Ionic Liquids for Clean Technology*

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Abstract: The use of room-temperature chloroaluminate(III) ionic liquids, specifically 1-butylpyridinium chloride–aluminium(III) chloride and 1-ethyl-3-methylimidazolium chloride–aluminium(III) chloride, as solvents for clean synthesis and catalytic processes, particularly those applicable to clean technology, is becoming widely recognised and accepted. The design principles for room-temperature ionic liquids, some of their properties, and the rationale for using these neoteric solvents, are discussed here, and an indication of the scope of these solvents for future industrial processes is given.

Key words: ionic liquids, molten salts, clean technology, clean synthesis, neoteric solvents, chloroaluminates(III)

1 PREAMBLE

Ionic liquids? Neoteric solvents? Molten salts for clean technology and catalysis? Are you serious?? Well, yes, I am serious, but yes there are questions to be answered. In 1982, I submitted a proposal to the then SERC which concerned the use of room-temperature ionic liquids to study catalytic processes which might have some industrial application. The proposal was rejected: referee 1 stated that the systems were far too complicated, and therefore would never have any application, referee 2 thought that the systems were far too simple, and the work was not worth doing, and referee 3 (clearly not having the correct proposal in front of him) wondered why we wanted to study the neutron diffraction patterns of vanadium bronzes!! Fortunately, the BP Venture Research Unit (headed by Prof. Don Braben) was more imaginative, and shortly afterwards awarded us a substantial grant to enable us to investigate the chemistry of ionic liquids. In 1996, thanks to this crucial grant, and with subsequent extremely generous support from BP Chemicals, Unilever, ICI, BNFL, IRTU and EPSRC (ROPA and Clean Synthesis awards), combined with the blood, sweat and tears of dozens of graduate students and postdoctoral fellows, we believe that the initial concepts and speculation have been vindicated, and that the industrial relevance of ionic liquids, especially for clean synthesis and clean catalysis, has been demonstrated (vide infra).

The purpose of this brief review is to give an introduction to the nature and properties of room-temperature ionic liquids, with particular emphasis being placed upon their potential as solvents for industrially relevant catalytic reactions, and (more generally) for clean technology. This account is neither comprehensive nor exhaustive, but is intended to whet the appetite of the reader, and perhaps encourage further interest in a subject that, until recently, had been generally considered as rather esoteric. This account centres around the use of room-temperature chloroaluminate ionic liquids as solvents, especially the systems 1-butylpyridinium chloride–aluminium(III) chloride, [NBupy]Cl–AlCl₃, and 1-ethyl-3-methylimidazolium chloride–aluminium(III) chloride, [emim]Cl–AlCl₃ (see Scheme 1): these are by no means the only systems which may be used for catalytic studies, but they are undoubtedly the archetypal systems. Much greater
3 RATIONALE: WHY USE IONIC LIQUIDS?

The question as to why use ionic liquids at all has recently been addressed in detail elsewhere, in a companion review, 8 which has been made available on a World-Wide Web site, 9 as a section of a dedicated ionic liquids database. 10 The relative merits of using ionic liquids, instead of the more common molecular solvents, are rehearsed there, and will not be repeated here. Moreover, the case for using room-temperature ionic liquids rather than high-temperature ionic liquids is also argued. To briefly summarise, ionic liquids suppress conventional solvation and solvolysis phenomena, and provide media capable of dissolving a vast range of inorganic molecules to very high concentrations. The low (i.e. ambient) temperatures suppress dissociation, disproportionation and degradation reactions, and the ionic environment tends to significantly extend the lifetimes of species (such as [RuCl$_6$]$_3^-$) 11 which are unstable in conventional molecular solvents.

4 ROOM TEMPERATURE IONIC LIQUIDS

4.1 Lowering the melting point

The melting points of the Group 1 chlorides are given in Table 1. 12 As can be seen, these are significantly above room temperature, and far too high to form a generic medium for reactive chemistry. However, the eutectic compositions of mixed ternary systems do melt at significantly lower temperatures than either binary component (see Fig. 1). Applying the understanding of lattice energies gained from the Kapustinskii equation, 13 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. Furthermore, as the sodium chloride–aluminium(III) chloride system shows compound formation at the 1 : 1 composition (viz. Na[AlCl$_4$]), the idealised phase diagram (Fig. 2) now exhibits two eutectic points. However, as these represent the lowest temperatures at which these

<table>
<thead>
<tr>
<th>System</th>
<th>Mole%</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>100</td>
<td>610</td>
</tr>
<tr>
<td>NaCl</td>
<td>100</td>
<td>803</td>
</tr>
<tr>
<td>KCl</td>
<td>100</td>
<td>772</td>
</tr>
<tr>
<td>CsCl</td>
<td>100</td>
<td>646</td>
</tr>
<tr>
<td>LiCl–CsCl</td>
<td>60–40</td>
<td>355</td>
</tr>
<tr>
<td>NaCl–KCl</td>
<td>50–50</td>
<td>658</td>
</tr>
<tr>
<td>CsCl–KCl</td>
<td>35–65</td>
<td>610</td>
</tr>
</tbody>
</table>
systems are liquids, it is necessary to bring the melting point down even further. This has been done by increasing the size of the cations: replacing the simple inorganic cations with unsymmetrical organic cations depresses the melting point to temperatures at or below room temperature, as illustrated in the following section.

**TABLE 2**

<table>
<thead>
<tr>
<th>System</th>
<th>Mole%</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>100</td>
<td>192</td>
</tr>
<tr>
<td>LiCl–AlCl₃</td>
<td>50–50</td>
<td>144</td>
</tr>
<tr>
<td>NaCl–AlCl₃</td>
<td>50–50</td>
<td>151</td>
</tr>
<tr>
<td>KCl–AlCl₃</td>
<td>50–50</td>
<td>256</td>
</tr>
</tbody>
</table>

The chemical and physical properties of the liquids are determined by the percentage of aluminium(III) chloride: those which have X(AlCl₃) greater than 50 mol% are referred to as acidic, whilst those with X(AlCl₃) less than 50 mol% are called basic. The exactly 50 mol% composition is referred to as neutral. It should be

### 4.2 Tetrachloroaluminate(III) ionic liquids

The development of ionic liquids that are fluid at room temperature by the groups of Osteryoung, Wilkes and Hussey has provided an ideal resolution to all of the problems presented above. Although the earlier work was based around the N-butylpyridinium cation, [NBupy]⁺, research now is almost exclusively based upon the 1-ethyl-3-methylimidazolium cation, [emim]⁺, or simple derivatives thereof. Undoubtedly the most studied system is 1-ethyl-3-methylimidazolium chloride-aluminium(III) chloride, [emim]Cl–AlCl₃, and its experimental phase diagram is shown in Fig. 3. The unsymmetrical nature of the cation is crucial; [NBupy]⁺ possesses a mirror plane missing from [emim]⁺, which only has C₁ symmetry (the ethyl group is not co-planar with the imidazolium ring). The 1-ethyl-3-methylimidazolium salts melt some 100 °C lower than their N-butylpyridinium analogues.

These chloroaluminate systems are governed by the following primary equilibrium, eqn (1):

\[2[AlCl₄]^- \rightleftharpoons [Al₂Cl₇]^+ + Cl^- \; K \approx 10^{-16.3} \] (1)

The chemical and physical properties of the liquids are determined by the percentage of aluminium(III) chloride: those which have X(AlCl₃) greater than 50 mol% are referred to as acidic, whilst those with X(AlCl₃) less than 50 mol% are called basic. The exactly 50 mol% composition is referred to as neutral. It should be

\[2[AlCl₄]^- \rightleftharpoons [Al₂Cl₇]^+ + Cl^- \; K \approx 10^{-16.3} \] (1)

† In the older literature, this cation is almost exclusively referred to (incorrectly) as 1-methyl-3-ethylimidazolium, and represented by [MeEtim]⁺. Its full, correct, systematic name is the 1-ethyl-3-methyl-1H-imidazolium cation.
TABLE 3
Principal Anions Present in the [emim]Cl–AlCl₃ Ionic Liquid System, as a Function of Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>[emim]Cl–AlCl₃</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic; X(AlCl₃) = 0–0.5</td>
<td></td>
<td>Cl⁻, [AlCl₄]⁻, [AlCl₅]⁻, [Al₂Cl₇]⁻, [Al₃Cl₁₀]⁻</td>
</tr>
<tr>
<td>Acidic; X(AlCl₃) = 0.5–0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very acidic; X(AlCl₃) = 0.67–0.75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

emphasised here that the terms ‘acid’ and ‘base’ refer to Franklin acidity and basicity, and not (as frequently assumed) to Lewis acidity and basicity. The ionic composition of the [emim]Cl–AlCl₃ system is displayed on a logarithmic scale (–pX) in Fig. 4, and on a linear scale in Fig. 5. There are three key features of note. Firstly, a clear parallel (both quantitative and qualitative) exists between the curves illustrated in Fig. 4, and standard pH curves in water. Secondly, the concentration of the tetrachloroaluminate(III) ion is approximately constant, and very high, across the whole compositional range. Finally, there is always exactly 50 mol% of the 1-ethyl-3-methylimidazolium cation present. Table 3 summarises the principal anions present as a function of composition: definitive evidence now exists for the existence of [Al₃Cl₁₀]⁻ in very acidic systems.²⁰,²¹

There is not the space here to enlarge further on the physical and chemical properties of these unique systems: the interested reader is referred to Hussey.¹,²

5 IONIC LIQUIDS FOR CLEAN CATALYSIS

Clean technology is concerned with reducing the waste from an industrial chemical process to zero. Its implementation will lead to a cleaner environment, and more cost-effective use of starting materials. It requires, in the majority of cases, the rethinking and redesign of many chemical processes that we currently think of as the industrial norm. Catalysis clearly has a central role to play in this process, with its potential for both high yields and high specificity.

The E-factor of a process is the ratio (by weight) of the by-products to the desired product(s).²² Table 4 illustrates that, contrary to popular perception, the ‘dirty’ end of the chemical industry, oil refining and bulk chemicals, is remarkably waste conscious. It is, surprisingly, the fine chemicals and pharmaceutical companies that are using inefficient, dirty, processes, albeit on a much smaller scale, and there will be increasing demand (political, economic, social and environmental) for the introduction of new clean technology. Industries that do not respond will die.

TABLE 4
By-products as a Proportion of Production for the Chemical Industry²²

<table>
<thead>
<tr>
<th>Industry</th>
<th>Production (tons p.a.)</th>
<th>E-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>10⁶–10⁸</td>
<td>0–1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>10⁴–10⁶</td>
<td>1–5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>10²–10⁴</td>
<td>5–50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>10¹–10³</td>
<td>25–100</td>
</tr>
</tbody>
</table>
Volatile organic solvents are the normal media for the industrial synthesis of organic chemicals (petrochemical and pharmaceutical), with a current worldwide usage estimated at £4 000 000 000 p.a. However, the environmental impact of these solvents is significant, and the Montreal Protocol has resulted in a compelling need to re-evaluate many chemical processes that have proved otherwise satisfactory for much of this century. A conspicuous example is the recent closure of one of the DuPont Hypalon® plants in Northern Ireland, which had been operating with chlorinated hydrocarbon solvents. There appear to be four main alternative strategies:

(1) solvent-free synthesis
(2) the use of water as a solvent
(3) the use of supercritical fluids as solvents
(4) the use of ionic liquids as solvents

It is the purpose of this review to stimulate interest in option (4), and to incite enough activity in this area to allow a meaningful evaluation. Ionic liquids possess, *inter alia*, the following desirable properties:

1. They have a liquid range of 300°C (cf. water, which has a liquid range of 100°C, and ammonia, with a liquid range of only 44°C), allowing tremendous kinetic control.
2. They are outstandingly good solvents for a wide range of inorganic, organic and polymeric materials (but, fortunately, they do not dissolve polythene, PTFE or glass!): high solubility implies small reactor volumes.
3. They exhibit Brønsted, Lewis and Franklin acidity, as well as superacidity. 23, 24
4. They have no effective vapour pressure.
5. Their water sensitivity does not restrict their industrial applications.
6. They are thermally stable up to 200°C.
7. They are relatively cheap, and easy to prepare.

Unlike water and other hydroxylic solvents, they will dissolve a wide range of organic molecules to an appreciable extent (benzene, for example, will form up to 50% (v/v) solutions), meaning much lower volumes of solvent are required for a given process. Exploratory work in our own laboratories (carried out in collaboration with BP Chemicals and Unilever Port Sunlight Research Laboratory) has demonstrated that a wide range of catalysed organic reactions (including oligomerisations, polymerisations, alkylation and acylations) occurs in room-temperature ionic liquids, and that these are serious candidates for commercial processes. 25, 26 For example, the oligomerisation of butenes to polyisobutene in a chloroaluminate(III) ionic liquid is a strong competitor for the Cosden process, which uses a supported or liquid phase aluminium(III) chloride catalyst. 27

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. For example, we have just reported upon a new series of ionic liquids that are also liquid crystals, with a phenomenal liquid range (up to 188°C) of smectic A phase stability, which offer a significant new ionic medium for studying the stereocontrol of reactions (e.g. polymerisation reactions) in liquid crystals. 28 This, quite literally, revolutionises the methodology of synthetic organic chemistry: it will never be the same again!

**ACKNOWLEDGEMENT**

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**REFERENCES**


