Defying the laws of physics?

Scientists working at the Institut Laue-Langevin (ILL) and the University Joseph Fourier in Grenoble, France, have discovered a crystal that appears to defy the laws of gravity. **Giovanna Cicognani** from ILL reports.

Equipment required: one inelastic neutron scattering instrument

One of our first encounters with physics is the mysterious transformation of water: from its solid state in the freezer to a liquid at room temperature and finally to a gas on the stove. Later we learn that although different substances have wildly different freezing and boiling points, just about everything can be transformed into these states – and the key is temperature. But what about something that melts when cooled and solidifies when heated?

Marie Plazanet, an instrument scientist at the ILL, and her colleagues have identified an aqueous solution that forms a milky-white solid when heated to about 60°C and that turns back into a homogenous, transparent liquid when cooled. The solution is a mixture of water, a sugar called alpha-cyclodextrine, and methylpyridine, a component of plastic.

To get a feeling for just how strange this is, says Giovanna Cicognani, Scientific Coordinator at the ILL, you could imagine a glass of Coca-Cola® with ice in it. "Everybody knows what would happen with time – the ice would melt and the Coca-

BACKGROUND

The recipe

To create the mysterious mixture discovered by the Grenoble scientists, mix 200 mg of alpha-cyclodextrine ($H_{60}C_{36}O_{30}$) with 1 ml of 4-methylpyridine (H_7C_6N) and a very small amount of water. The mixture should be liquid at room temperature. When heated, it should become solid.

Neither the mixture nor its constituents are dangerous, but 4-methylpyridine is very smelly.

BACKGROUND

Hydrogen bonds

Water is a member of a group of substances called the Group VI hydrides. Many of these are vile-smelling gases: hydrogen sulphide, hydrogen selenide and hydrogen telluride - each more repellent than the next. Is that true of all of the Group VI hydrides? Well, not quite. Hydrogen oxide is an exception in several ways: for one thing, it is odourless; for another, it is a liquid. Of course, it too can be dangerous: prolonged contact with the solid form can cause tissue damage, and in gaseous form, it can cause severe burns. Nonetheless, hydrogen oxide – water – is also essential to life on earth.

So what makes water so different from the other Group VI hydrides? Principally, hydrogen bonds.

A hydrogen bond is an attractive force which exists between polar molecules of opposite charge. As the name implies, one part of the bond involves hydrogen atoms. Water molecules, for example, are polar molecules which have a partial negative charge (the oxygen atom) and a partial positive charge (the hydrogen atoms). When water molecules are close together, their positive and negative charges attract each other.

The hydrogen bonds that form between water molecules account for some of the essential – and unique – properties of water. It is the attraction due to hydrogen bonds that keeps water liquid over a wider range of temperatures. This is because the energy required to break multiple hydrogen bonds causes water to have a high heat of vaporisation; that is, a large amount of energy is needed to convert liquid water, in which the molecules are attracted through their hydrogen bonds, to water vapour, in which they are not.

Cola would cool down a bit. In this case, though, when you heat the glass to 60°C, the whole thing would solidify."

The scientists investigated the substance using neutrons generated by a nuclear reactor operated for research purposes at the ILL. A chain reaction in the reactor produces neutrons, which are collected in a controlled, tightly focused beam that is aimed at crystals or other materials. The neutrons in the beam collide with neutrons in the sample, creating a diffraction pattern that can then be reinterpreted into a high-resolution picture. This yields an atom-by-atom map of the sample.

"We used neutrons to probe the inner properties of our solution, showing that, in the solid phase, a rigid and ordered structure is formed, even though another part of the mixture remains liquid," explains Ralph Schweins, an ILL scientist and a member of the experimental team.

The Grenoble scientists believe that this change of state can be explained by the formation and breakage of hydrogen bonds. Above 60°C, hydrogen bonds form between either the cyclodextrine and the methylpyridine, or the cyclodextrine and the water molecules, maintaining the stability of the solid. At lower temperatures, these hydrogen bonds break and new hydrogen bonds form between the cyclodextrine molecules, which result in the solid becoming a liquid again. Modelling of the molecular movements in the solution has confirmed these findings.

So the substance doesn't really defy the laws of physics after all. But it does give some interesting insights into hydrogen bonds, which play a vital role in our lives – not just when it's cold outside and we're hoping for snow!

Resources

The findings are reported in more detail in: Plazanet M et al. (2004) Freezing on heating of liquid solutions. *Journal of Chemical Physics* **121**: 5031-5034, doi: 10.1063/1.1794652

With its international funding and expertise, the Institut Laue-Langevin (ILL) offers scientists and industry the world's leading facility in neutron science and technology. From its Grenoble site in south-eastern France, the institute operates the most intense neutron source on earth. For information about ILL, its research and events, visit: www.ill.fr

Information on the Université Jacques Fourier in Grenoble can be found at: www.ujf-grenoble.fr

The Institut Laue-Langevin

CLASSROOM ACTIVITY

Discussion:

1. Can you think of a practical application for the newly studied mixture?
2. Can you think of any other mixtures that might behave in the same way?
3. Explain hydrogen bonding in your own words.
4. Why is hydrogen bonding so strong in water but not in other Group VI hydrides?
5. Do you know any other examples of hydrogen bonding?
6. Are you aware of any uses of state change?
7. How much do you know about neutron analysis? How much can you find out on the worldwide web?

REVIEW

The laws of physics are seemingly defied. In a humorous style, we learn that the gaseous state does not necessarily follow the liquid state as temperature increases. Instead, some substances melt when cooled. This article gives a nice example of investigating an old topic (hydrogen bonds) in the light of recent discoveries.

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