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*Ionic liquids can be made in a range of colours. QUILL is the Queen's University Ionic Liquid Laboratories in Belfast.*

# IONIC LIQUIDS

The discovery most likely to shape the 21st century

## Key words

liquids  
ions  
solvents  
green chemistry

A new class of fluids, called ionic liquids, are revolutionising the world of chemistry. In 2013, they were voted as the British innovation most likely to shape the 21st century, in a nationwide poll organised by the Science Museum (image 1). In 2014, they were also featured in the prestigious Royal Society Summer Science Exhibition. Ionic liquids are currently being used in industry and in our homes, and they have also won many awards for their pollution-fighting abilities. But what exactly are these liquids, and why are they taking the world by storm?

## What are ionic liquids?

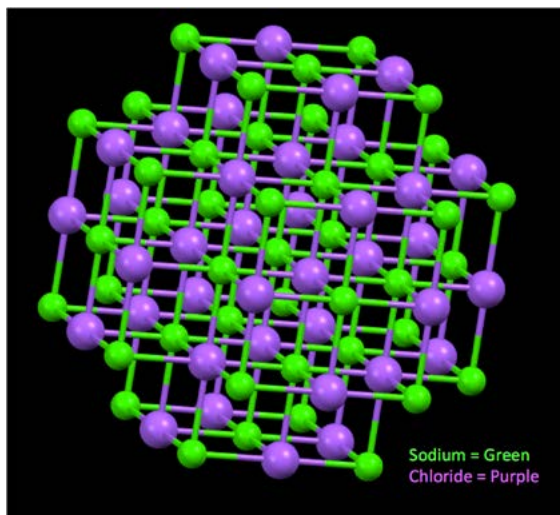
Ionic liquids are, quite simply, salts that are liquid at, or near to, room temperature. Just like table salt, that consists only of ions (sodium cations,  $\text{Na}^+$ , and chloride anions,  $\text{Cl}^-$ ), ionic liquids also consist only of ions (positively charged cations and negatively charged anions). In table salt, the sodium cations and chloride anions pack together tightly because they are small, 'beautiful' and symmetrical, which is why table salt must be heated to  $801^\circ\text{C}$  (similar to the temperature of volcanic lava) before it will melt. In ionic liquids, the cations and anions are typically big, 'ugly' and unsymmetrical, and cannot get close enough together to crystallise. This inability to form a solid is known as frustrated crystallisation and, as a result, many ionic liquids are fluid at room temperature.

A screenshot of the 'GREAT BRITISH INNOVATION VOTE' website. The page features a navigation bar with 'home', 'past innovations', 'future innovations', 'about this vote', and 'press'. Below the navigation, there's a main heading: 'We asked the public what they thought was the most important innovation of the last 100 years and the recent one most likely to shape our future.' There are two buttons: '1 View all Past Innovations' and '2 View all Future Innovations'. A large image of yellow spheres is visible. Logos for 'ROYAL SOCIETY OF ENGINEERING', 'Department for Business Innovation &amp; Skills', 'INNOVATION IS GREAT', 'SCIENCE PLUS', 'EngineeringUK', and 'THE ROYAL SOCIETY' are present. A red banner at the bottom says 'Ionic liquid chemistry' and 'was voted the British innovation most likely to shape the 21st Century'. To the right, it says 'Voting has ended' and 'Over 50,000 votes were cast. Thanks to everyone who took part.' Below this, a list of top 5 innovations is shown: 1. Ionic liquid chemistry (30% of votes), 2. Raspberry Pi (22% of votes), 3. Organ printer (12% of votes), 4. Graphene (11% of votes), and 5. Discovery of the Higgs boson (8% of votes).

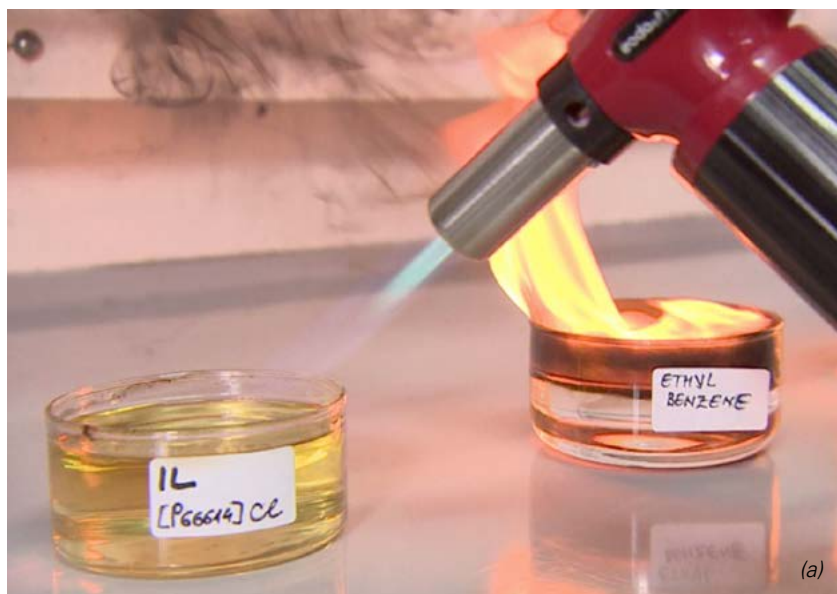
Great British Innovation Vote website showing ionic liquids selected as the winner



Sodium chloride (table salt)



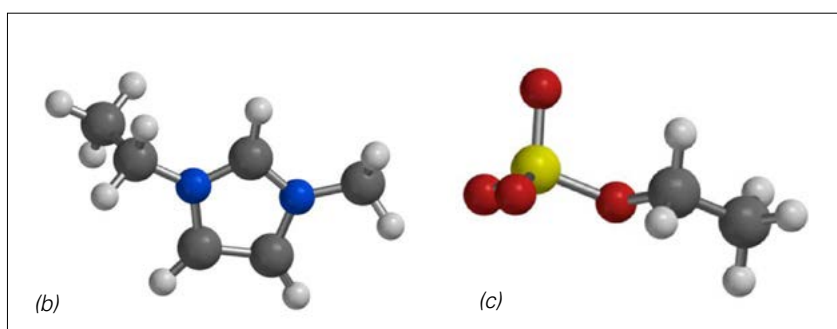
Sodium chloride crystal lattice



(a)



An ionic liquid (1-ethyl-3-methylimidazolium ethylsulfate; melting point  $< -20\text{ }^{\circ}\text{C}$ )



(b)

(c)

(a) Ionic liquids cannot burn because they do not release vapours. Here, a phosphonium ionic liquid will not ignite while ethylbenzene, found in petrol, burns. Below, the molecular structures of two ionic liquids: (b) ethylmethylimidazolium ethylsulfate and (c) a phosphonium liquid.

## Super solvents

So, ionic liquids do not evaporate and have far lower melting points than traditional salts, but so what? The answer is that they are extremely good at dissolving things – they are excellent solvents. The vast majority of solvents in use today are molecular and their biggest weaknesses are that they release vapours into the atmosphere, known as VOCs, they can burn, and they cannot dissolve many substances. For example, only ionic liquids can dissolve coal. It is not possible to use high melting salts to dissolve coal (and most other substances for that matter) because working at molten lava-type temperatures would simply incinerate most compounds of interest.

With ionic liquids, we can work close to room temperature, which has opened up a treasure chest of opportunities to dissolve many substances that are traditionally considered insoluble. We can also access chemistry that wasn't possible before, simply because we couldn't dissolve the reactants. It is very fortunate that ionic liquids do not dissolve glass or stainless steel, otherwise we would not have any reaction vessels in which to use them! In addition to their 'green', super-solvent abilities, there is yet another reason why ionic liquids are such extraordinary materials.

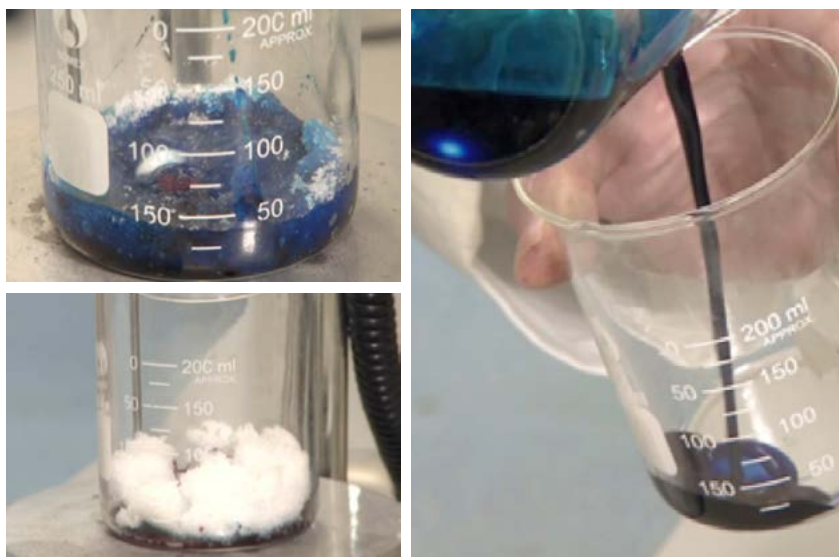
Ionic liquids turn our understanding of the nature of liquids on its head. Most liquids we are familiar with, such as water and alcohol, are molecular, meaning they are composed of neutral molecules. When molecular liquids are heated, the molecules at the surface gain enough energy to enter the gas phase and they evaporate into the atmosphere. In contrast, ionic liquids, which are composed only of ions, cannot pollute the atmosphere because they do not evaporate under normal conditions when they are heated – this fundamental, ever-present, characteristic of ionic liquids is one of the reasons why they are called 'green' solvents. An added bonus of not being able to evaporate is that ionic liquids cannot burn, and they are thus much safer to use in industrial plants which need large quantities of solvents.

VOCs are Volatile Organic Compounds

## Designer, green solvents

Ionic liquids can be tailor-made to exactly meet the needs of virtually any application! By carefully manipulating their cations, anions, or both, ionic liquids can be designed to possess specific properties e.g. they can be magnetic or luminescent. It is not possible to tailor-make molecular solvents since their properties cannot be easily tuned, and so their applications range is limited too. In addition, there are only about 300 conventional, molecular solvents used in industry today, while there are at least a million (1 000 000) possible simple ionic liquids!

There are so many ionic liquids available because of the ability to combine various different cations with various different anions. If we mix two ionic liquids, there are at least a billion (1 000 000 000 000) options, and if we mix three, at least  $10^{18}$  possible choices! Making ionic liquids in the laboratory is also quite easy - some of them are simply made by mixing two solids. There are now many companies throughout the world that are manufacturing and selling ionic liquids on very large scales.



Preparing the ionic liquid, cholinium tetrachlorocobaltate(III),  $[\text{NMe}_3(\text{CH}_2)_2\text{OH}]_2[\text{CoCl}_4]$ , in the laboratory. **a** Combine two solids, cholinium chloride and cobalt(III) chloride. **b** Mix them for 15 minutes at room temperature. **c** Pour the ionic liquid product.

It is important to be aware that, although ionic liquids can be tailor-made to be non-toxic and biodegradable, the flip side of the coin is that we can also design ionic liquids to be toxic. This might seem contradictory to the green aims of ionic liquid science, but actually has important implications for applications such as fighting hospital superbugs like MRSA and *C. difficile*. The key concept to be kept in mind is design - this process is constantly being refined so that we have better control of what properties an ionic liquid will possess, ranging from environmentally-friendly to toxic.

Access to so many ionic liquids, in addition to their green credentials, has caused a major shift in the way we approach chemistry, particularly its green application, but where and how are ionic liquids being used?

## Ionic liquid applications

Although you may not realise it, ionic liquids are probably already 'in' or 'on' your home - some fabric softeners and household paints contain them. Industrial applications range from using ionic liquids to capture greenhouse gases such as carbon dioxide, making new products, 'trapping' and transporting hazardous gases, cleaning metal surfaces, using them in safer batteries (which do not catch fire), as well as using them to remove toxic mercury from natural gas (to be discussed in a later issue of CATALYST).

Ionic liquids can also be used on smaller scales as, for example, less volatile and therefore safer fluids for studying gems and minerals, to dissolve biomass in the quest for producing biofuels, and even as replacements for toxic and smelly formaldehyde for embalming corpses! In conjunction with NASA, they are also planned to be used as the basis of a massive Lunar Liquid Mirror Telescope, which would enable us to see much, much further into space and time than is currently possible. The possibilities seem almost endless, and they are - wherever a conventional liquid can be used, an ionic liquid, designed to be better, can replace it.



Lord Browne of Madingley (chief executive of BP from 1995 to 2007) with a collection of luminescent ionic liquids

## The ionic liquid bottom line

Since nearly every product in use today has had a molecular solvent of some kind involved in its manufacture, replacing these solvents with ionic liquids would have a massively beneficial effect on lowering atmospheric pollution and, at the same time, would make industrial applications greener, cleaner, more economic, and more efficient.

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### Look here!

For more information about ionic liquids see: What are ionic liquids? <http://bit.ly/1wqTH79>

Ionic liquids at the 2014 Royal Society Summer Science Exhibition

Video: <http://tinyurl.com/pczn8fl>

Podcast: <http://tinyurl.com/ozur5yh>