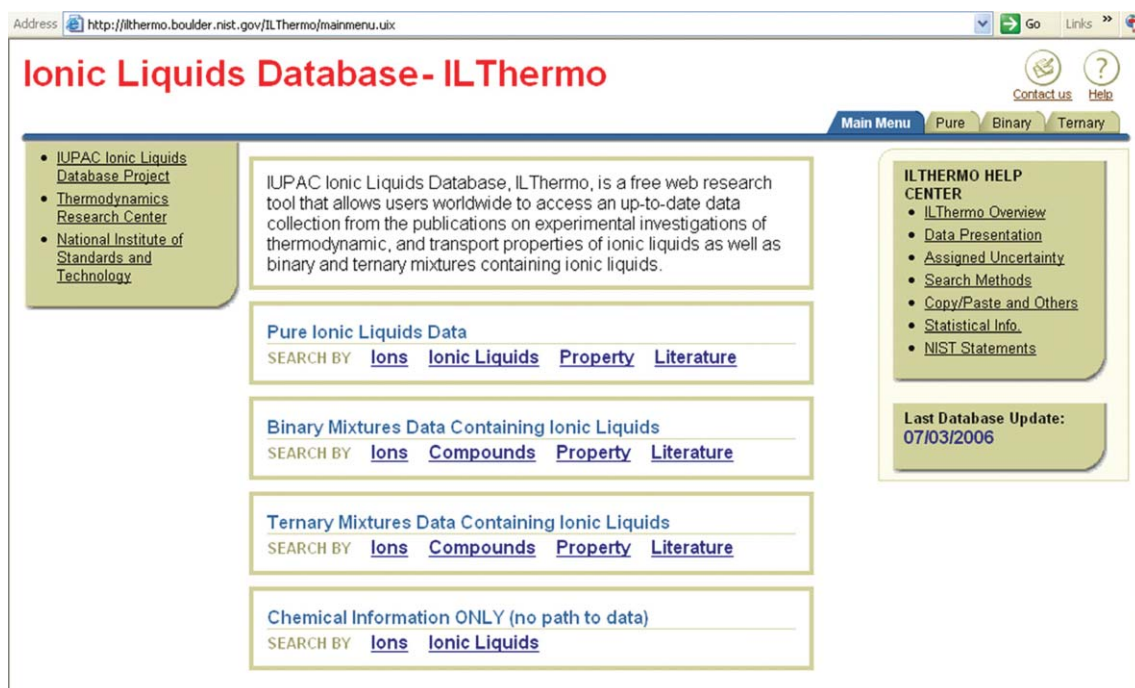
Fig. 14 The home page of the IUPAC Ionic Liquids Database.

sponsored by NATO and entitled "Green Industrial Applications of Ionic Liquids", a round table was held. It outlined, in detail, a strategy for the development of ionic liquids for industrial applications and set criteria that would have to be met:[52]

(a) Ionic liquids are intrinsically interesting and worthy of study for advancing science (ionic *vs.* molecular solvents) with the expectation that something useful may be derived from their study;

(b) Combined with green chemistry, a new paradigm in thinking about synthesis in general, ionic liquids provide an opportunity for science/engineering/business to work together from the beginning of the field's development;

(c) Readily available, well characterised ionic liquids, free of intellectual property, are needed to encourage development of applications.

(d) Toxicity, biodegradation, bio-accumulation, safety, health, and environment (SHE) impact data are needed immediately;

(e) Ionic liquid research should include cost/benefit, economic, and life-cycle analyses;

(f) Regulatory road blocks to ionic liquids implementation should be tackled now;

(g) A public (free), verified, web-based database of physical, thermodynamic, and related data (*i.e.* not process specific) is needed, and work should start immediately on identifying the best methods to accomplish this;

(h) There is an urgent need to increase the number, but especially the areas of expertise, of ionic liquids researchers. A model of open collaboration needs to be encouraged;

(i) International collaboration, communication, and education regarding the results are needed; and

(j) A brochure should be developed to advance the understanding of ionic liquids and their applications.

Now, in 2007, it can be seen that this was a very precise set of guidelines; all of the criteria have come to pass, especially (d),[53] (g)[54] (see Fig. 14) and (j),[55,56] and we have recently expanded on the relationship between ionic liquids and green chemistry.[57,58] The rate of publication in the open literature has been rising at a greater than exponential rate for years (see Fig. 15), and this is tracked by the rate of appearance of patents (see Fig. 16).[59]

Within the rest of this review, examples of applications of ionic liquids in industry will be shown. In retrospect, the Crete meeting can be seen as a crossroads§ in the development of ionic liquids, where the right path was chosen: it was attended by a healthy mix of academics and industrialists.

1.8 Out of the labyrinth

Daedalus designed it; Theseus emerged victorious from it, having slain the Minotaur, by following Ariadne's thread. To enter the world of ionic liquids, with over 8000 papers having been published in the last decade, can seem as daunting as the task which faced Theseus: what is needed is the aid of Ariadne. The required threads come in the form of the recent books published on the subject,[52,60,61] and some useful reviews.[25,36,62] But even here, a thread is needed: remarkably, a review of ionic liquids appears every two-to-three days, and papers are appearing faster than forty per week. The second edition of "Ionic Liquids in Synthesis" will be a welcome addition to the literature, and this is due to appear later this year.[63]

Unlike the six hundred conventional solvents that are extensively used in industrial processes, ionic liquids represent a different paradigm. As there are at least a million simple ionic liquids (and a trillion ternary systems), they can be
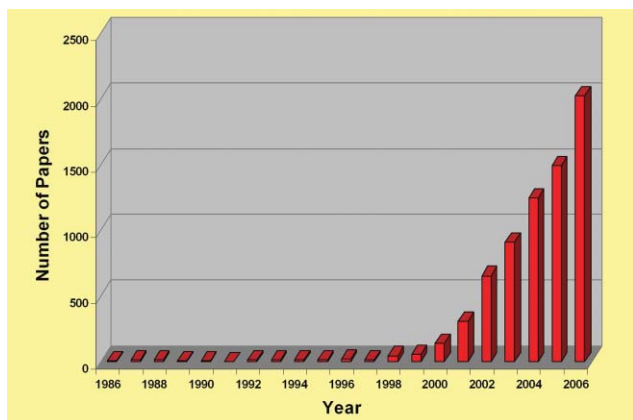
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§ But, thankfully, not Tyburn!

Fig. 15 Steeper than exponential growth of ionic liquid publications, 1986–2006.[59]
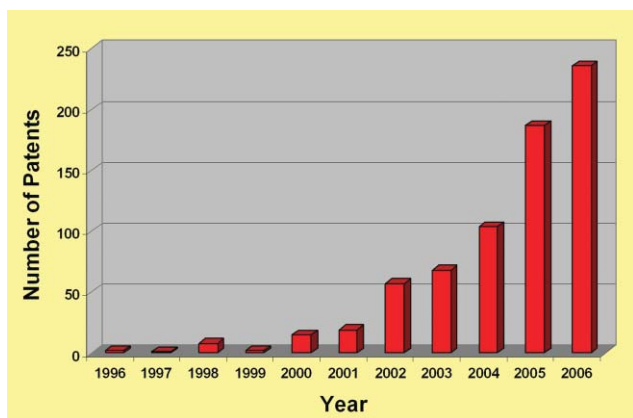

Fig. 16 Annual growth of ionic liquid patents, 1996–2006.[59]

designed to optimise a specific reaction, for example to deliver maximum yield and purity of the isolated product. This is why ionic liquids¶ have been christened "designer solvents".[64] To give a simplistic example, ionic liquids can be composed of ions of low toxicity (even edible, in some cases),[65] or conversely they can be made from such ions as cyanide or paraquat to produce exceptionally poisonous ionic liquids (gainsaying spurious claims that ionic liquids are intrinsically green).

It is essential to use solvents with negligible vapour pressure, and there are a few alternatives. One of the options is ionic liquids, which minimise the risk of atmospheric contamination and reduce associated health concerns. That is why ionic liquids are frequently called "green solvents", as they can help to reduce the amount of solvent or catalyst in a chemical reaction, too. However it should be noted that one property of low vapour pressure does not make ionic liquids green. If ionic liquids are toxic and not biodegradable, they are not green.

It was almost universally believed that ionic liquids could not evaporate. However, recently, a paper by Earle *et al.* was

¶ Ionic liquids are also called room temperature molten salts, fused salts, NAILs, OILs, liquid organic salts, or ionic fluids; these are currently being phased out. They are sometimes grouped with supercritical fluids under the broader term of neoteric solvents.

published that demonstrated that, under the appropriate conditions of high temperature and low pressure, it was possible to distil ionic liquids, and that indeed mixtures of ionic liquids could be separated by fractional distillation.[66] There was immediate doubt cast upon these findings, both in many e-mails addressed to the authors, and in a more open format, such as an article entitled "Are ionic liquids REALLY volatile?".[67] This was because the myth of involatility was so deeply embedded in the ionic liquid community that it was difficult to accept, especially as it seemed to cut across an almost theological creed that it was the lack of vapour pressure that made ionic liquids green.[58] However, Wasserscheid, in commenting on this paper, states:[68] "Do these developments bring into question the view that ionic liquids are 'green solvents'? That reputation is built largely on their non-volatility, because they do not create the atmospheric pollution that can result from the volatility of classic organic solvents. The answer is no: Earle and colleagues clearly state that the vapour pressure of ionic liquids remains negligible at near ambient conditions, and many ionic liquids show no signs of distillation below the temperature of their thermal decomposition. What the proven volatility of some thermally stable ionic liquids under relatively mild (and close to technically realistic) conditions will most assuredly do, however, is make these substances more useful for us. New purification methods and reactions that use ionic liquids in the gas phase are territories that are now ripe to be explored. The possibility of separating two ionic liquids by distillation will, in particular, unlock the door to new routes towards the manufacture of ionic liquids, and towards the regeneration of spent ionic liquids from technical processes". Now, a year on, the volatility of some ionic liquids is now widely accepted, and the nature of the gas-phase species has been established as tightly bound, discrete ion-pairs (and not clusters).[69]

Ionic liquids are intrinsically excellent candidates for industrial applications compared to volatile organic solvents. Organic solvents have been known for several centuries, and obviously occupy most of the solvent market in industry. However if the properties of ionic liquids and organic solvents are to be compared (see Table 4), it could be anticipated that industry may be a natural environment for ionic liquids. Since a lot of properties of ionic liquids have yet to be discovered, at the current level of development ionic liquids can nicely complement, and even sometimes work better than, organic solvents in a number of industrial processes. This statement should not however diminish the fact that ionic liquids have plenty of academic applications, and their unique properties due to their structure, which will be discussed later in this review, make them exciting compounds for theoretical and computational studies.[71] A companion review for organic synthesis in an academic environment will appear in this journal later in 2008.[72]

1.9 All things are ready, if our minds be so

As has been mentioned before, there are about 600 conventional solvents used in industry, compared to at least one million (10^6) simple ionic liquids that can be easily prepared in the laboratory.[35] But that total is just for simple primary

**Table 4** Comparison of organic solvents with ionic liquids[a]

Property	Organic solvents	Ionic liquids
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius–Clapeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means "designer solvents"
Cost	Normally cheap	Typically between 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0.2–100	22–40,000
Density/g cm^{-3}	0.6–1.7	0.8–3.3
Refractive index	1.3–1.6	1.5–2.2

[a] The data summarised in this Table are not comprehensive, nor do they represent outliers; they are meant to give a brief visual comparison of typical values. Detailed values can be found elsewhere.[70]

systems. At the moment only about 300 ionic liquids are commercialised, so one can imagine how many opportunities in this field are still undiscovered and why this field of chemistry is so tempting. If there are one million possible simple systems, then there are one billion (10^{12}) binary combinations of these, and one trillion (10^{18}) ternary systems possible!! And in case this seems like a cock-and-bull story, it is entirely plausible that to generate the required combination of reactivity, solubility and viscosity, industrial applications will need to work with ternary systems.[49] At a zeroth order approximation, the cations in ionic liquids are responsible for their physical properties (such as melting point, viscosity, and density), whereas the anions control chemical properties and reactivity.[36] Indeed, the choice of ionic liquid can control the outcome of a reaction; if the reaction between toluene and

nitric acid is performed in three different ionic liquids, then three different products are formed (see Fig. 17).[73]

So, why are the ternary systems needed? The first choice, from a million, is to control and define the chemistry. Then, a second ionic liquid (now defining the solvent to one in a billion) may be added to fine tune the physical properties of the system (*viz.* viscosity, density, or thermal conductivity). Finally, a third cheap (but inert) ionic liquid (now defining the solvent to one in a trillion) can be added to lower the cost of the system. This means, as a new paradigm in chemistry, that the solvent can be fine-tuned to optimise the chemistry, the chemical engineering, and the cost of the system. Therefore ionic liquids can legitimately be called "designer" solvents, and offer a freedom and flexibility for process design previously unknown and undreamt.[38,40,55,64]
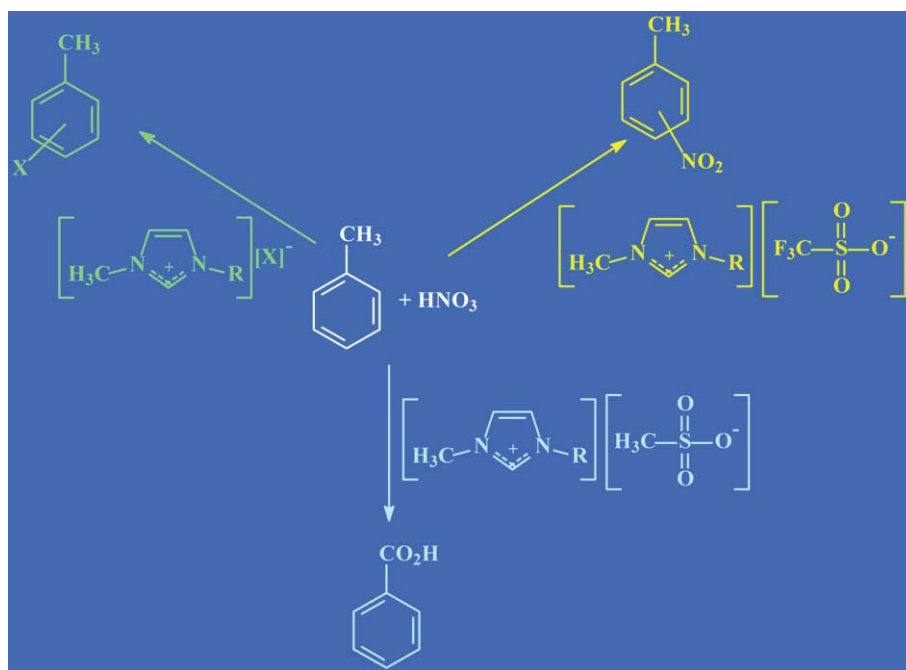
Fig. 17 The reaction between toluene and nitric acid produces three different products in three different ionic liquids, each at better than 99% conversion.[73]
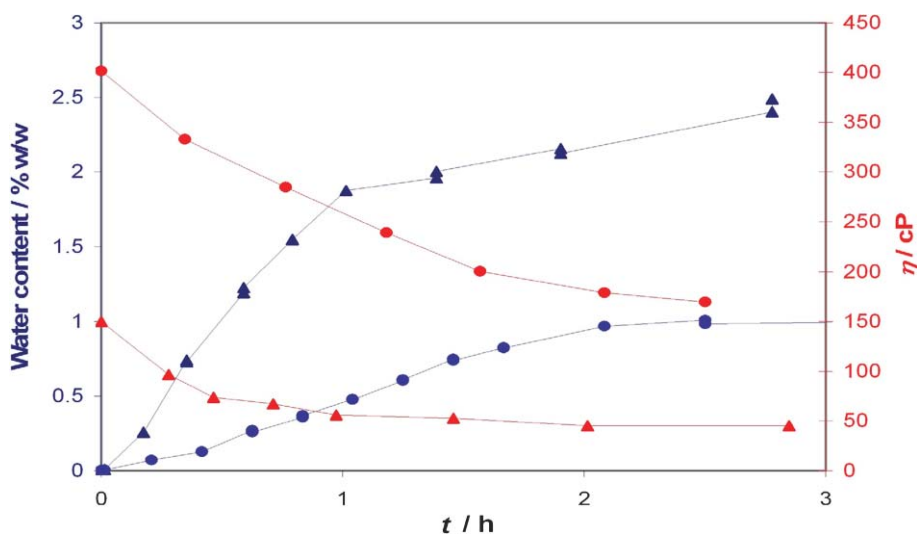
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Fig. 18 Water absorption from the atmosphere as a function of time for [C$_4$mim][BF$_4$] (△) and [C$_4$mim][PF$_6$] (○).[75]

2 Suppliers of ionic liquids

2.1 To thine own self be true

It is self-evident that if one wants to use an ionic liquid, one has to have one. So, how do you get them? If working on a small scale, in academia or in industry, the best source of ionic liquids is to make them yourself. They are simple to prepare, and by controlling the synthesis, one controls the purity too. These routes have been discussed extensively elsewhere,[36,60,74] and are outside the scope of this review, but it is crucial to monitor the purity of the ionic liquid, and to report it in all publications. As a bare minimum, all reports should include, in addition to NMR and MS analysis:

(a) The method of synthesis of the ionic liquid

(b) The water content of the ionic liquid

(c) The halide content of the ionic liquid

Disgracefully few papers include this information, and this adds to the rather poor quality of many publications in this area.

The only viable alternatives to making them oneself are to either obtain them from a trusted synthetic collaborator, or to purchase them from a commercial supplier. In either case, it does not obviate the need for assessing the analytical purity of the ionic liquids as received and used. It is not always appreciated that even very hydrophobic ionic liquids absorb water rapidly from the atmosphere, and two examples of this are given in Fig. 18.

2.2 The price of everything, and the value of nothing

Obviously the important issues for industry are security of supply and cost.[56] Considering firstly supply, this is no longer an issue as there are now many suppliers of ionic liquids, from the gram scale to the multi-ton scale {but it was a concern in 2000, see Section 1.7, point (b)}. Some of the key suppliers are listed in Table 5.

Whilst it may be invidious to single out an individual supplier, it must be said that the Merck website is remarkably useful, containing an easily searchable database of ionic liquids, and summarising (and being searchable by) key physical properties: a typical search result is shown in Fig. 19. Moreover, Merck are unique in supplying ionic liquids at three different levels of specified purity, and have more ionic liquids in their catalogue than all the other suppliers combined. Merck further distinguishes itself with a

Table 5 Some of the major suppliers of ionic liquids

Supplier	Website
Merck KGaA/EMD Chemicals	http://ildb.merck.de/ionicliquids/en/startpage.htm
BASF	http://www.basionics.com
Cytec	http://www.cytec.com/
SACHEM	http://www.sacheminc.com/products-and-services/ionic-liquids.html
DuPont	http://www.dupont.com/fluorointermediates/pdf/k15303.pdf
Scionix	http://www.scionix.co.uk
Solvent Innovation	http://www.solvent-innovation.com/index_overview.htm
IoLiTec	http://www.iolitec.de/ionic_e.htm
Accelergy	http://www.accelergy.com/
ACROS	http://www.acros.com/_Rainbow/pdf/AO_IonicLiqui_Eur_def.pdf
Sigma-Aldrich	http://www.sigmaaldrich.com/catalog/search/TablePage/16255866
Kanto Chemical Co.	http://www.kanto.co.jp/english/
Nippon Gohsei	http://www.nichigo.co.jp/english/pro/chemical.html
Solchemar	http://www.solchemar.com/
Chemada	http://www.chemada.com/cat0.htm

Fig. 19 A typical screen capture from the Merck Ionic Liquids Database.

focus on ionic liquids systems containing electrochemically stable anions, such as tris(pentafluoroethyl)trifluorophosphate and tetracyanoborate. Other sources worthy of highlighting are Cytec, who specialise in tetraalkylphosphonium ionic liquids, SACHEM, who specialise in tetraalkylammonium ionic liquids, BASF, who specialise in ionic liquids derived from 1-methylimidazole, and Scionix, who specialise in ionic liquids for electroplating and related processes, especially those derived from choline. All five of these suppliers can supply multi-ton quantities of ionic liquids.

Since ionic liquids are designer solvents, they can be based on ions of a very wide range regarding costs. For example, *de facto*, ionic liquids containing gold[76] will be very expensive, and even more familiar ionic liquids based on the 1-alkyl-3-methylimidazolium cation, can also be quite costly, especially when coupled with the bis{(trifluoromethyl)sulfonyl}amide (or bistriflamide) ion. However not all ionic liquids are expensive, especially on an industrial scale: some ionic liquids, *e.g.* choline-based and tetraalkylphosphonium or tetraalkylammonium salts,[77] are intrinsically less expensive than others.

Even getting ballpark figures for the cost is not straightforward: many of the websites only provide prices on application. However, some generalisations can be made; choline chloride sells at approximately the same price as toluene. On the Solchemar website, at the time of writing, 25 g of [C$_4$mim]Cl was €25, but 2500 g was €599 (*ca.* £400, or £160 per kg) – four times cheaper per gram – which makes it only five times more expensive than dimethyl sulfoxide. So, to generalise, ionic liquids normally fall in the range of 5–20 times more expensive than molecular solvents, on a laboratory scale, but there are those which are cheaper, and those which are much more expensive. However, as it is at the heart of green chemistry to recycle ionic liquids, 10–20 recycles gives them the same cost

per cycle as conventional organic solvents, and over 50 recycles makes them significantly cheaper.

3 I am come to survey the Tower this day

To return to the recent distorted view of the industrial development of ionic liquid technology,[2] we will survey the Ivory Tower, but casting its walls wider than academia (where be these warders that they wait not here?)! The processes (either commercialised or pilot) will be considered according to the Company that has taken the work to scale, in no particular order.

3.1 BASF

Of all the industrial giants, BASF has done the most publicly to implement ionic liquid technology. They possess the largest patent portfolio, have the broadest range of applications, and work openly with leading academics.

3.1.1 The BASIL™ process. Probably, currently, the most successful example of an industrial process using ionic liquid technology is the BASIL™ (**B**iphasic **A**cid **S**cavenging utilising **I**onic **L**iquids) process.[78] This first commercial publicly-announced process was introduced to the BASF site in Ludwigshafen, Germany, in 2002.

The BASIL™ process is used for the production of the generic photoinitiator precursor alkoxyphenylphosphines (see Fig. 20). In the original process, triethylamine was used to scavenge the acid that was formed in the course of the reaction, but this made the reaction mixture difficult to handle as the waste by-product, triethylammonium chloride formed a dense insoluble paste. Replacing triethylamine with 1-methylimidazole results in the formation of 1-methylimidazolium chloride, an ionic liquid, which separates out of the reaction mixture as
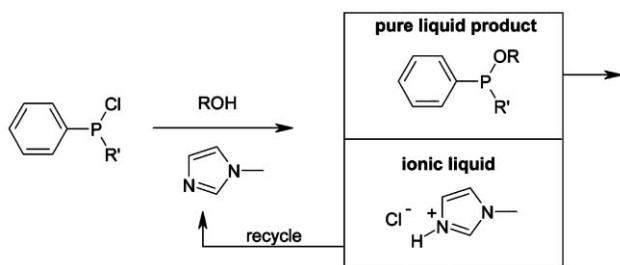
Fig. 20 The BASIL™ process.

a discrete phase. This new process uses a much smaller reactor (see Fig. 21) than the initial process; the space-time yield is increased from 8 kg m^{-3} h^{-1} to 690,000 kg m^{-3} h^{-1}, and the yield increased from 50% to 98%. 1-Methylimidazole is recycled, *via* base decomposition of 1-H-3-methylimidazolium chloride, in a proprietary process.[79] The reaction is now carried out at a multi-ton scale, proving that handling large quantities of ionic liquids is practical. Its success was almost immediately recognised: the process won the ECN Innovation Award in 2004.[80]

3.1.2 Breaking azeotropes. Ionic liquids as entrainers, or separation enhancers,[81] have been used to break common azeotropes, such as water–ethanol and water–tetrahydrofuran (see Fig. 22).[82] The costs of separation and recycling of the entrainer are significantly reduced.

3.1.3 Replacing phosgene. BASF is pursuing ionic liquids in many different directions: another that is under development is "nucleophilic HCl". As seen in Fig. 17, QUILL showed that hydrogen chloride can act as a chlorinating agent towards arenes, generating chloroarenes.[73,83] In a parallel development, BASF demonstrated that hydrogen chloride in ionic liquids can act as a phosgene substitute.[84] The reaction of butan-1,4-diol with phosgene[85] generates 1,4-dichlorobutane in essentially quantitative yield:
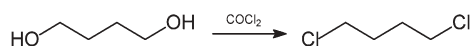

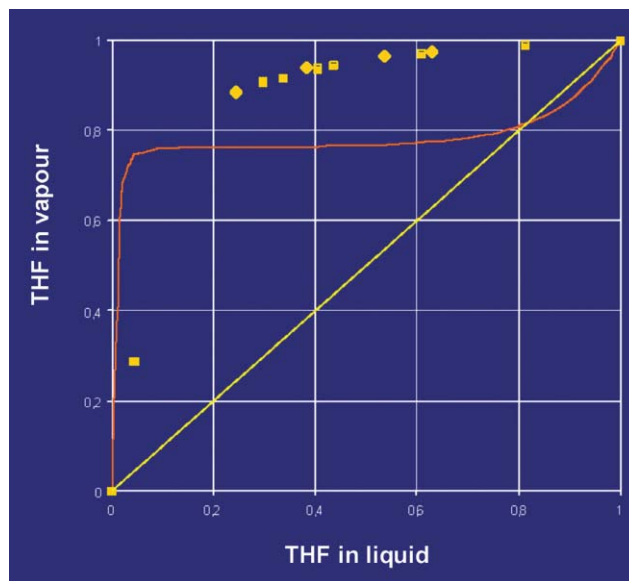Fig. 21 The BASIL jet stream reactor (© BASF 2007).

Fig. 22 The phase diagram for the water–tetrahydrofuran system. The solid orange line represents the pure two component system; the yellow points represent the effect of adding the ionic liquid (© BASF 2007).

If the reaction is attempted with hydrogen chloride instead of phosgene, four products are formed, and the desired 1,4-dichlorobutane is only a minor by-product, the major products being tetrahydrofuran and 1-chlorobutan-4-ol:
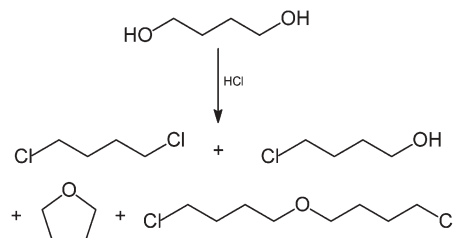
However, if the hydrogen chloride is dissolved in an ionic liquid, then almost pure 1,4-dichlorobutane is obtained (98% selectivity).[84]

3.1.4 Cellulose dissolution. Working in collaboration with Prof. Robin D. Rogers (formerly of the University of Alabama, now transferred to QUILL as co-director),[86] BASF has licensed the exclusive use of various intellectual property rights, developing from the original extensive work in Alabama.[87,88] This is a model of academic–industrial collaboration (again, where be these warders that they wait not here?). There is estimated to be 7×10^{11} tons of cellulose in existence, making it the earth's most abundant natural organic chemical and, hence, the most important bio-renewable resource on earth, as about 7.5×10^{10} tons of cellulose grow and disappear each year.[89] Interestingly, these developments hark back to 1934 (see Section 1.2).[6]

3.1.5 Aluminium plating. Like the previous application on cellulose processing, the aluminium plating process[90] relates to early work too, dating back to 1948 (see Section 1.3).[7] Also,

like the previous application, this work was developed with a leading academic, Frank Endres.[91] The quality of the films can be seen in Fig. 23.

3.2 Eastman Chemical Company

Although the BASIL™ process (see Section 3.1.1) was the first publicly announced room-temperature ionic liquid process, and was launched with a significant amount of publicity, Eastman Chemical Company had been running a process for the isomerisation of 3,4-epoxybut-1-ene to 2,5-dihydrofuran since December 1996.[92,93]
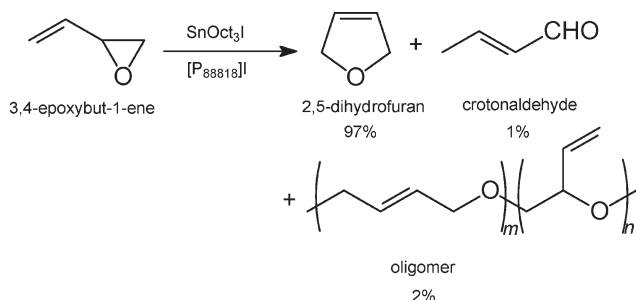
This was operated by the Texas Eastman Division, in a plant with a 1400 metric tons per year capacity (see Fig. 24), at Longview until the end of 2004. The epoxidation of butadiene to 3,4-epoxybut-1-ene had been discovered in 1986 by Dr John R. Monnier of the Eastman Kodak Research Laboratories,[94] and its isomerisation to 2,5-dihydrofuran was later discovered in 1988 by Dr Stephen N. Falling and coworkers of the Eastman Chemical Company.[95] This isomerisation process critically requires a Lewis acid catalyst, and a Lewis basic ionic liquid, $[P_{888\ 18}]I$ (*ex* Cytec). It operated with three continuous, stirred-tank reactors, a wiped-film evaporator, a distillation train, and a continuous, counter-current, liquid–liquid extractor for recovery of the catalysts from December 1996 to December 2004.[95] The phosphonium ionic liquid was selected over its ammonium analogue because of its greater thermal stability. The plant is now idle, because the market for the product has declined.
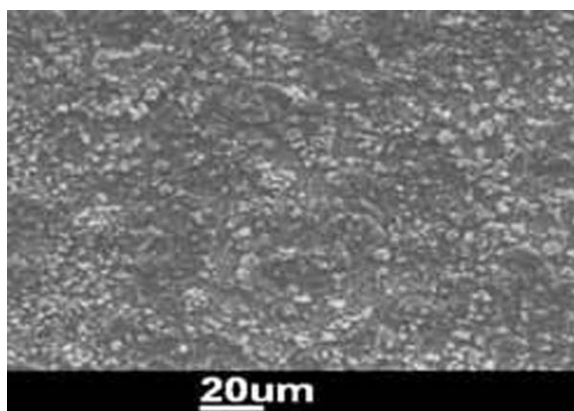
Fig. 23 SEM photo of aluminium deposited on sheet steel from $[C_2mim][AlCl_4]$ at room temperature (© BASF 2007).

Fig. 24 Texas Eastman Division *EpB* Chemical Semiworks Plant, Longview, Texas (© Eastman Chemical Company 2007).

3.3 IFP (Institut Français du Pétrole) – Axens

Whereas Eastman Chemical Company and BASF commercialised the first ionic liquid processes, IFP was the first to operate an ionic liquid pilot plant.[96] The Dimersol process, based on traditional technology, consists of the dimerisation of alkenes, typically propene (Dimersol-G) and butenes (Dimersol-X) to the more valuable branched hexenes and octenes.[97] This is an important industrial process, with thirty-five plants in operation worldwide, each plant producing between 20,000 and 90,000 tonnes per year of dimer, with a total annual production of 3,500,000 tonnes.[1,98] The longer-chain olefins produced in the dimerisation process are usually hydroformylated to alcohols (*e.g.* isononanols): isononanols are then converted into dialkyl phthalates, which are used as poly(vinyl chloride) plasticisers.

The dimerisation reaction is catalysed by a cationic nickel complex of the general form $[LNiCH_2R'][AlCl_4]$ (L = PR$_3$) and is commonly operated without solvent. However, it has been found that the catalyst shows greater activity when it is dissolved in undesirable aromatic or halogenated hydrocarbons.[1,97]

The use of chloroaluminate(III) ionic liquids as solvents for these nickel-catalysed dimerisation reactions has been developed and pioneered at IFP (France), especially by Nobel laureate Yves Chauvin and Hélène Olivier-Bourbigou.[99,100] The reaction can be performed as a biphasic system between −15 °C and 5 °C, as the products form a second layer that can be easily separated and the catalysts remains selectively dissolved in the ionic liquid phase. The activity of the catalyst
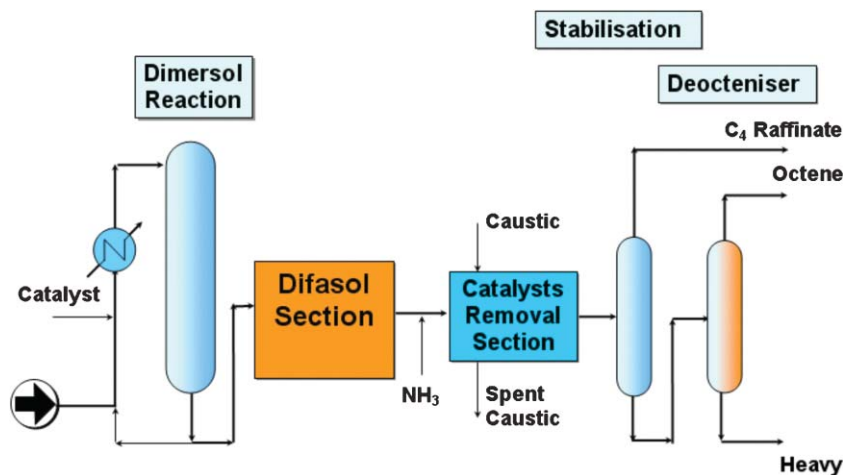
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Fig. 25 Process scheme integrating Dimersol and Difasol.[99]

is much higher than in both solvent-free and conventional solvent systems, and the selectivity for desirable dimers is enhanced. This process has been patented as the Difasol process and can be retro-fitted (see Fig. 25 and Fig. 26) into existing Dimersol plants; it is operated by Axens, an IFP subsidiary, and is described in Chauvin's Nobel lecture.[1]

The combined Dimersol–Difasol process was described for dimerisation of 2-methylbut-2-ene under laboratory conditions:[99] the biphasic system is clearly superior (see Table 6).

In comparison with the homogeneous Dimersol process, the advantages of the biphasic Difasol system are:

• a much better use of the catalyst and therefore a reduced catalyst disposal and cost

• a better dimer selectivity

• a higher yield into dimers can be achieved in a single step even with a low concentration alkene feed

• a possible extension of the Dimersol process to higher less reactive olefins

• from an engineering point of view, the reactor size is much smaller than in the homogeneous system

When the Difasol reactor, which involves the use of an ionic liquid, was added to the existing Dimersol reactor, the process (Fig. 25) became much more efficient. The process uses a biphasic mixture (cf. the BASIL process, Section 3.1.1), which results in a much better use of the catalyst, and therefore a reduced catalyst disposal cost, and a better dimer selectivity. A higher yield into dimers can be achieved in a single step, even with a low-concentration alkene feed, and from an engineering point of view, the reactor size is much smaller than in the homogeneous system. Moreover, this new process can be possibly extended to higher, less reactive olefins.

3.4 Degussa

Like BASF (see Section 3.1), Degussa are developing ionic liquids on several distinguishable fronts. They also own a minority stake in Solvent Innovations.

3.4.1 Hydrosilylation. The process of hydrosilylation of a polydimethylsiloxane can be represented as:
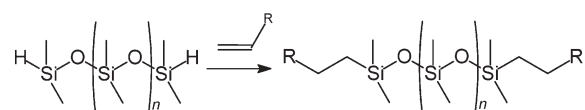
The hydrosilylation of the C=C double bond with silane-functionalised polydimethylsiloxanes is a widely applied reaction in industrial synthesis for the production of organo-silicon compounds on a technical scale. Degussa have used ionic liquids as a means of catalyst heterogenisation: the
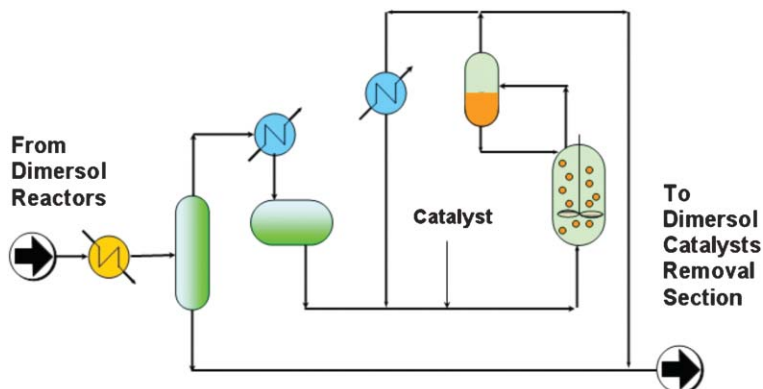

**Fig. 26** Difasol process scheme.[99]

**Table 6** Dimerisation of 2-methylbut-2-ene in a laboratory batch experiment

Operating conditions	Homogenous	B©iphasic
Catalyst	Ni^{II} + $AlX_{3-x}Et_x$	Ni^{II} + [C_4mim][$Al_2Cl_{7-x}Et_x$]
Catalyst consumption (ppm/feed)		
Ni	62	20
Al	2000	1000
Reaction time/h	8	2
Conversion/wt%	17	81
Dimer selectivity/wt%	>85	>90

catalyst (ionic) is dissolved in the ionic liquid, from which there is no significant leaching, but in which the product is insoluble (see Fig. 27). Their aim was the synthesis of polyethersiloxanes, an important class of surface active compounds which find use in a broad range of industrial applications. The experimental procedure is rather simple, and can be described as a one-pot biphasic synthesis (Fig. 27).[101,102]

Silane-functionalised polydimethylsiloxanes with different chain lengths and functionality patterns, and polyethers and ethers with different ethylene and propylene oxide content, were studied:[101,103]

n = 18, 28, or 78

m = 5; *n* = 43

400EO: *x* = 0, *y* = 7.5
540: *x* = 3, *y* = 5.8
400PO: *x* = 7.4, *y* = 0

AGE
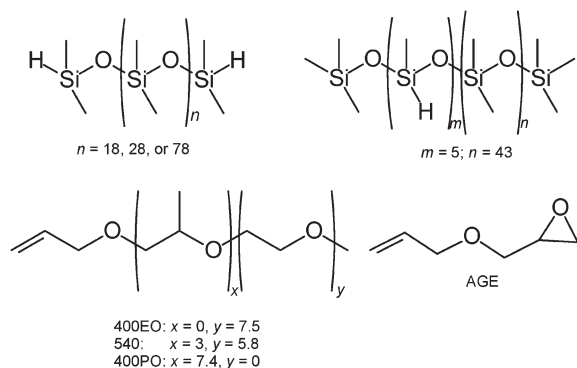
The catalysts used were $H_2[PtCl_6]$ (ionic) and [(μ-Cl)$_2${PtCl-(cyclohexene)}$_2$] (molecular), and the ionic liquids studied were 1-butyl-4-methylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium chloride, 1,2,3-trimethylimidazolium methylsulfate, and TEGO® IL K5MS (see Fig. 28). Hydrosilylation reactions in the presence of ionic liquids based on 1,3-dialkylimidazolium cations did not give the desired polyethersiloxanes, as the 2-H position of the cation was too reactive.
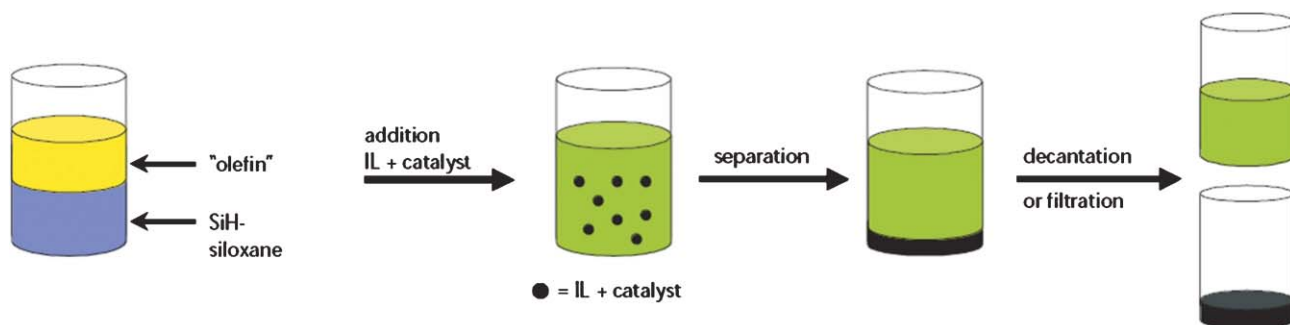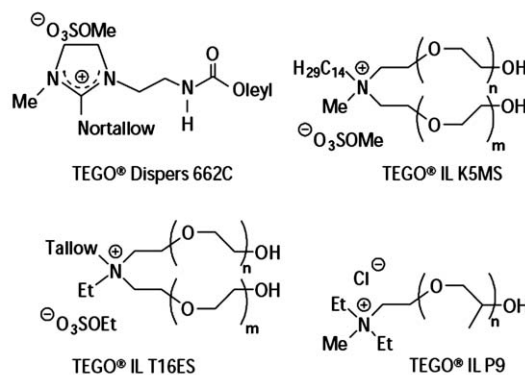
Fig. 28 Ionic liquids used as paint additives for the Pliolite® range.[102]

Factors affecting the reaction included the influence of the hydrophilicity/hydrophobicity of the substrates and corresponding products on the catalytic performance of the various catalyst/ionic liquid solution combinations and, even more importantly, on the separation behaviour of the ionic liquid at the end of the reaction. A clean separation of the ionic liquid from the products is essential for the partitioning of the catalyst between the two phases. Naturally, without a clean separation and a much better solubility of the catalyst in the ionic liquid phase than in the product phase, a complete retention of the catalyst in the ionic liquid and the desired recovery of the catalyst cannot be achieved. The reaction was found to give high conversions (>99%) in short time periods, under most conditions. The principal conclusion was that the nature of the catalyst was the key variable. When the molecular catalyst, [(μ-Cl)$_2${PtCl(cyclohexene)}$_2$], was used, it leached from the ionic liquid, and this leaching increased with increasing concentration of catalyst. However, using an ionic catalyst, $H_2[PtCl_6]$, the leaching was below detectable levels (<1 ppm), and independent of catalyst concentration. It is now generally accepted that ionic catalysts in ionic liquids are anchored even more strongly than catalysts chemically attached to oxide or polymer surfaces.[101,103]

The hydrophobicity of the organosilicon products increases with increasing chain length and decreasing silane-functionalisation of the polydimethylsiloxane. The polyethers are more hydrophobic, the higher the content of propylene oxide. The ionic liquid phase separates more easily

Fig. 27 Schematic for the hydrosilylation process (yellow = alkene; blue = silane; green = product; black = catalyst dissolved in ionic liquid phase).[102]

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from the organosilicon products the more hydrophobic they are.

3.4.2 Paint additives. Degussa are also using ionic liquids as additives to a new range of paints, for improved finish, appearance and drying properties.[102,104] The range is marketed under the name TEGO® Dispers, and added to the Pliolite® paint range.[102] The accentuated physical robustness and colour stability to a rub-out test can be seen in Fig. 29. By using these ionic liquids as secondary dispersing agents, universal, water-based pigment pastes can be used for all types of paints and coatings. This will allow a reduction in the use of volatile organic substances in paints and coatings in the future.

3.4.3 Lithium-ion batteries. Degussa, within its unit Creavis, has been investigating the use of ionic liquids in lithium batteries as substitutes for volatile and flammable mixtures of organic solvents, *i.e.* ethylene carbonate and dialkyl carbonates.[93,102,105] This is a pre-commercial study, and results (as publicly available) look promising.

3.5 Air products

Undoubtedly the talk which aroused the most interest at the first International Congress on Ionic Liquids (COIL-1) in Salzburg,[93] was a presentation by Dan Tempel of Air Products.[106] He revealed a new Air Products technology,[107] which is based around entrainment by the complexing of reactive gases in ionic liquids. It produces at least twice the performance of the main rival process, which relies on the physical adsorption of gases on solids, and provides a method to deliver these reactive and hazardous gases in a safe, effective, more easily handled way, reducing both the risks and hazards in the work place – a true green chemistry success. The gases can be stored and transported at sub-atmospheric pressure (see Fig. 30), instead of the normal pressurised cylinders, adding dramatically to safety. It is marketed as Gasguard® Sub-Atmospheric System, Complexed Gas Technology (CGT); the gas is removed from the cylinder by the application of vacuum.[108]

The system is based on the inherent Lewis acidity or basicity of the gases; Lewis acidic gases (such as boron(III) fluoride) are

Fig. 29 Painted surfaces with paints with and without added ionic liquids (© Degussa 2007).

Fig. 30 CGT $^{11}BF_3$ and CGT PH_3 commercial offerings (2.2 litre cylinders) (© Air Products 2007).

stored in Lewis basic ionic liquids (such as $[C_nmim][BF_4]$), whereas Lewis basic gases (such phosphine, PH_3, or arsine, AsH_3) are stored in Lewis acid ionic liquids (such as $[C_nmim][Cu_2Cl_3]$ or $[C_nmim][Cu_2Br_3]$). It can thus be used to deliver high purity gases to the electronics market.

3.6 Central Glass Co., Ltd., Japan

The Central Glass Company[109] are, to the best of our knowledge, the first firm to produce pharmaceutical intermediates using ionic liquid technology, although a two-step synthesis of pravadoline had been described earlier in the open literature.[110]

Sonogashira coupling is a palladium–copper catalysed reaction of aryl halides and terminal alkyl- or aryl-alkynes, allowing preparation of alkyl, aryl-, and diaryl-substituted alkynes, which can be used in optical, electronic and pharmaceutical applications. It is typically carried out in organic solvents (such as toluene, tetrahydrofuran, or *N,N*-dimethylmethanamide), and a stoicheiometric amount of base is required to trap the HX produced in the reaction. The Sonogashira coupling reaction in ionic liquids had been described several times in the open literature,[111] but each time in the highly undesirable $[C_4mim][PF_6]$ (the anion hydrolyses to release HF even in mild conditions).[36]

The following reaction was studied in detail by the Central Glass Co., Ltd.:
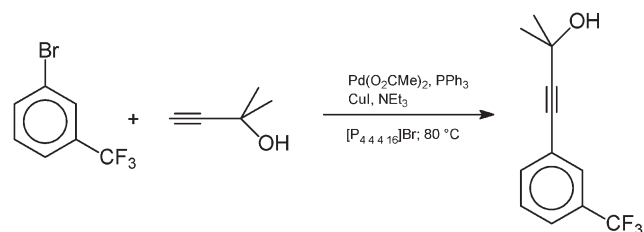
What they discovered was the use of 1,3-dialkylimidazolium cations led to reactions which were demonstrably less efficient than when conventional solvents were used (presumably due to
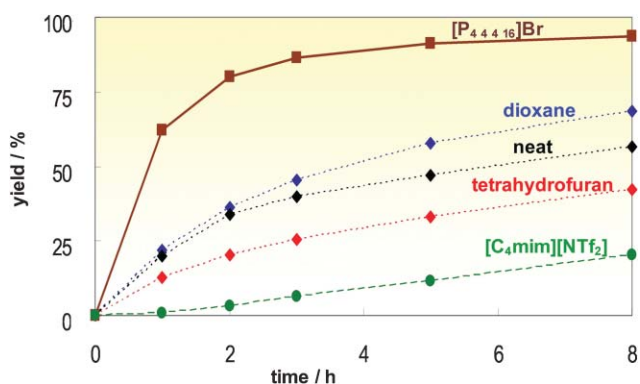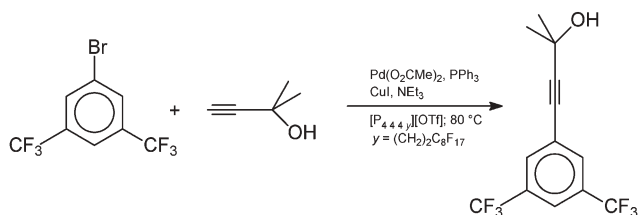
Fig. 31 The Sonogashira reaction in various media.

carbene formation,[36] *cf.* Section 3.4.1). However, when tetra-alkylphosphonium ionic liquids were used, the reaction was much more efficient than when carried out in organic solvents, or with neat reagents (see Fig. 31). From these results, the following reaction was developed and commercialised:

The product is separated from the catalyst-containing ionic liquid phase by extraction with hexane, and the by-product salt, $[HNEt_3]Br$, removed with a counter-current flow of water. The remaining ionic liquid-catalyst solution can be recycled several times with little loss of catalytic activity, and a microflow reaction system can also be used for this reaction.

3.7 IoLiTec

IoLiTec (**Io**nic **Li**quids **Tec**hnologies) are an interesting new company specialising in marketing ionic liquids (see Table 5),

Fig. 33 A spray nozzle for aqueous solutions of sodium chloride (left) and a hydrophilic ionic liquid (right), each after 10 h of operation (© IoLiTec 2007).

and developing applications.[112] They have developed a practical and efficient technology to clean high value and sensitive surfaces, using ionic liquids as antistatic cleaning agents (see Fig. 32), the brush bristles being moistened by a fine spray of aqueous solution. Conventionally, dilute aqueous sodium chloride solutions have been used as the wetting agent, but the effect of replacing this with an ionic liquid is dramatically demonstrated in Fig. 33.

IoLiTec has also interests in the application of ionic liquids in medicine (coated implants), food analytics, sensors, and heat pumps,[112] and is currently involved in the development of various green applications based on ionic liquids, *e.g.* electrolytes for dye-sensitised solar cells (Grätzel cells or DSSCs),[32,113] and phase change materials (PCMs)[114] for the storage of solar energy and for sorption cooling media for "solar cooling". Pilot installations for both DSSC and PCM applications are currently being constructed.

3.8 SASOL

South African company SASOL has been investigating the potential of ionic liquids in metathesis[115] and olefin trimerisation.[116] This metal-catalysed reaction of two alkenes was the subject of the 2005 Nobel Prize in Chemistry,[117] and an excellent set of books exist.[118] The reaction focused upon is the self-metathesis of oct-1-ene to yield tetradec-7-ene and ethene:
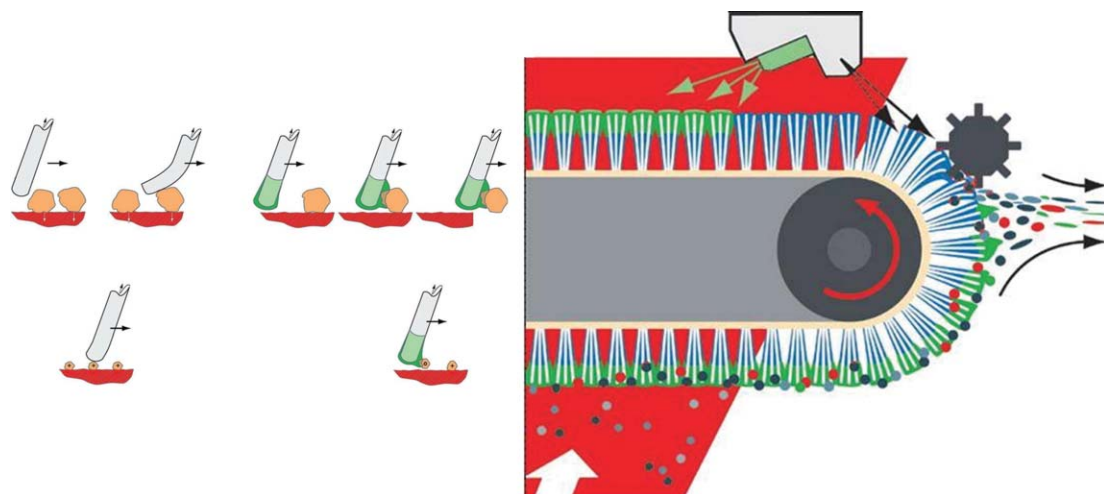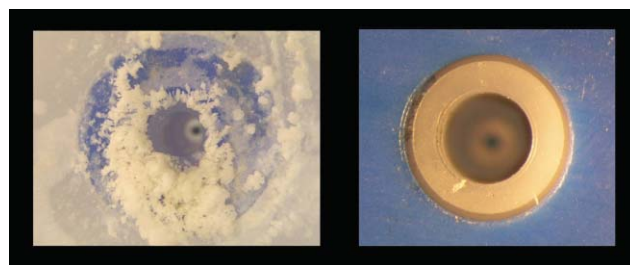

Fig. 32 The removal of dust particles by brush bristles (left), which is much more efficient if they are coated with a conducting liquid film, applied by a spray from a fine nozzle (right) (© IoLiTec 2007).
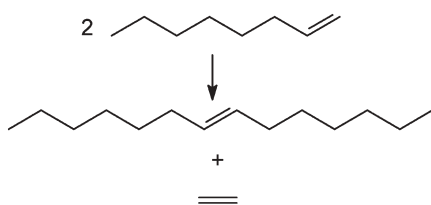
SASOL investigated this reaction in conventional solvents, with neat reagents, and in a range of ionic liquids.[115,119] They used the conventional Grubbs catalyst, a second generation Grubbs catalyst, and a Grubbs-Hoveyda (third generation) catalyst:
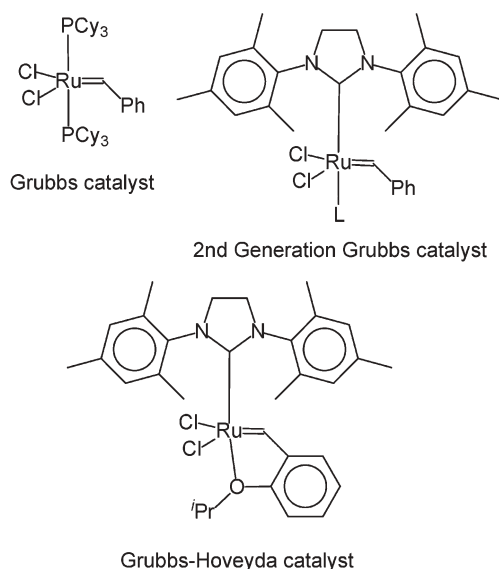
Experiments combining the conventional Grubbs catalyst with ionic liquids were less than promising, but with the second generation catalyst dissolved in [C$_2$dmim][NTf$_2$] remarkable improvements were observed: the yield of tetradec-7-ene was over 20% higher than with either the neat reagents or with toluene as a solvent. Moreover, the selectivity towards tetradec-7-ene was stable with time, whereas it dropped with time in conventional solvents. However, the use of a Grubbs–Hoveyda catalyst (see above) gave an even more spectacular result: the results of the neat reaction and the reaction performed in [C$_2$dmim][NTf$_2$] are compared in Fig. 34. The ionic liquid performs better in every way. Moreover, SASOL investigated the effect of the chain length of the alkyl group on the imidazolium cation upon the formation of the product, with again a dramatic difference being noted: the shorter the chain length, the better the result (see Fig. 35). The reaction is homogeneous, and very selective, with little or no isomerisation. Operating conditions are mild, from ambient temperature up to about 80 °C, and high activity and long life can be obtained from the catalysts, in this case ruthenium, which is cheaper than either rhodium or palladium.

3.9 BP

BP have heavily invested in ionic liquid technology, as is apparent in their patent portfolio,[49,50,120] and in an article in their in-house magazine (see Fig. 36).[121] But there have been few public announcements about processes. From the article in Frontiers,[121] we learn from Steve Koonin (BP's chief scientist) "Ionic liquids represent a fascinating new area of fundamental science, and one that has the unusual potential for direct and immediate impacts on a number of our businesses. For processing applications that BP uses in areas such as refining, petrochemicals, upstream and reservoir activities, ionic liquids could replace most of the processing steps that we use today."

However, they have revealed some details of their aromatic alkylation process in chloroaluminate ionic liquids.[122] Most importantly, they gave a detailed description of an ethylbenzene manufacturing plant (see Fig. 37), in which benzene is treated with ethene in Franklin acidic compositions of the [C$_n$mim]Cl–AlCl$_3$ (n = 2, 4 or 8) ionic liquid system at pressures up to 60 bar and 170 °C.[122] In a conclusion which reflects the theme of this review, they stated that "calculations suggest that for any reaction catalysed by AlCl$_3$, the increased cost of substituting ionic liquid, currently estimated as a factor of 5–6, could only be justified by a decrease in catalyst usage of a similar order, resulting from a combination of desirable features such as superior activity, selectivity and recyclability. The authors conclude that there is considerable scope for further ionic liquid formulation development for aromatics alkylation, requiring the combined skills of industry and academia working in collaboration."[122]

3.10 ExxonMobil

Like BP, ExxonMobil have made no public pronouncements of their interests in developing ionic liquid processes, but they have a significant patent suite, and have been publishing in the open literature. Most of the work seems to be led by Dr Christian Mehnert. Areas of interests include biphasic carbonylation catalysis using conventional rhodium catalysts in Lewis-acidic ionic liquids,[123] the electrochemical oxidation of sulfur compounds in naphtha,[124] the use of supported ionic liquids,[125,126] catalytic hydroformylation,[127,128] hydrogenations,[126,128] aldol condensations,[129] and even ionic liquid synthesis.[130]

3.11 Chevron and Chevron Phillips

Chevron, like BP and ExxonMobil, have used ionic liquids for a number of processes, but there are again no public statements about their state of commissioning. They have an extensive patent portfolio,[131–136] and the main themes running through these are refinery alkylation,[136] emulsification and high shear mixing,[134] oligomerisation[132,133] and hydrotreatment[133] of alkenes (often to prepare lubricating oils), and removal of carbon dioxide from gas streams.[135]

3.12 PetroChina

Unlike the other petrochemical companies, PetroChina have publicly announced a major process employing ionic liquids.[137,138] The process, given the rather inharmonious name of Ionikylation,[137] has been tested at pilot plant, and retrofitted into an existing 65,000 tonne per year sulfuric acid alkylation unit in China. The chemistry, alkylation of
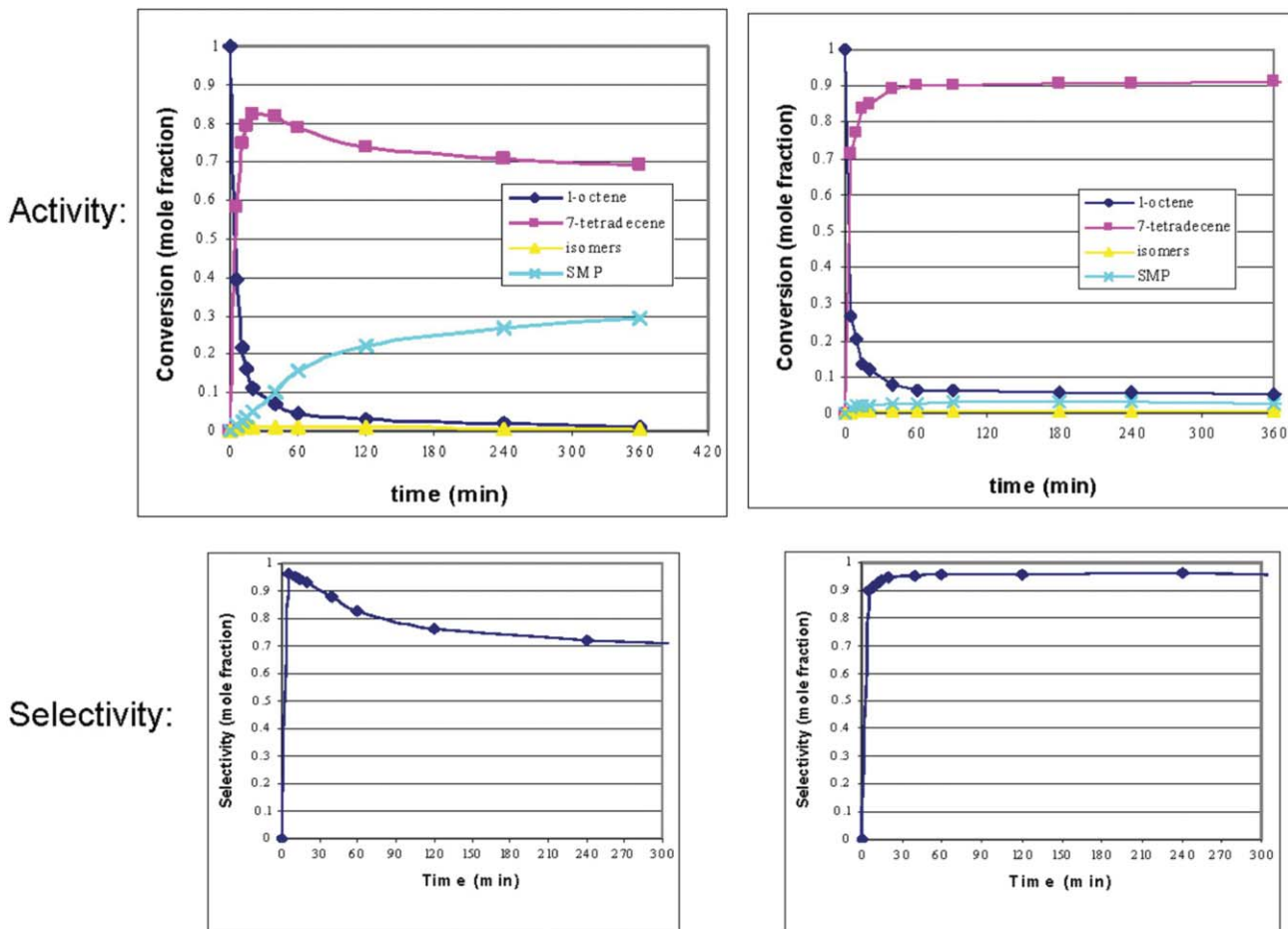
Fig. 34 The results of the self metathesis of oct-1-ene in the presence of a Grubbs–Hoveyda catalyst with neat reagent (left) and in [C$_2$dmim][NTf$_2$] (right), activity being the upper set of graphs, and selectivity being the lower.

isobutene, parallels early BP and IFP work, in that it occurs in a strongly Lewis acidic ionic liquid based on aluminium(III) chloride. The retrofit not only increased the yield of the

process (compared to sulfuric acid), but increased the process units capacity by 40% (to 248 tonnes per day), with attractive economics. This is by far the largest commercial usage of ionic
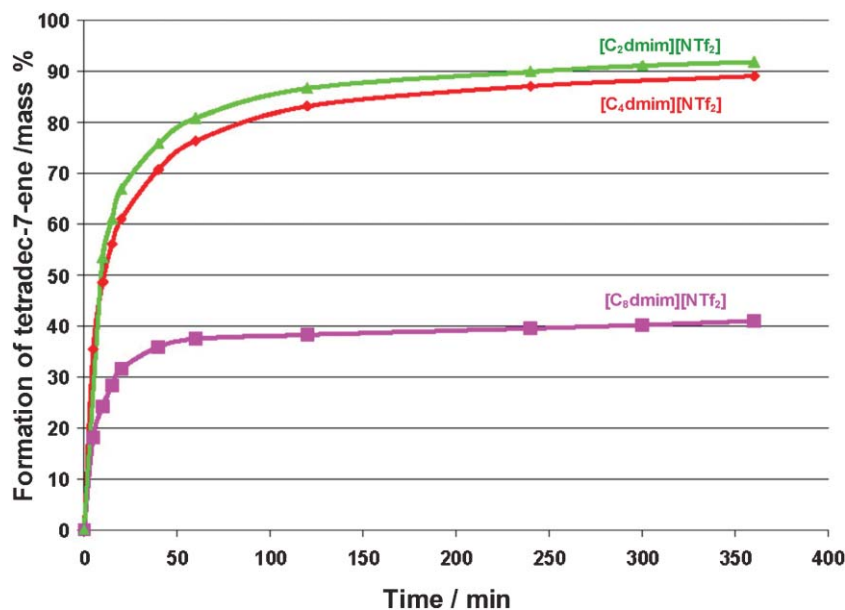

Fig. 35 The results of the self metathesis of oct-1-ene in the presence of a Grubbs–Hoveyda catalyst in various ionic liquids, [C$_n$dmim][NTf$_2$].
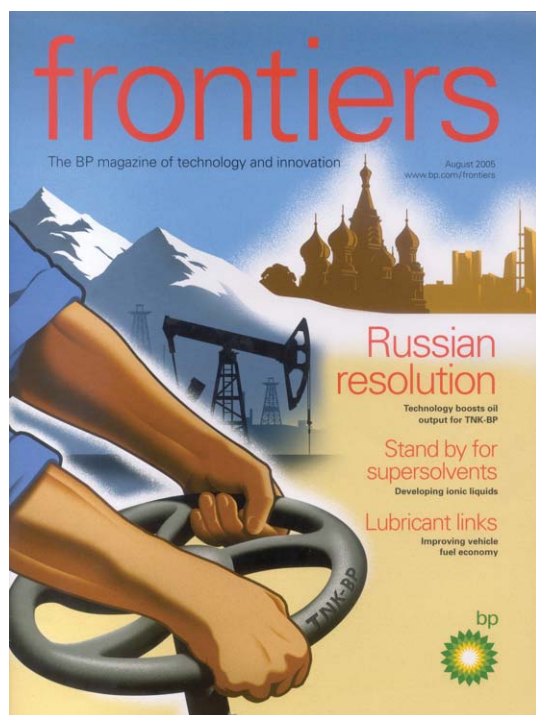
Fig. 36 Ionic liquids featured on the cover of the BP in-house magazine (© BP 2006).

liquids reported to date, and is certainly a forerunner of other commercial petrochemical processes.

3.13 Eli Lilly

Eli Lilly have described a process for demethylating an aryl ether to quantitatively generate a phenol, on both a twenty-two litre and a 190 litre pilot plant scale.[139] 4-Methoxyphenylbutanoic acid is demethylated in three hours at 180 °C when melted with pyridinium hydrochloride,

[pyH]Cl.[139] 4-Hydroxyphenylbutanoic acid, which is the product, is an important pharmaceutical intermediate.
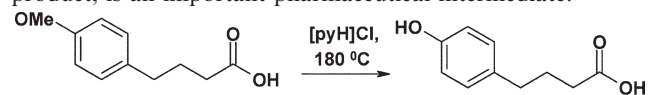
3.14 Pionics

Pionics is a Japanese firm specialising in lithium batteries.[140] In association with Trekion,[141] they have developed a very efficient and safe lithium battery. Pionics is now constructing a mass-production commercial plant in Shiga, Japan to produce self-extinguishing lithium ion rechargeable batteries, which should be in production by late 2007.[142]

3.15 Scionix

Scionix,[143] a University spin off from the University of Leicester and Whyte Chemicals, have developed a chromium electroplating process based on choline-chromium(III) derived ionic liquids.[144] It is a high efficiency, low power, process, avoiding the conventional, toxic, chromium(VI) process. It is presently running at pilot plant scale, and is ripe for commercialisation. Scionix have also developed an interesting process for the electropolishing of stainless steel.[145] Although not all the Scionix media are true ionic liquids, some being better described as deep eutectics (mixtures of ionic liquids and molecular components), many of the principles are similar. These choline-based systems have the huge advantage of being very cheap.

3.16 Linde

Linde have developed a device that they call an "ionic compressor".[146] It is a machine for compressing gases at constant temperature (isothermal compression) and high pressure, using the ionic liquid as a type of liquid piston (ionic liquids have a very low compressibility). Linde state that "in
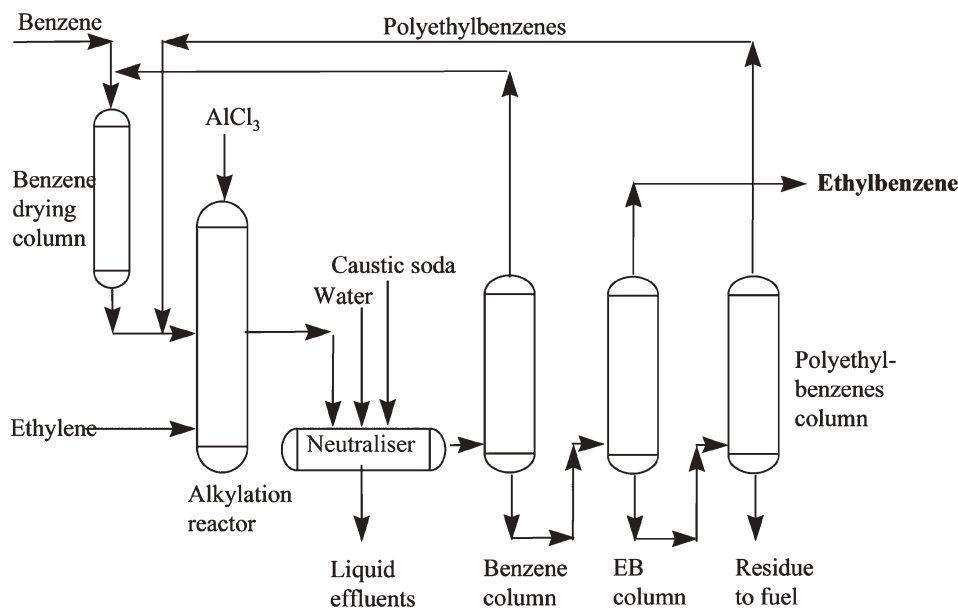

Fig. 37 Schematic of an ethylbenzene manufacturing plant.[122]

Fig. 38 Causeway to the future‖.

contrast to a conventional piston compressor, with some 500 moving parts, we now need only eight." The system maintains a constant gas pressure of 250 bar while delivering 500 cubic meters of natural gas per hour. The proposed early applications are dihydrogen and natural gas filling stations.

4 Where does the future of ionic liquids lie

The field of ionic liquids is growing at a rate that was unpredictable even five years ago. The range of commercial applications is quite staggering; not just in the number, but in their wide diversity, arising from close cooperation between academia and industry. The concepts and paradigms of ionic liquids are new, and still not fully accepted in the wider community: it is hard for conservative scientists to throw away thousands of years of concepts grown from the fertile ground (ocean?) of molecular solvents, and if chemists are conservative, then chemical engineers are even more so. But, there is always a flipside, a mirror image, and there are now many laboratories all over the world (and the growth in China is spectacular) that work with ionic liquids. To restate the opening quote of this review: "*If you want to find something*

new, look for something new!". We predict that ionic liquids will be used commercially in all of the fields illustrated in Fig. 38.

A close examination of Fig. 38, however, reveals that these predictions are not haruspicy, but a natural extrapolation of where we are now. It is thus not really prediction but expectation. Pharmaceutical applications will burgeon;[147] wider use will be made of the unique physical properties (they may even be sent to the moon);[148] applications for their newly discovered volatility will be found;[66,69] more petrochemical applications will be realised. But the most exciting applications will be the unpredictable ones. As ionic liquids can, in principle, replace conventional liquids wherever they are used, we have barely scratched the surface of the possible. The next few years will be truly fascinating.

Acknowledgements

‖ The diagram of ionic liquid applications is represented as a hexagon, the most perfect crystalline structure in nature. The authors of this review live in Northern Ireland, where the Giant's Causeway is a World Heritage site. Composed of over 40,000 hexagonal basalt columns, it was formed from cooling molten salts, and is evocative of the ubiquity of ionic liquids, here a medium for crystal growth.

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