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Green solutions

Many reactions take place in solution. Water is a familiar solvent but there are many others. In this article we explore some of these, including a rather surprising one — carbon dioxide — which is a non-polluting 'green' solvent.

GCSE key words
Solvent
Particle theory
Solution
Carbon dioxide

The chemical industry relies on solvents to produce many everyday products we take for granted, such as medicines and plastics. The covalent organic starting materials used in these products often will not dissolve in ionic water (just as oil and water don't mix — think of salad dressings). Instead of water, industry uses solvents called **volatile organic compounds** (VOCs).

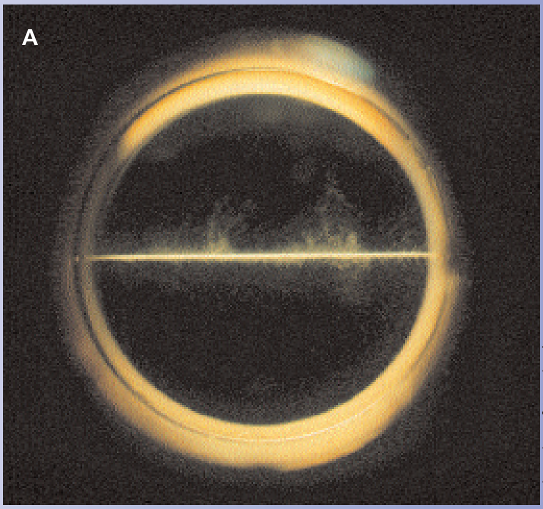
VOCs are derived from petrochemicals. This means they are produced from oil, which is a non-renewable resource. They are also associated with hazards, for example many are highly flammable. When the chemical reaction is complete, the solvent is either recycled or disposed of by incineration. But incineration can cause atmospheric pollution which can damage the environment and our health.

ALTERNATIVE SOLVENTS

Researchers are trying to find alternatives to using VOCs as solvents. In our research at the University of Nottingham, we have used carbon dioxide as a solvent for many different types of chemistry and now industry is starting to use it too. Carbon dioxide is a gas at room temperature (it is a constituent of air and it makes the bubbles in carbonated drinks). It is not very good at dissolving organic compounds because gas molecules have weak attractive forces and cannot force the reactants together to produce a chemical reaction. However, if we compress carbon dioxide and heat it a little, it becomes a **supercritical fluid** and a much better solvent.

SUPERCRITICAL FLUIDS

Imagine boiling some water in a sealed container. As the water heats up, some of the molecules gain enough energy to break the attractive forces of the



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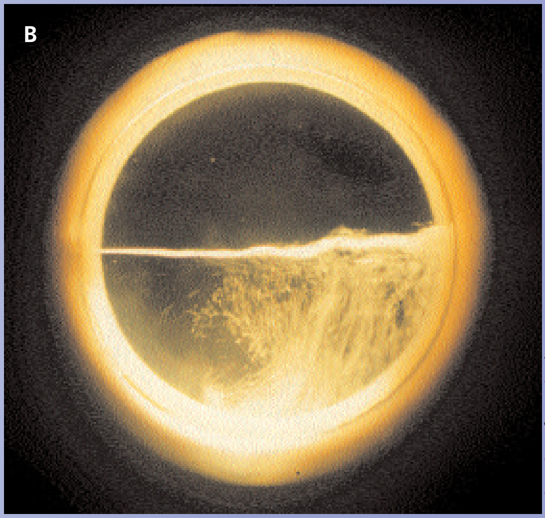

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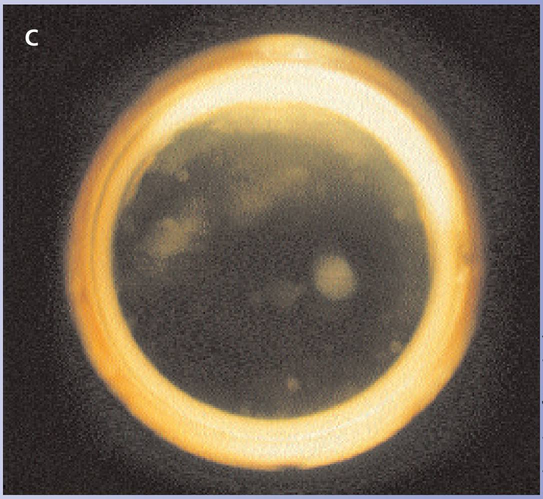

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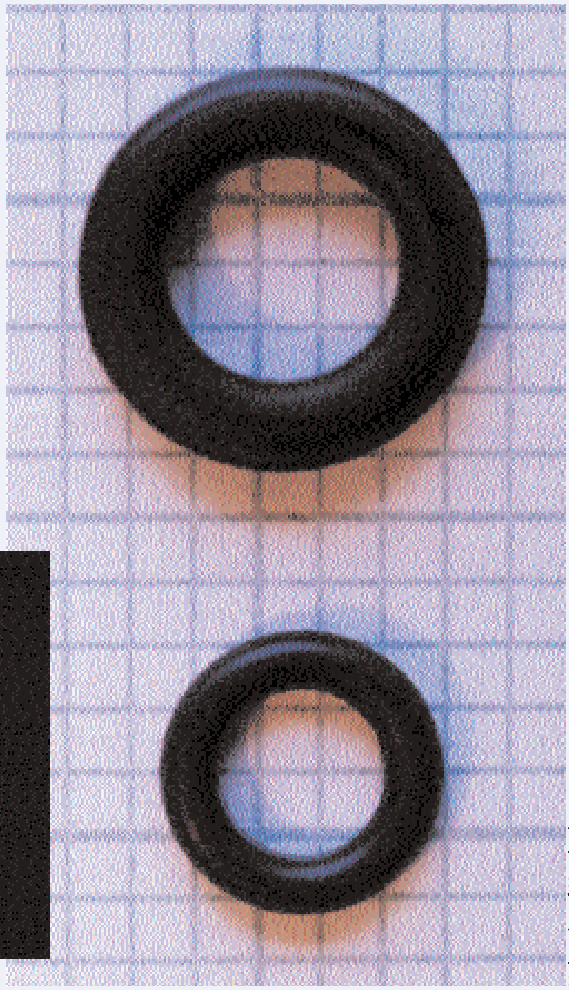
These three photographs show liquid being heated in a sealed vessel. You can see the liquid 'boiling' (B) and, at a certain temperature and pressure, it becomes a supercritical fluid (C)

Never try heating anything in a sealed container yourself. A large amount of pressure will build up and burst open the container with lethal force. Researchers use specially designed stainless steel equipment and follow rigorous safety procedures.

Right: *Carbon dioxide has swelled the polymer ring at the top. Do you know how to test for the presence of carbon dioxide? The equation for the reaction is in Box 1*

Below: *The top ring has been put in limewater and as the carbon dioxide comes out of the ring (you can see the bubbles), it reacts to form calcium carbonate, which is a white solid and makes the water cloudy*



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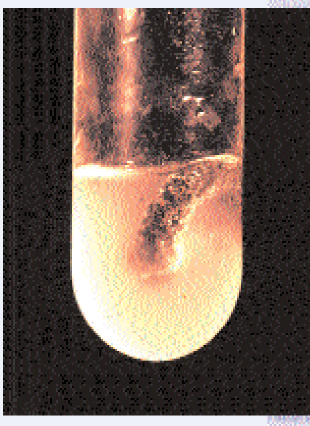


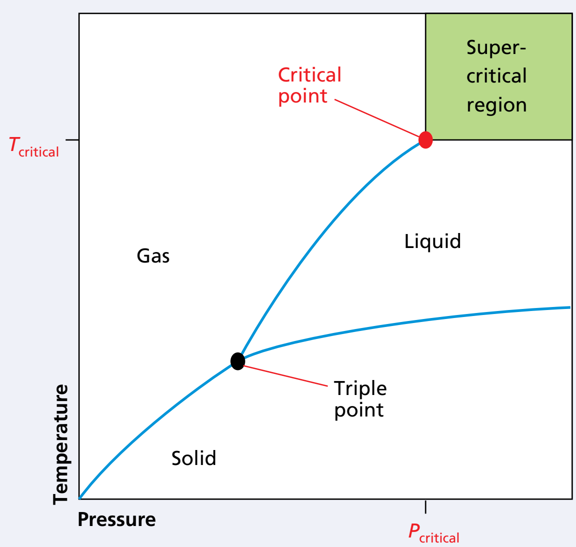


Figure 1 *A temperature–pressure plot for all matter. The triple point is the temperature and pressure at which a substance can exist in equilibrium in the solid, liquid and gaseous states. The triple point of water (0.01°C and 0.006 atmospheres) is used to calibrate thermometers. At the critical point, the liquid and gaseous states become identical. The critical temperature for carbon dioxide is 31°C and the pressure needs to be 73 times atmospheric pressure, while for water, the temperature needs to be 374°C and 218 atmospheres*

BOX 1 SOLVENTS

Chemical reactions are normally carried out in a solvent. Solvents are needed to mix the chemicals together and to remove any heat produced during the reaction. Without solvents, the reaction may give the wrong product or even blow up!

You will have used water as a solvent in the laboratory to dissolve ionic compounds. For example, calcium hydroxide is a solid and must be dissolved in water to help it react with carbon dioxide. This produces calcium carbonate, which is used to treat heartburn and indigestion. The equation for the reaction is

$$Ca(OH)_2(aq) + CO_2 \rightarrow CaCO_3 + H_2O$$

neighbouring molecules and so become a gas — the water starts to evaporate. The density of the liquid decreases (as molecules leave) and the density of the gas increases (as molecules enter) until liquid and gas have the same density. At this point, the meniscus (the surface separating the liquid and the gas) disappears and a different state of matter, called a supercritical fluid, is formed.

A supercritical fluid is a state of matter between a gas and a liquid and has some of the properties of both. For example, like a liquid, a supercritical fluid can dissolve things, but, like a gas, it can also diffuse through a solid. We can take advantage of these properties to make useful organic compounds that would be hard to make in conventional solvents.

POLYMER PROCESSING

A **polymer** is a chain of repeating units, called **monomers**. Polymers are all around you, from your baked potato (starch) to everyday plastics such as those in carrier bags (polyethene) or protective packaging (polystyrene). Using supercritical carbon dioxide ($scCO_2$) to process polymers not only replaces harmful conventional solvents but also allows new types of polymers to be made. When a polymer and $scCO_2$ are mixed together, the carbon dioxide is forced into the polymer and causes the polymer to swell up like a balloon. Substances can then be added into the polymer.

One possible application of $scCO_2$ is in modifying the plastic used for artificial hip joints. If the material can be made harder, then it may last longer in the body. We are trying to achieve this by adding metal particles to the polymer using $scCO_2$. Another area of our research using $scCO_2$ involves mixing drugs into biodegradable polymers. These new products can be taken by the patient as a pill. The pill slowly degrades in the body and the drug is released in a controlled way over a set period of time.

Supercritical carbon dioxide is an ideal solvent for processing polymers for medical applications because, unlike liquid VOCs, the carbon dioxide gas

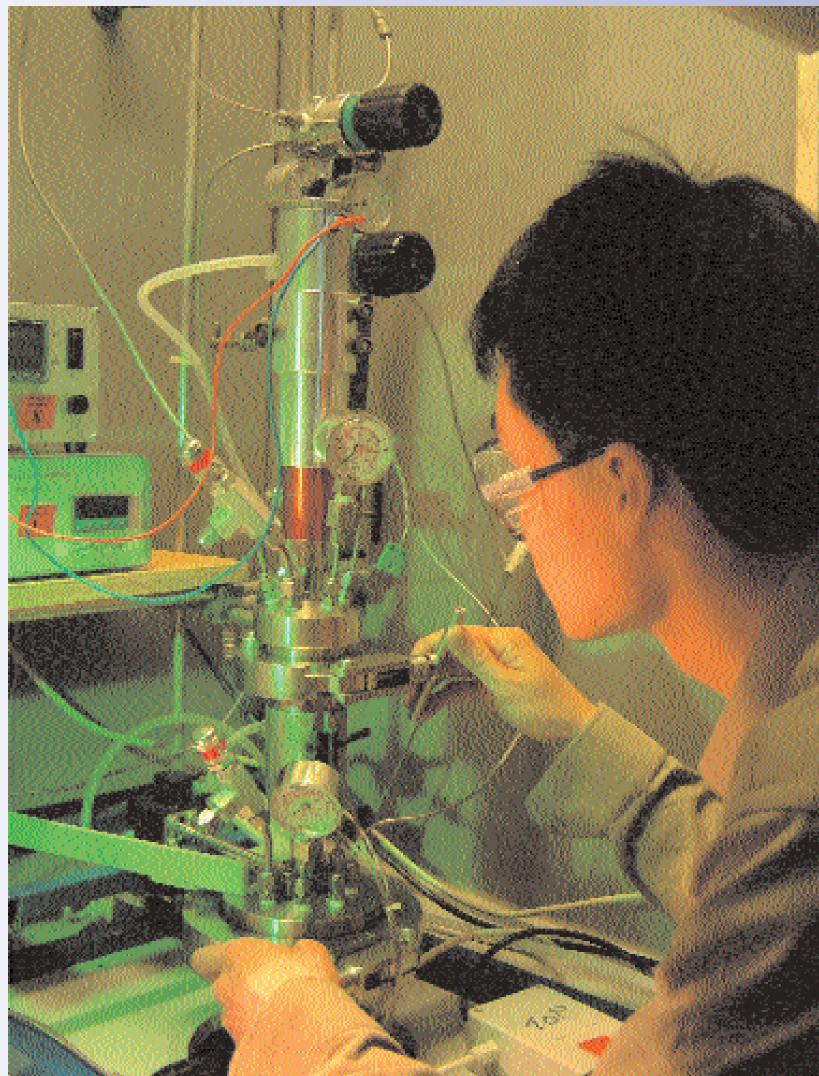
diffuses out of the polymer and leaves no toxic residues behind.

GREEN CHEMISTRY

You might think carbon dioxide is not really a 'green' solvent because it is a so-called greenhouse gas, and increased levels of carbon dioxide in the atmosphere contribute to global warming. However, for our work we take carbon dioxide from companies that produce a lot of it (e.g. the brewing industry) and reuse it over and over again. We rarely emit it into the atmosphere. At the end of a reaction, the carbon dioxide is separated from the product by allowing it to expand to a gas and then compressing it again, ready for reuse.

Research carried out at the University of Nottingham is now being applied in industry to make new processes 'green' and existing processes 'greener'. Using green solvents is just one area of green chemistry, which aims to use less harmful chemicals and increase the efficiency of chemical processes.

For example, if the starting materials are harmful, green chemists try to find alternative starting materials to make the same product. If the product is harmful, green chemists try to find a different product that performs the same function. Using a catalyst speeds up the reaction so less energy is required — for this purpose organisms are being used to convert reactants to products, utilising their enzyme systems.



A researcher uses high-pressure equipment to process biodegradable polymers using supercritical carbon dioxide. When the pressure is released slowly, the carbon dioxide leaves holes or pores inside the polymer. Polymers of this type may, in the future, be used to support the growth of new cells, such as liver or bone cells, in damaged tissue in the body. The polymer degrades over time in the body, leaving behind the new tissue. The photograph on the left shows small pieces of our porous polymer that have supported the growth of bone cells in the laboratory

Industry is starting to realise that it is cheaper to use green chemistry than to comply with the ever-tightening regulations on the use and disposal of hazardous chemicals, and this is good news for the environment. The University of Nottingham is the first in the UK to offer an undergraduate degree in green chemistry, so a new generation of students will be helping our planet become a healthier place to live!

BOX 2 WEBSITES

Find out more about our supercritical research at:
http://www.nottingham.ac.uk/supercritical
and about biodegradable polymers, which support new tissue growth at:
http://www.nottingham.ac.uk/pharmacy/tissue-eng
Go to a cyber wonderland of polymer fun at:
http://www.psrc.usm.edu/macrog
More on green chemistry can be found at:
http://www.epa.gov/opptintr/greenchemistry and
http://www.chemsoc.org/networks/gcn
while for wider environmental issues look at:
http://www.environment-agency.gov.uk

***Lucinda Dudd** is studying for a PhD in supercritical water at the University of Nottingham. **Kelly Morley** has completed her PhD and now works for the Green Chemistry Network promoting all areas of green chemistry.*