appeared on 17th April 2013

Water when things get rough

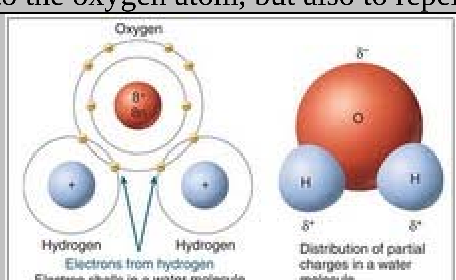
There are many sides to plain old H_2O, says S.Ananthanaryanan

The presence of water is the crucial factor in many of the wonders of our earth, including the presence of life itself. But water also exists in forms quite different from what living things are familiar with, to make possible other, non-life-related features of the earth. These include different crystal structures when water is in the form of ice and also forms of liquid, when water is at high temperature and under pressure.

Christoph J. Sahle, Christian Sternemann, Christian Schmidt, Susi Lehtola, Sandro Jahn, Laura Simonelli, Simo Huotari, Mikko Hakala, Tuomas Pylkkänen, Alexander Nyrow, Kolja Mende, Metin Tolan, Keijo Hämäläinen, and Max Wilke, of Germany, Finland and France report in the journal, ***Proceedings of the National Academy of Sciences***, that water undergoes structural changes at the molecular level, which makes it an aggressive solvent, at high pressure and temperature,. These conditions exist deep under the surface of the earth and knowing how water behaves is vital to understand the movement of metals and minerals and the formation and composition of the earth's mantle and crust.

The wonders of water

Water is known as the ***universal solvent***, because a great number of substances (though not all) dissolve in water. This property is because of the structure of the water molecule. While water is H_2O, or two hydrogen atoms connected to one oxygen atom, there are peculiarities which make this combination unique. One is the balance created by the relative mass of the atoms – the oxygen atom is about 16 times heavier than a hydrogen atom. As the atoms join because the two hydrogen atoms share their individual electrons with the oxygen atom, which reaches a stable state with the help of the two electrons of the hydrogen atoms, the hydrogen atoms in combination are positively charged, while the oxygen atom is negatively charged. The charge makes the hydrogen atoms get attracted to the oxygen atom, but also to repel each other. The result is that the hydrogen atoms are



on opposite sides of the oxygen atom. But being directly opposite is an unstable condition and the hydrogen atoms can be a little nearer to the oxygen atom, but kept that way because they are also nearer to each other, if the hydrogen atoms are a little to the side, shaped something like a shallow 'V'.

The result of this shape of the water molecule is that it is lop-sided, the two positive charges are to one side and the negative charge is to the other. The water molecule, when seen from a distance, is not an uncharged body, like a molecule should be, but is like a pair of separate charges – the two hydrogen atoms on one side and the oxygen atom on the other. This form of the water molecule has a powerful effect on other molecules. The separation of charges creates an electric field, which weakens the bonds between the components of other molecules. It is almost like molecules are prised open, like a clam shell, and materials dissolve in water. Water thus becomes a medium where chemical reactions can take place and water is the medium of choice for life processes.

Other properties, like low viscosity, which allows water to flow freely, and surface tension, which enables water to rise in the narrow channels in plants, have resulted in all forms of life on earth evolving to use processes that use water. An important condition for this use to be available is that water should be in liquid form. Life forms are hence usually found within the narrow temperature range when water is liquid, or the life form burns food to maintain such a temperature. For the same or similar reasons, life forms can be expected only in planets which have surface temperature where water could be liquid – or in ***earth-like*** extra-solar planets.

Self organizing

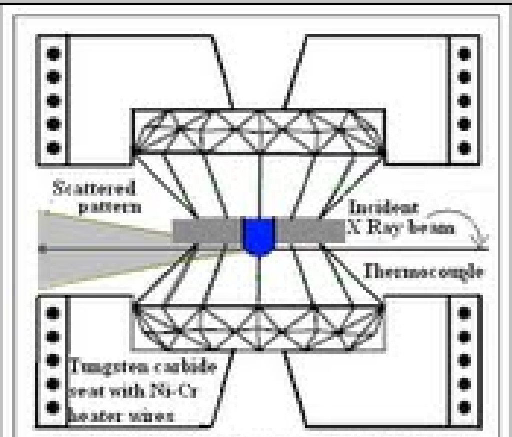
As water is thus a form of entities like pairs of charges, which are free to move as in a liquid, it can be expected that the charged-pair nature would affect the way water molecules orient themselves. The weak electric force between water molecules, called the ***H-bond***, causes water molecules to form into small, ordered structures, which get less structured as one moves away from them, The H-bonds create a hexagonal crystal form when water freezes, into ice, a form that is a little less closely packed than liquid water at 4˚C. The result is that water expands when it freezes, an effect that has profound effect on the survival of aquatic life and also in the weathering of rocks, when water that freezes in cracks causes rocks to split open. Ice crystals are known to take innumerable forms, depending on the process of their formation, but as ice is held together by H-bonds, ice is a material with negligible mechanical strength.

The area of interest is how water behaves, at the microscopic level in the liquid and gaseous forms, under different conditions. Studies have been conducted by scattering X Rays or beams of neutrons, which are uncharged subatomic particles, by samples of water. The studies are inconclusive, and the question of whether the structure of water is the same everywhere or whether there are patches of H-bond distortion surrounded by a regular structure, is open. In the work now reported, significant information has come from studies of changes in structure as conditions change have been carried out till very high temperatures and pressures.

The nature of liquids is that they form a surface, above which the substance exists in the vapour phase. When the temperature is increased, molecules gather energy and leave the bound, liquid state, to enter the vapour state. So long as this process is going on, the liquid will not rise in temperature, but only change phase, from liquid to vapour. But at a very high temperature and pressure, the surface separating the liquid and the vapour disappears and the liquid can be said to be in both phases at once. This temperature and pressure is called the ***critical point***, at which small changes in pressure or temperature can lead to large changes in the other as the molecules absorb or give up the heat of vaporization. Above the critical point, the vapour cannot be liquefied by increasing the pressure alone and should thenceforth be referred to as a gas. The critical point for water is about 374˚C, when water liquefies at a pressure of about 218 atmospheres. And as a powerful solvent, water above the critical point is used for chemical processes, destroying waste, recycling plastic and processing biomass.

But the structure of water in these conditions has rarely been studied, despite its importance to understand geophysical processes, volcanic action, petroleum formation, even studies of the origin of life. For creating a water sample at high pressure and temperature, Dr Max Wilke and colleagues used a diamond cell, sealed with a gasket made of rhenium, a rare metal that has a very high melting point and finds use in jet engines. Water was contained in a half a millimeter wide and a tenth of a millimeter deep cell and electrically heated. The temperature was measured using a thermocouple and the density and pressure measured by observing a vapour bubble in the liquid.

The micro structure of water was tested using scattering of X Rays and it was found that the structure evolves from being water-like at room temperature and pressure, to a gas-like structure at high temperature and pressure. Comparison of the results with what was calculated suggests that high temperature/pressure conditions created uniform, or homogenous structure, rather than a formation of clusters of H-bonds. The results represent important progress for analysis of processes in the condition deep under the surface of the earth.



Hydro-thermal Diamond Anvil Cell