Water-based storage

Confined in a Cage of Water

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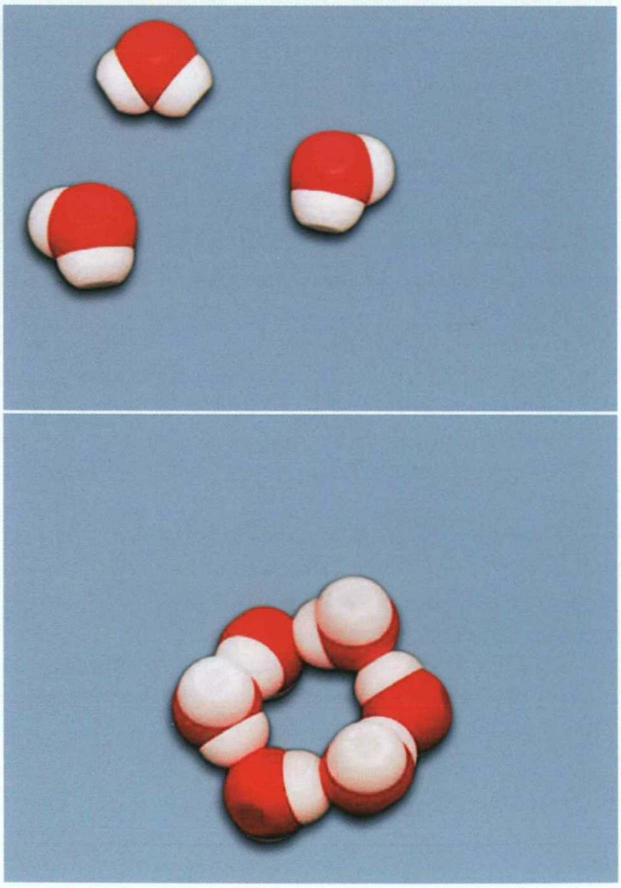
Whenever we drink our coffee, brush our teeth or swim in a lake, we usually do not realize how remarkable a substance water really is

We are accustomed to the fact that water is one of the most ubiquitous substances in our lives, yet most people are unaware that its properties are in fact remarkable and in many respects atypical. Ice floats on water, which means that the former is less dense than the latter. This property is extremely rare among substances (whose solid forms usually have greater density than their liquid counterparts) and it enables numerous water-inhabiting organisms to survive during the winter, since water reservoirs do not freeze all the way to the bottom. The considerable high value of water's heat of vaporization is of fundamental importance for processes that regulate the body temperature of living organisms as well as for maintaining a sufficient water content within them. Seas and oceans act as reservoirs of heat, due to the fact that they see considerably less fluctuation in temperature over the course of the year than observed on land. Water functions, therefore, to moderate the climate. Many of water's other physical properties are also atypical - in fact, there are more than 40 such special properties of water, usually connected with its unique structure.



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Models of water molecules and of the undulated hexagon they form, as an element of the ice structure

A unique molecule

Indeed, it is the structure of water that is crucial for understanding its properties. The water molecule is small: it consits of one oxygen atom and two hydrogen atoms. Yet it is useful to view this molecule from a somewhat different angle, namely treating it as an oxygen 'nucleus' plus two hydrogen atoms and two electron pairs, all arrayed in a tetrahedral fashion. Each of these four elements can form bonds with 'neighboring' molecules: each hydrogen atom can form a bond with the electron pair of a neighboring molecule, whereas each electron pair 'receives' such a bond from its surroundings. That is why the water molecule is referred to as a donor of two hydrogen bonds and an acceptor of another two hydrogen bonds. This results in a system of four hydrogen bonds that are usually impossible to differentiate later on.

The tetrahedral configuration of the bonds around the oxygen atom is of fundamental importance. Bear in mind here that the incredible diversity of the crystal lattice structures seen in organic compounds results from the tetrahedral arrangement of bonds around the carbon atom. Water manifests similar structures, yet hydrogen bonds are far weaker than the covalent bonds present in organic compounds. Thus, structures made up of water molecules are bonded more weakly, can be created more easily, and can decompose into their components more easily.

Stored in water

An important feature of tetrahedrons is that there are always free places between them: taken alone, such shapes simply cannot be arranged to pack space fully.

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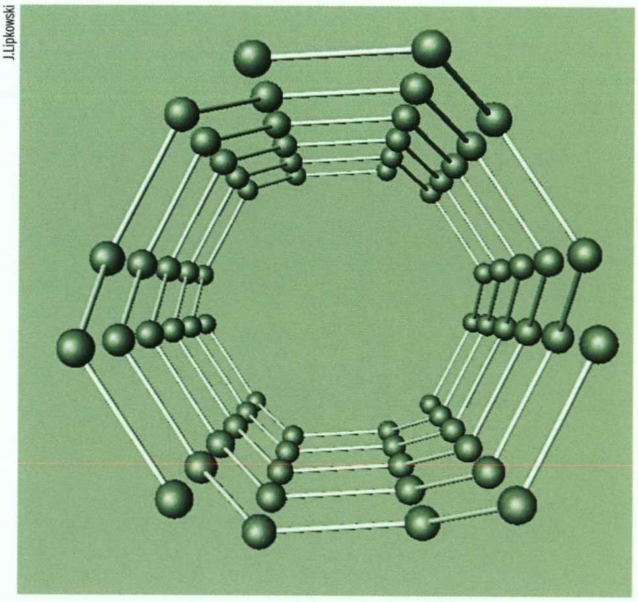
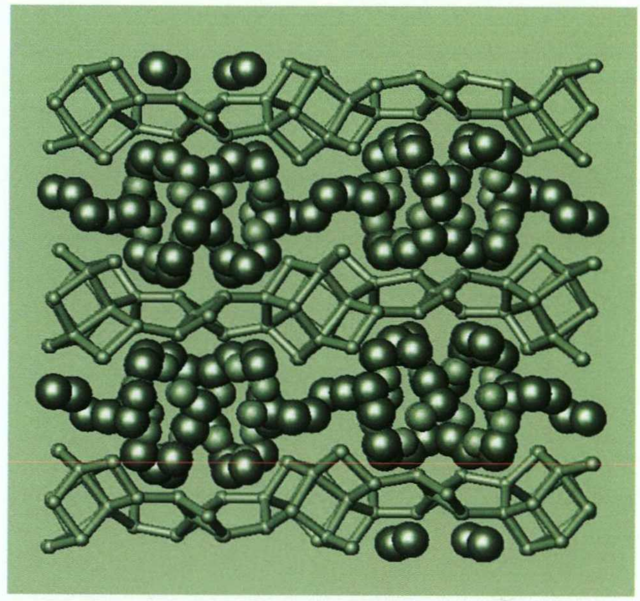


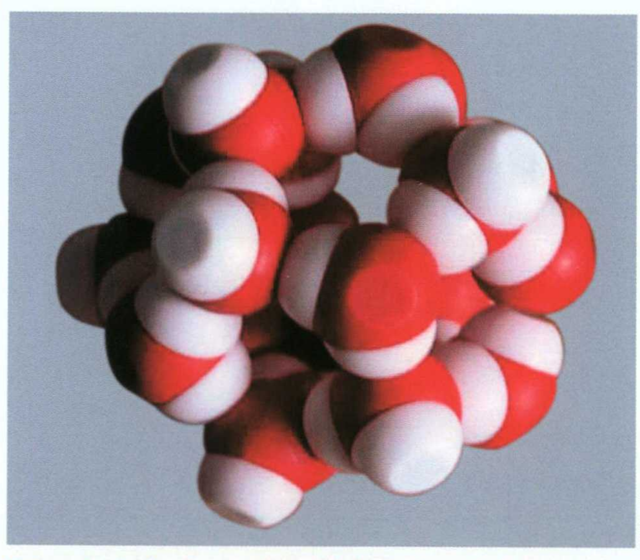


On the left: the structure of a channeled hydrate containing as its 'guest' a molecular complex called 18-crown-6 with methylammonium fluoride. On the right: the layered structure of the molecular complex hydrate called 1-crown-6 with n-propylammonium fluoride

This fact can be easily demonstrated if we compare the densities of water and the liquefied form of neon, an atom whose weight and size are similar to that of the water molecule, yet whose symmetry is spherical. Liquid neon's density proves to be about 1/4 greater. In other words, about 1/5 of water's volume consists of unfilled spaces due to the characteristic arrangement of the bonds between water molecules.

Water does 'strive' to fill those free spaces, essentially in two different ways. The first, a relatively trivial way, involves the structural deformation of intermolecular bonds. This is what happens when we push an ice-skate down on the ice: its structure is deformed, it starts melting, and the density of the entire system increases. The other way occurs only if an additional component takes part in forming the structure. If the shape of this other component enables it to fill in the 'natural' gaps in the structure formed by the primary component, i.e. water, then what consequently arises are two-component structures that can indeed be closely packed together in space. Simultaneously, these structures enable water molecules to create bonds with one another without deforming the tetrahedrally arrayed hydrogen bonds. This additional component's role is reduced to filling in the free spaces in the lattice of its 'host,' thus being only a 'guest,' yet one of essential importance: it enables the entire structure to appear and holds it together.

One of the most distinctive structural elements of so-called 'porous' water is the pentagonal dodecahedron, a shape that is one of the five Platonic solids. Here it is important that all the water molecules that form such an arrangement are, in terms of their hydrophilic functions (their ability to form hydrogen bonds), turned towards the outer part of the dodecahedron, its inner part being surrounded with water in a way that precludes hydrogen bonds from forming there. This special property makes it possible for the free interior of the dodecahedral space to be filled in by atoms or molecules that have no distinct ability to form specific bonds with water molecules. This free space can be filled in with atoms of the noble gases, which remain confined there until the lattice is destroyed when the crystal is melted, or by such organic molecules as hydrocarbons, otherwise known not to react with water. The prerequisite for this is that their shape and size



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Water molecules forming a pentagonal dodecahedron – the fundamental structural element in clathrate hydrates

must match the free space available in the host's structure. Substances held together by means of such connections are referred to as clathrate compounds (from the Latin word clathratus meaning cage-like) and are some of the most intriguing types of chemical compounds.

Researchers are now considering how to use water to store gases for practical purposes, especially with a view to eliminating the basic greenhouse gas, namely carbon dioxide. A series of patents have been developed in the field of technologies for disposing of waste carbon dioxide by stashing this unwanted gas away at great underwater depths. From the physicochemical point of view, this goal is considerably more complex than the common natural phenomenon whereby methane combines with water. The conditions necessary for water/CO_2 clathrates to be stable are relatively complex, and so these technologies are not yet of practical use.

One very hot topic in contemporary chemical research involves 'supramolecular water assemblies,' associated molecules made up of water molecules and other substances, held together without covalent bonds, i.e. by means of intermolecular forces. Classic examples are here clathrate hydrates of gasses, such as the noble gases and the aforementioned methane. An important limitation for such structures is the size of the free space present inside the structure of water: there is not enough room for molecules larger than toluene (C_7H_8). Yet as far back as in the 1960s, researchers discovered that it was possible to create clathrate structures in a way that allowed the individual 'cages' to join together, thus creating sizable spaces capable of taking in relatively large molecules or molecular ions.

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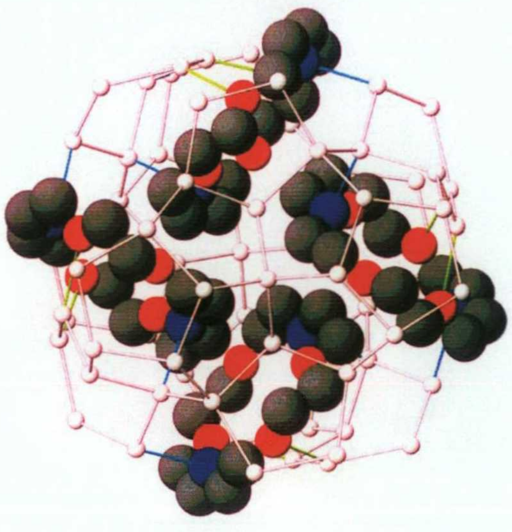

The structure of a hydrate called 1,10-diaza-18-crown-6, depicted as to show its structural analogy with clathrate hydrates (the 'cage' is in this case incomplete)

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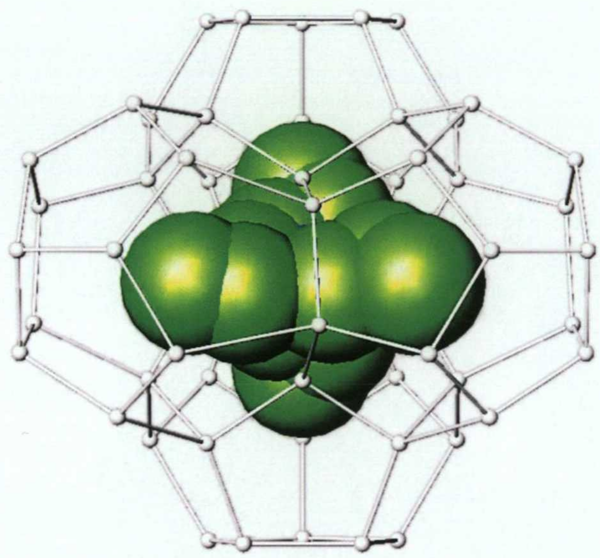

A model of a large clathrate 'cage' made up of four symmetrically situated dodecahedrons composed of water molecules and containing a tetra-n-propylammonium cation as its 'guest.' The small, light-colored balls symbolize the oxygen atoms of the water molecules, whereas hydrogen atoms are not shown, their position being on the lines between the oxygen atoms

For more than a decade, supramolecular water assemblies have been the subject of research carried our in our laboratory at the PAN Institute of Physical Chemistry, in cooperation with the Russian Academy of Sciences' Institute of Inorganic Chemistry in Novosibirsk and the Academy of Sciences of Moldova's Institute of Applied Physics in Chisinau. Our research results have shown that very interesting hydrates with a structural topology that differs from that of clathrates can be created, demonstrating layered, channeled and zeolite-like structures. They have been successfully obtained in crystalline form, and their structure identified.

The structural properties of water which this article describes constitute only a fraction of our basic knowledge on water molecules; this sample has been selected in order to highlight certain natural properties. Our understanding of the processes that involve water molecules is still far from comprehensive, yet one thing is certain: but for the distinctive properties of water, neither we, nor the Earth as we know it, would exist. ■

*based on a paper submitted by Janusz Lipkowski, selection and editing by Weronika Śliwa

Further reading:

'Water Structure and Behavior' http://www.lsbu.ac.uk/water/

Lipkowski J. (2003) Hydrophobic hydration of macrocyclic host molecules and their complexes. *XXVIII International Symposium of Macrocyclic Chemistry*, Gdańsk.