# Fullerene Hydration

Fullerene hydration is an interesting but lesser known fact concerning the C_{60} and C_{70} fullerenes. Contrary to expectations due to their apparently hydrophobic character, they may be dissolved in water. (C_{60}-I_h)[5,6] fullerene C_{70} can be dispersed in water (> 2 mM [303]) by transferring from an organic solvent using sonication without the need of stabilizers (for example, γ-cyclodextrin [944]) or chemical modification [271] (normally its solubility direct from solid is eleven orders lower at about 20 fM). It has also been solubilized by ultrasonication in strong aqueous inorganic acids [579] as has C_{70}[1718]. The result is a kinetically-stable molecular colloidal solution also containing a variety of negatively charged clusters.[d]It forms a transparent orange solution with a broad absorption band (400-500 nm). This fullerene is an electronegative molecule showing some aromatic behavior in the twenty six-membered (but not the twelve five-membered) rings with the pi-orbitals electron density biased outwards [301].[c] C_{60} has been shown to have a high free energy of hydration and hence a high affinity for water [1851].

(H$_2$O)$_{20}$ dodecahedral cage   **(C_{60}-I_h)[5,6] fullerene**


0.95 nm   0.88 nm
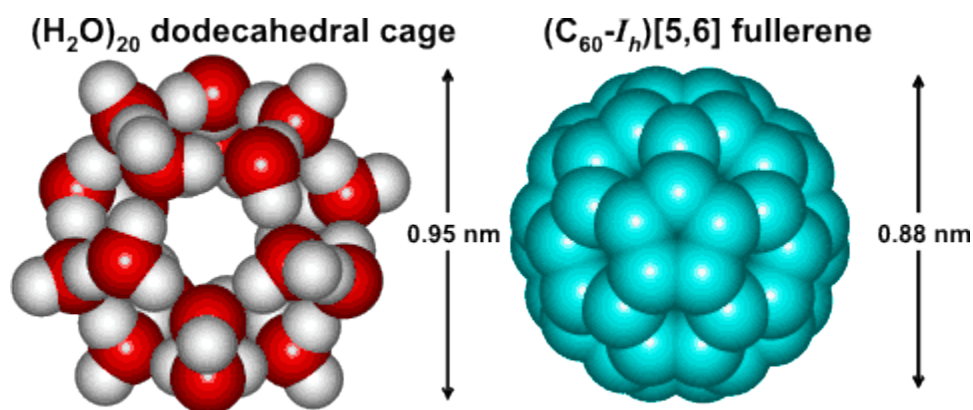
The solubility of single C_{60} molecules may be explained if the fullerene may sit (ideally) in an icosahedral water cluster (ES) missing its inner water dodecahedron. The size of the C_{60} molecule and the central aqueous dodecahedron are similar (see opposite).[e]

The inner twenty remaining water molecules are ideally situated to form -OH···pi hydrogen bonds[a] to each of the twenty 6-membered rings in the fullerene, by positioning directly over these rings; the optimum such positioning for the hydrogen bond to a benzene molecule. These 20 water molecules can then be linked through the 60 fully hydrogen bonded water molecules from the next shell of the icosahedral (ES) cluster. This arrangement would present a negatively charged surface to the environment, as found experimentally. In such a structure the carbon atoms would be centers of electron-deficiency and capable of interacting with lone pair electrons donated by extra water molecules. Such water molecules have room to sit under the outer shell water molecules to which they can hydrogen bond if some outer shell hydrogen bonds are broken or distorted. The strong hydration around the monomeric C_{60} molecules has been proposed to prevent the occurrence of toxic reactions [687].[b] The surrounding water in this complex can be partially replaced by disaccharides such as lactose [1904].

An increased tendency to ionize by these carbon-linked water molecules would increase the negative charge on the C_{60}molecules, make the C_{60} solution acidic as found [303] and give rise to the orange color of solutions. The resultant symmetrical positioning of six hydroxide ions (see below right)

increases the electron density so strengthening the -OH···pi-electrons hydrogen bonding. The corresponding hydrogen ions may be associated with the water in the immediately surrounding shell or the bulk
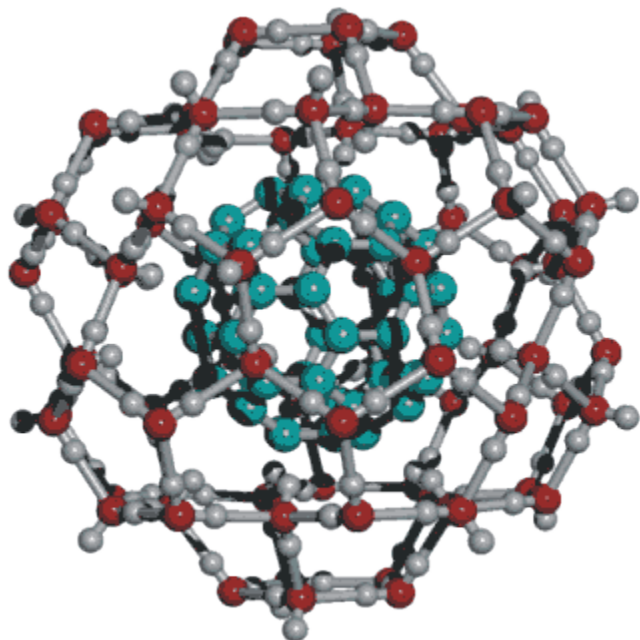

$C_{60}(H_2O)_{80}$
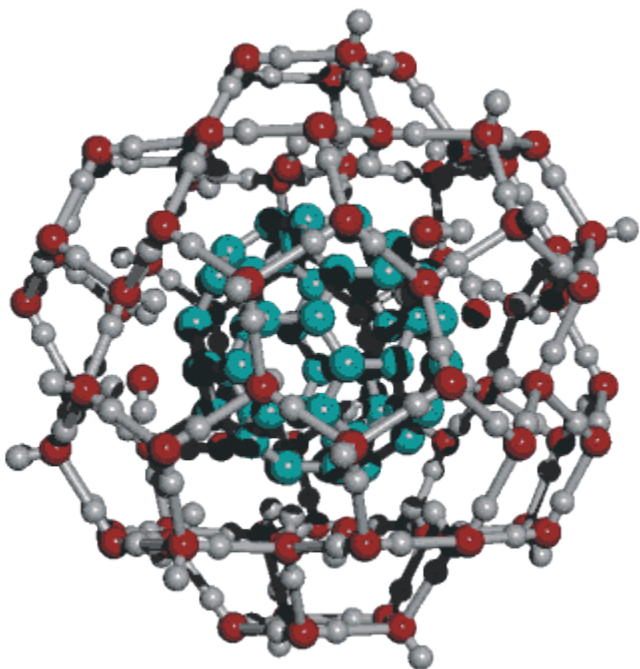
$C_{60}(OH^-)_6(H_2O)_{80}$

In the structures given above only the innermost 80 water molecules in the icosahedral cluster are shown to clarify the structuring. Recent spectroscopic studies are consistent with this structure even though the authors propose $C_{60}(H_2O)_{60}$[602]. Interactive structures are given (Jmol). Without water hydrogen bonding to the outside of these clusters, they will collapse.

A potential arrangement of six electron-donating hydroxide ions (as above right), shown blue, and the 20 hydrogen atom-donating hydrogen bonds, shown red, is given on the connectivity map of C_{60}; also showing the most important Kekulé structure [946a].[f] These 20 positions are also the most prominent positions given by molecular dynamics simulations using a state-of-the-art quantum mechanical polarizable force field [1754].
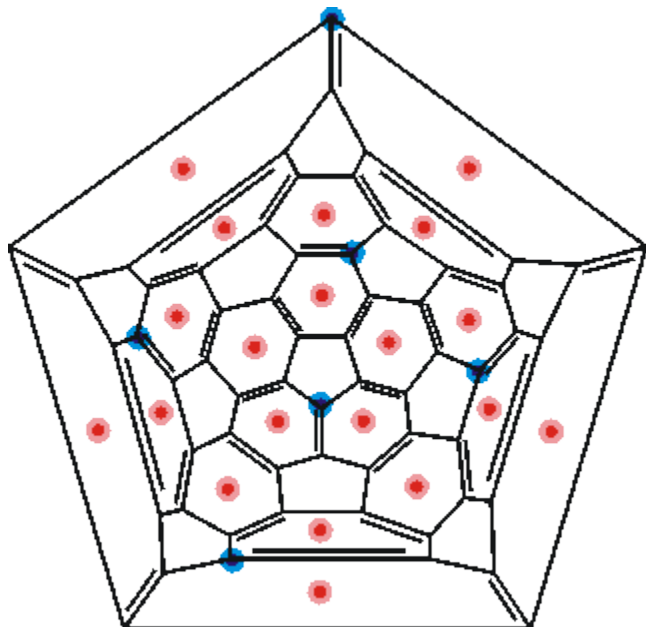
C_{60} molecules in aqueous solution form colloidal clusters based on 3.4 nm-sized icosahedral arrangements of 13 C_{60} molecules [271], where water separates the C_{60} molecules [303].
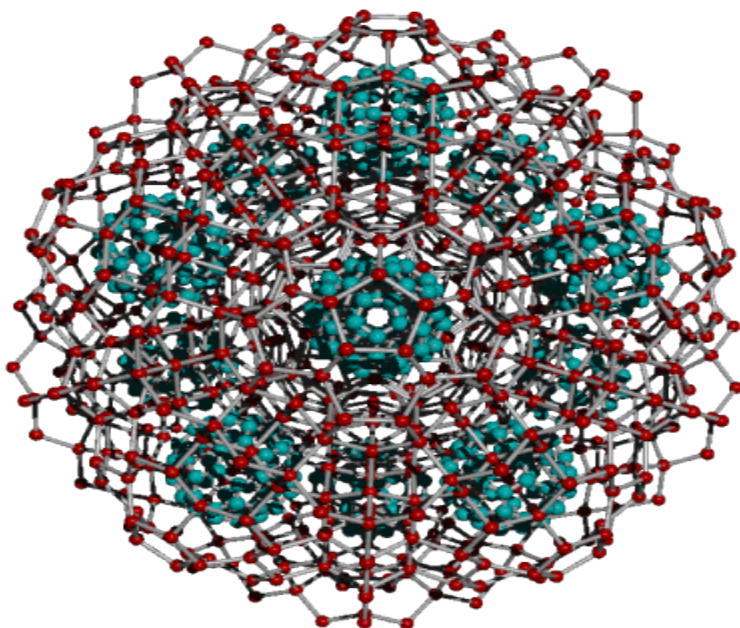
Such an arrangement is shown opposite within an expanded (but now strain-free) cluster of water icosahedral clusters. The water network is formed by fully tessellated tetrahedral tricyclo decamer $(H_2O)_{10}$ structures (see below for one). The diameter of the cluster (carbon atoms) opposite is slightly larger at 3.5 nm. Ions that destroy the expanded water network also coagulate such C_{60} hydrosols (see the Hofmeister series) [302].
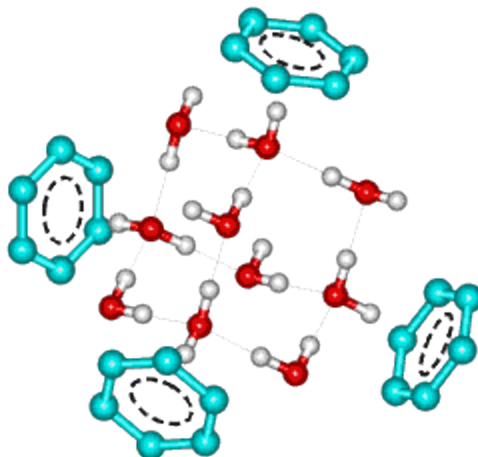
The structure is also compatible with recent findings by Grigoriy Andrievsky using piezogravimetry [303] (20 - 24 H_2O per C_{60}). This result agrees with low temperature differential calorimetry [305] where two types of water were evident, fully hydrogen bonded water melting at 0 °C (~60 H_2O per C_{60}) showing required hydrogen-bonding to hydrogen-bond deficient water, melting at -2.3 °C (19 ± 1 H_2O per C_{60}) with 30% less enthalpy change. The ratio of inner sphere to outer (second) sphere water molecules varies between 1:3 for single molecules and 2:3 for infinite sized aqueous C_{60} clusters.

Interactive structures are given (Jmol).

Theoretical calculations show that a water molecule may be placed inside the (C_{60}-Ih)[5,6] fullerene cage with stabilization (relative to the isolated molecule) due to stronger -OH···π hydrogen bonding than found in the hydration sphere surrounding the fullerene [809]. Although there is room for more water molecules inside the cage, positioning them there is energetically unfavorable due to poor hydrogen bonding caused by the cramped environment [809].

(C_{70}-$D_{5h(6)}$)[5,6] fullerene can also be dissolved in water [1146]. Solution is achieved using a mixture of sulfuric and nitric acids with or without ultrasonic irradiation; the soluble product proven to be unchanged C_{70} by mass spectrometry. The hydration of C_{70} may be similar to that of C_{60} as above, involving aqueous icosahedral clusters, and utilizing -OH···pi-electrons hydrogen bonds[a]. In this case the icosahedral water cluster (ES), again missing its inner water dodecahedron, is split into two halves hydrating the top and bottom parts of the C_{70} (see below). Around the middle of the molecule an incomplete hydration shell may form which naturally involves five water molecules (asterisked below) that are ideally placed to hydrogen bond to the five extra π-centers in the extra five six-membered rings that C_{70} possesses over the 20 in C_{60}.
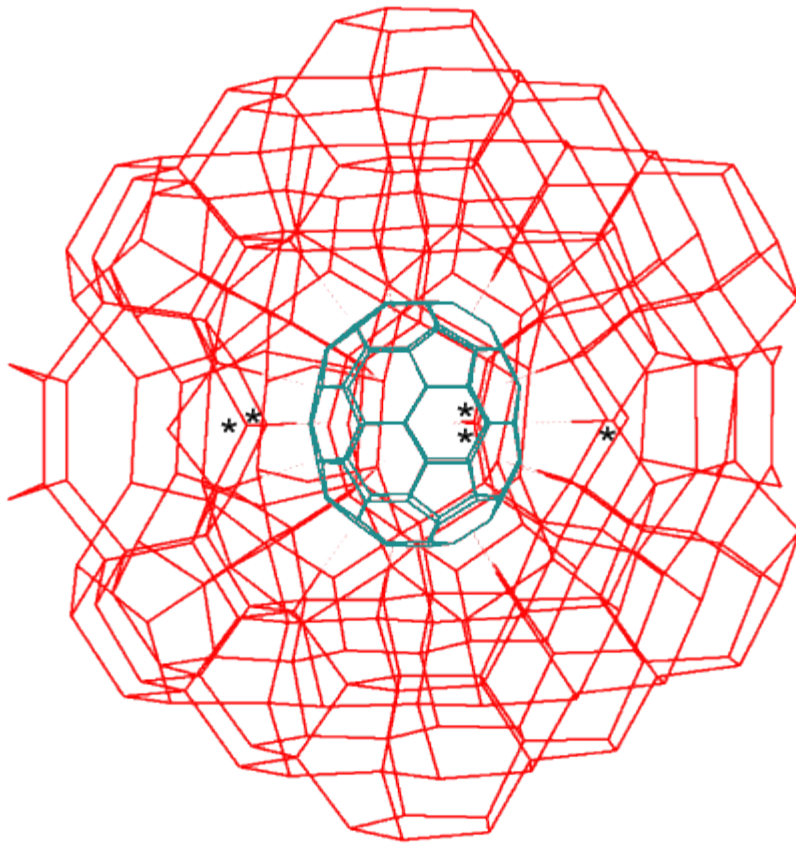
$C_{70}(H_2O)_{280}$ cluster
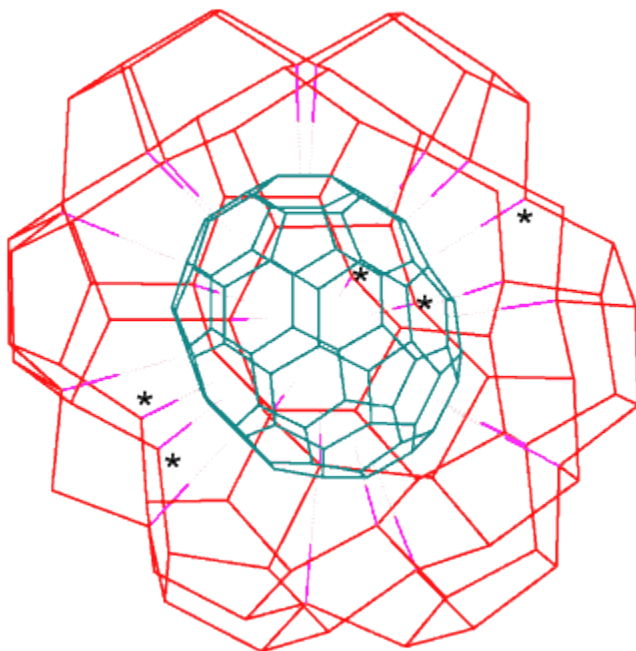
Inner aqueous sphere only, $C_{70}(H_2O)_{90}$; C_{70} shown as blue-green, -OH···pi-electrons hydrogen bonds shown as violet-dashed with hydrogen bonds between the water molecules shown as red links, hydrogen atoms are not shown.
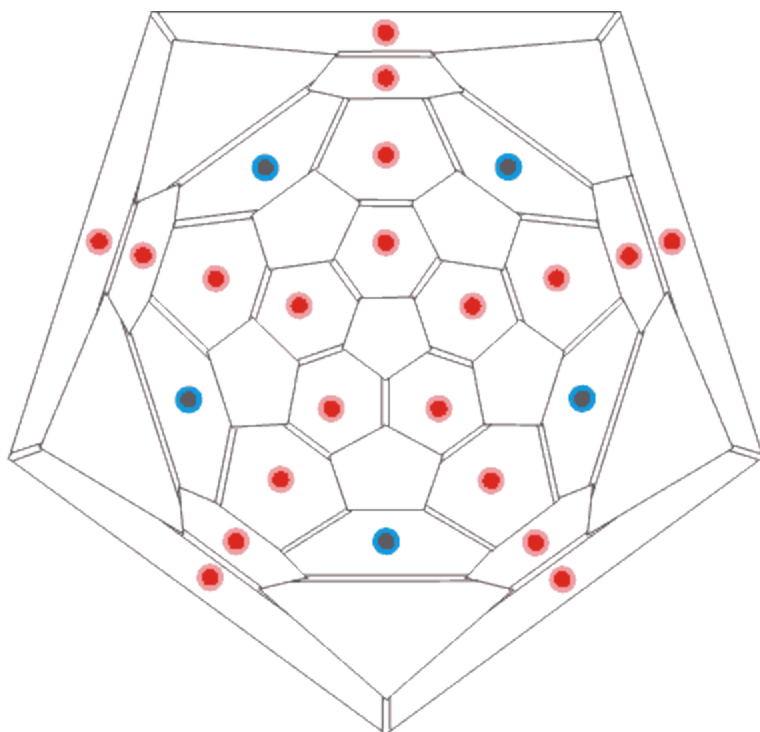
The connectivity map for $(C_{70}\text{-}D_{5h(6)})$[5,6] fullerene is shown opposite indicating the electron rich centers that may hydrogen bond to water in the surrounding aqueous cluster. The blue dots show the positions of the additional sites (compared with $(C_{60}\text{-}I_h)$[5,6]) for hydrogen bonding. It is clear that the -OH···π hydrogen bonds are not equivalent in C_{70} whereas they were in C_{60} as there are now three different environments for the electron-rich six-membered rings (in the ratio of 10:10:5).

An interactive structure of $C_{70}(H_2O)_{90}$ is given (Jmol).

Footnotes

[a] Such -OH···pi-electrons hydrogen bonds have been found to possess about half the binding energy of -OH···O hydrogen bonds with, optimally, the -OH atoms centrally and vertically placed and the distances from the oxygen atom to the aromatic centroid of about 3.1-3.7Å (compare 3.2Å for all 20 such bonds/fullerene in the above model) [325]. They have been found as the optimum structure of $C_{60}(H_2O)$ [1068]. Water-benzene -OH···π hydrogen bonds are evident below 340 °C [945] and are responsible for the higher than expected solubility of benzene in water. [Back]

[b] Although disputed from some quarters, the toxicity widely reported for some C_{60} preparations may be solely due to the presence of significant amounts of solvent or impurities [687]. Tests for physiological harm should be experimental as modeling studies may ignore this hydration effect (for example, [956]). Other work has shown that hydrated fullerene may have some health benefit [1317]. [Back]

[c] Although C_{60} has been modeled (by some) as a purely hydrophobic structure possessing no electrostatic interactions, it is important to recognize that there are effective charge separations between the (positive) carbon atoms and the (negative) centers of the six membered rings and also

that the C_{60} molecule is polarizable. Without allowing for these factors, such modeling is likely to be unreliable. [Back]
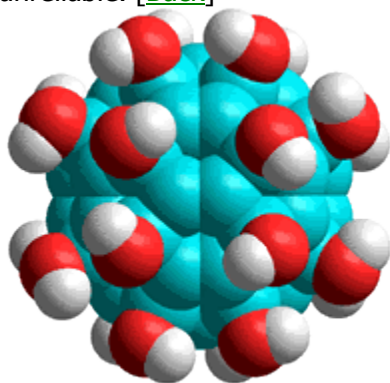
[d] Other work only produces colloidal clusters [1370]. [Back]

[e] A derivative of the C_{60} fullerene, $C_{60}(OH)_{24}$ (see right) dissolves and hydrates well in water. In this molecule the hydroxyl groups are closely arranged and encourage high density water forming around the fullerene, with limited (but strong) hydrogen bonding to the hydroxyl groups (<2 per OH group compared with the preferred hydration of 3 per OH group) and consequentially there are many broken hydrogen bonds in the surrounding water [1370]. [Back]

[f] The 30 double bonds actually have bond orders of 1.44 and the 60 single bonds (all 12 pentagons) have bond order of 1.28, so using the 'spare' P_z electrons donated from each of the 60 carbon atoms [946b].

Source: http://www1.lsbu.ac.uk/water/buckmin.html