Super solvents

Want an environmentally friendly solvent that can dissolve plastics and rock? *David Bradley* writes that QUB researchers are developing new ionic solvents that could revolutionise the chemical industry, and even make cleaner fuels for cars

Pick a salt, any salt. Sodium chloride? Potassium iodide? Salts are made of charged particles (ions) and exist as tough, crystalline solids. They dissolve in water, but need serious heating to several hundred degrees to melt them. For example common table salt, sodium chloride, melts at a sweltering 806^{o}C.

But in the late 1940s Frank Hurley and Tom Weir, working at the Rice Institute in Texas, discovered that they could make some salts liquid at close to room temperature. They mixed and gently warmed a powdered organic salt known as alkylpyridinium chloride, with another salt, aluminium chloride, and found the two powders reacted together quickly and formed, amazingly, a clear, colourless liquid an ionic liquid.

Hurley and Weir's ionic liquid remained a chemical curiosity for decades. Now, though, the chemical industry is under pressure to find cleaner alternatives to the volatile, toxic and flammable organic solvents that are currently used. And pockets of research had hinted that ionic liquids might have useful properties, such as being able to dissolve almost anything including coal, plastics, metals and even rock. Moreover, ionic liquids cannot evaporate, do not burn, are fairly non-toxic and can be easily recycled. All of which would make them attractive solvents.

Now, Ken Seddon of Queen's University Belfast (QUB) and his team have taken ionic liquids off the shelf to develop clean and efficient chemical reactions that avoid noxious solvents and could revolutionise the industry. Earlier this year their college also established the Queen's University Ionic Liquid Laboratories (QUILL) so that any developments made there could also be used in the real industrial world. "This is the first centre in the world focusing on ionic liquids", enthuses Seddon.

Petrochemical giant BP Amoco is the latest to join QUILL, making 17 members so far. Other firms who believe that ionic liquids could be important, and who have also joined QUILL, include ChemVite and DuPont in Northern Ireland; US companies Chevron and Biopolymer Engineering; Britain's BNFL, ICI and Merck; Sasol of South Africa, and Schering Plough (Ireland).

Seddon's team has already made ionic liquids, based on chemical cousins of Huirley and Weir's original powders, that can dissolve the components of some crucial industrial reactions. The Friedel-Crafts reaction, for instance, is used industrially to add alkyl and acyl groups to molecules containing aromatic rings, such as benzene and pyridine, and other carbon molecules like dodecene, resulting in more complex compounds such as ketones.

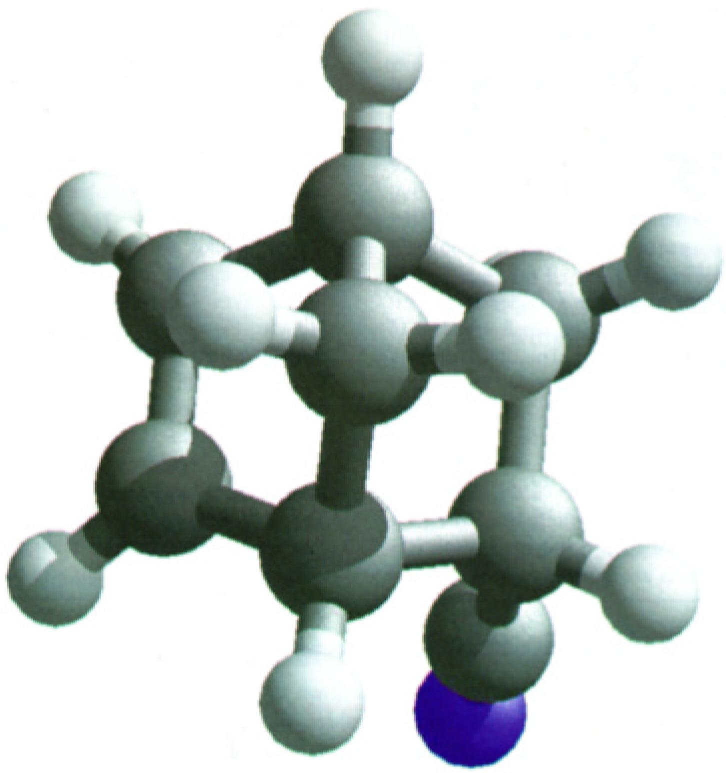
"These compounds", Seddon explains, "can be used as precursors to make pharmaceuticals, agrochemicals and even flavourings and perfumes." indeed, Seddon's team has already synthesised the musky fragrance molecules, traseolide and tonalid, in this way.
So, ionic chemistry might save the musk deer, currently threatened with extinction because of the demands of the perfume industry.

Another important aspect of this new chemistry is that reactions in ionic liquids are cooler than their current industrial counterparts. And lower temperatures mean less energy, which reduces costs and makes the processes even more environment friendly.

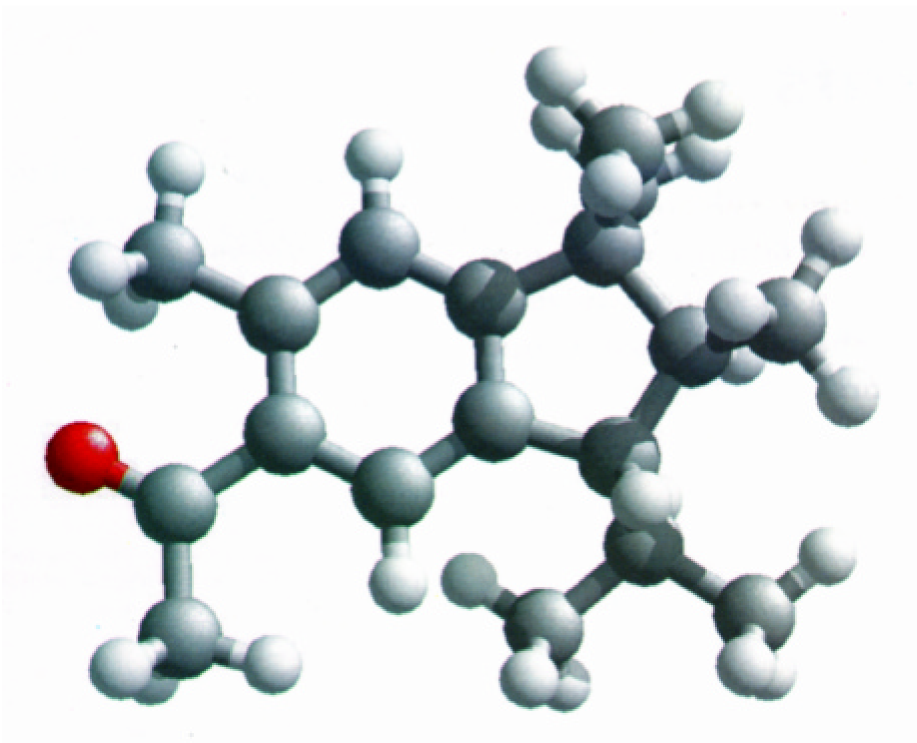
One common industrial reaction is the Diels-Alder reaction. This stitches together a carbon compound containing two double bonds with another compound that has one double-bond, to form a ring. Chemists can produce all sorts of complicated molecules using this reaction simply by changing the peripheral chemical groups attached to the double bonds in the starting materials.

The ring cycle

Seddon, Martyn Earle and Paul McCormac have used ionic liquids to carry out the Diels-Alder reaction of cyclopentadiene, a ring shaped molecule with two double bonds. By reacting other molecules containing their own double bond, this molecule can be used as a starting point to synthesise a range of useful two-ring compounds. The products are themselves useful in the petrochemical and pharmaceutical industries. Alternatively, they can be converted into other products. For instance, cyclopentadiene reacts with acrylonitrile to



The Diels-Alder molecule: the QUB research team has made ionic solvents that can synthesise this molecule faster and more cheaply than using conventional techniques.



An almost infinite range of ionic liquids can be made by varying the ions used.

make a bicyclic compound which is used as a pharmaceutical precursor. The Diels-Alder reaction can also be used to make poly-isobutene, a synthetic rubber used as a thickening agent for lubricants and a filler in the construction industry. Significantly, Seddon claims that their product is purer than the current commercial material.

Yet another advantage, adds Seddon, is that ionic liquids do not mind small amounts of impurities, such as water. The tiniest drop of water will normally wreck Diels-Alder reactions, so the first step is always to ‘dry’ everything thoroughly. Using ionic liquids avoids this inconvenience.

The ionic liquid version of the Diels-Alder reaction is also more efficient than the commercial industrial counterpart, especially as the products are easily separated from the solvent: they float to the top of the reaction vessel and can be skimmed off, like cream from milk. The solvent itself can then be reused. This ease of separation means that no complicated processing is needed to retrieve products, unlike reactions involving organic solvents.

Ionic liquids are beginning to attract interest around the world. Yves Chauvin at the French Petroleum Institute (IFP) near Paris is making ionic liquids at room temperature. Chauvin and colleagues use powdered nickel catalysts to speed up reactions involving simple hydrocarbon compounds known as alkenes. This way they turn a cheap starting material into a valuable commodity chemical.
For instance, they can couple alkenes together, add hydrogen atoms and convert them into oxygenated versions. Such compounds are useful precursors for plastics, perfumes, medicines and agrochemicals. IFP has already commercialised one of its ionic liquid processes, which they call DIFASOL. This converts butene, the four-carbon alkene, into iso-octene, an important step in transforming raw PVC into plastic.

Jairton Dupont and his team at the Federal University of Rio Grande do Sul, Brazil, are using ionic liquids to dissolve palladium catalysts. These catalysts can be used to turn organic compounds such as butadiene into complex alcohols for use in pharmaceutical and dye manufacture.

Ionic liquids could also be used to produce cleaner fuels for cars. Tom Welton of Imperial College, London, is working with York University’s Paul Dyson on oil-derived fuels, such as petrol and diesel. These fuels contain large amounts of cancer-causing and polluting ‚aromatic’ compounds, such as benzene and phenanthrene, which incidentally burn less efficiently than straight hydrocarbons.
By adding hydrogen atoms to these molecules during fuel refining they can be converted into ‘saturated’ hydrocarbons. This boosts the fuel’s efficiency and reduces sooty emissions from engines. Inexpensivemethods of carrying out this process have proved elusive, but Welton and Dyson found that, using a catalyst dissolved in an ionic liquid, they can add hydrogen atoms to these aromatic compounds at room temperature, and so convert the fuels into leaner burning compounds very cheaply.

Ionic liquids cannot evaporate, don’t burn, are non-toxic and easily recycled

An almost infinite range of ionic liquids can be made by varying the ions used, explains Seddon: by selecting the positive and negative ions, new ionic liquids can be tailor-made for countless reactions. “In fact there are at least 1018 possibilities, which is plenty for most chemists to be going on with!” It will be possible to ‘custom-design’ ionic liquids for any application, or modify their properties (such as viscosity, density, and solubility).

Chemists are constantly creating new ionic liquids by trying different ion mixes, and discovering just how smoothly and efficiently their reactions can proceed. They are close to producing an ionic liquid for almost any reaction that would normally use a noxious organic solvent. And with several groups now working on the technology, including QUILL in Northern Ireland, the chemists should soon clean up.

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How do they do that?

HOW can an ionic material be liquid? It boils down to bonds and packing. in an everyday crystalline ionic lattice, like that found in table salt, the positive sodium and negative chloride ions behave like so many sticky apples packed neatly in a crate. However, if instead of tiny uniform ions, a material is made from bulky and asymmetric organic ions, then the ions cannot pack so neatly together - one might think of trying to pack Coke bottles with bananas - and no amount of rearranging will pack them neatly. In fact, the charges on each ion are held so far apart by their bulkiness that they do not stick well together at all, let alone pack. This lack of sticking means they do not form a solid. Should they ever begin to form solid crystals, a little jostling heat will readily break them apart again, into a liquid. “What it boils down to”, explains Tom Welton of Imperial College, “is that an ionic liquid is a salt that doesn’t make a very good solid”. In the liquid state the individual ions can move freely around and interact, and easily dissolve chemicals added to the reaction flask.