

## UNUSUAL PROPERTIES OF WATER

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Water has been known for its unusual properties from antiquity when, e.g. was found that hot water freezes faster than cold water. Presently, on the web page 'water' Martin Chaplin [1] lists sixty seven properties of water which may be considered 'anomalous' when comparing to 'normal' chemical substances. Much of this can be attributed to the spatial structure of hydrogen bonding in condensed phases of water. Hydrogen bonding constitutes about 2/3 of cohesion energy of water. However, the remaining 1/3 is definitely not negligible. Combination of the two leads to properties of water in the systems where it plays a role. The very comprehensive range of such systems and common presence of water make the enormous variety of structures and properties of water-containing compounds. In the present paper the non-hydrophilic component of properties of water will be emphasized in combination with the structural aspects of supramolecular bonding of water molecules.

### Basic physicochemical characteristics

**Structural features.** Inclusion of hydrophobic species in porous structure of water is closely associated with the idea of clathrate inclusion compounds. Although clathrate formation was first observed early in the last century [2], the physicochemical nature of clathrate compounds was not understood until the middle of the last century [3]. The concept of guest molecules '*closed or protected by cross bars of trellis*' was originally proposed by Powell [4]. The presence of guest species in clathrate cavities is not simply of a fortuitous nature. Thermodynamic theory has made clear that guest-host intermolecular interactions are of primary importance, and the guest species may (as often happens) influence the host in such a way that the 'imprisonment' becomes more effective or is even made possible.

During the past five decades the chemical definition of **clathrate** has been extended to cover **inclusion-type interactions** in the solid state, and in liquid (or solution) phases. The latter issue seems to be one of the most important recent developments in the field because of its relevance to biological and geological systems.

In recent years the term '**lattice inclusion**' has been widely used [5] to describe, in a rather general manner, the situation whereby a foreign (guest) species is accommodated in a crystalline lattice of the host component. In such a way the distinction between pure '*clathration*' or '*complexation*' becomes less important, while special emphasis is put on the steric fit between the two components, i.e. the crystalline host and the guest species. The latter may be monomolecular or oligomeric, electrically neutral or ionic. If the crystal is a molecular solid, the term '**lattice inclusion**' is equivalent to description of the compound as interstitial. And, in turn, it follows that we consider *interstitial solid solutions* of the guest in the host lattice (provided there is no significant chemical bonding forces between the components, otherwise we should speak of *interstitial complexes*).

It is convenient to distinguish between two basic structural types of clathrate inclusion compounds. These are:

- (i) *framework host structures*, in which building blocks (molecules) of the host are interconnected by directional bonds in such a way that some space is left empty, and thus available to incorporate foreign (guest) species, and
- (ii) *packing structures*, in which close packing cannot be attained in a chemically homogeneous composition or, put in other words, the host molecules are of size and shape that preclude efficient packing. Thus, the unfilled intermolecular space which remains between the host molecules can be used to include a suitable guest.

A common characteristic of the two above mentioned structural types is that the host itself cannot form close packed crystal structures, and packing efficiency is attained by using a second (i.e. guest) component. As a rule, an '*empty*' clathrate (i.e. a '*clathrate without any guest*') is thermodynamically unstable and may only be prepared as a metastable, and in rather rare cases only. Accordingly, one may consider desorption of a guest component from a clathrate structure as a possible strategy towards preparation of new polymorphic (metastable) structures of the host compound.

It is commonly assumed that no specific chemical bonds exist between the host and guest in clathrate compounds. There is even a system of nomenclature of inclusion-type compounds [6] in which the term *clathrate* is meant as the opposite of *complex*. In other words, *clathration* refers to *physical incorporation* rather than *chemical bonding*, for which the term complex is more appropriate.

**Clathrate Hydrates - Supramolecular Architecture of Water as Host.** Water molecule is commonly known to form, in condensed phases, four hydrogen bonds, donating two and acting as the acceptor of the other two. The resulting tetrahedral geometry of the intermolecular bonding may be realized in the dodecahedral arrangement of water molecules in which oxygen atoms occupy vertices while hydrogen bonds lie along edges of this regular figure. Indeed, almost a

perfectly regular dodecahedron may be found in clathrate hydrates [7], and has also been found as a *building block* of composite cavities [8]. It is interesting to note that such a geometric figure formed by water molecules has been identified in molecular beam experiments [9]. Accordingly, it may be taken as a proof that water molecules have inherent tendency to form dodecahedral cavity structure. An even more striking observation coming from the cited above experimental work is that the cavity contains an extra water molecule (or  $\text{H}_3\text{O}^+$  ion) enclathrated inside the  $(\text{H}_2\text{O})_{20}$  cavity. Such a model has been suggested by L. Pauling in his theory of the structure of water. (An *extra* molecule inside the cavity might, presumably, be the reason for water's increasing density upon melting of ice and, bonded in a hydrophobic manner, contribute to the dynamic properties of liquid water, although this has never been confirmed by any solid state structure of water or its clathrates. The structures of  $(\text{H}_2\text{O})_{20}$ ,  $\text{H}^+(\text{H}_2\text{O})_{20}$  and  $\text{H}^+(\text{H}_2\text{O})_{21}$  were also analyzed theoretically [10] and their stabilization energies calculated. Water molecules can be replaced by methanol up to  $(\text{H}_2\text{O})_{13}(\text{CH}_3\text{OH})_8$  with the formation of clathrate-like structures of mixed water-methanol  $(\text{H}_2\text{O})_n(\text{CH}_3\text{OH})_m\text{H}^+$  clusters [11].

Packing of dodecahedra leads to the formation of additional cages, since five-fold symmetry of the dodecahedra does not allow efficient space-filling in a crystalline form. Put in other words, packing of dodecahedra produces crystal structures which contain some additional cavities, usually larger than the dodecahedral ones. The simplest solution, known in the literature as hydrate type I, contains a combination of dodecahedra and tetrakaidecahedra in the proportion 3 : 1. Internal cavity radii of the cavities are approx. 3.9 Å (small cavity = dodecahedron) and 4.3 Å (large cavity), respectively. Common description of cavity structure of hydrates is  $5^{12}$  for dodecahedra and  $5^{12}6^2$  for tetrakaidecahedra what means the former is built of 12 pentagons and the latter of 12 penta- and 2 hexagons. This kind of notation is commonly used, thus, e.g.  $5^{12}6^8$  represents icosahedron observed in hydrates type H, thus far the largest (radius = 4.06 Å) single cavity found in clathrate hydrates [12]. Clathrate hydrates type II are built of the  $5^{12}$  and  $5^{12}6^4$  cavities in proportion 2 : 1, the internal radius of the hexaidecahedron is equal 4.7 Å.

When considering the ability of hydrophobic molecules to form hydrates of the structures mentioned above, it is common to use, as the first approximation, geometric fit of molecular sizes to the cavities. Small molecules, like nitrogen  $\text{N}_2$ , may enter both small and large cavities but their contribution to stabilize the cavities is not high, however. On the other hand, methane or hydrogen disulphide fit very well to the dodecahedral cavities, thus being efficient hydrate 'formers'.

Although hydrate types I, II and H are commonly listed as the basic ones for hydrophobic hydration, the complete structural information may still be far from completeness. Although this problem will not be discussed here, it seems important to mention that basic structural chemistry of gas hydrates is still an open field for interesting discoveries.

Very important and interesting is the formation of large polyhedra, typically combined of, four basic units, which take on open structures in which the tetrahedral, intermolecular bonds of water molecules, are preserved only partially. This leads to a variety of possible three-dimensional structures.

Guest-host interactions. In recent years much new information concerning clathrate hydrates has been provided both from experimental and theoretical studies. In the latter a major breakthrough may be consideration of the host-guest coupling in the normal mode analysis for the accommodation of large (relative to the cavity size) guests [13] when cage distortion occurs (like  $\text{CF}_4$  guest molecules in the small cavities of clathrate hydrates). The classic theory of van der Waals and Platteeuw is based on an ideal solid-solution model and thus ignores the guest-host vibrational coupling and host lattice distortions. These contributions cannot, in real structures, be neglected. By taking them into account [14] the stability of Xe and  $\text{CF}_4$  clathrate hydrates could be calculated. Encaging non-spherical propane molecules required taking into account the anharmonicity of vibrational free energy associated with the non-spherical nature of the guest. The calculated thermodynamic properties are, reportedly, better approximation to the experimental data [15] than those previously available. By examining the temperature dependence of the dissociation pressure of Xe and Ar clathrate hydrates it has been concluded that the predicted pressures agree well with experiments at higher temperature range [16].

It has also been demonstrated, in an elegant series of advanced NMR studies, that the distribution of guest species (Xe) between small and large cages is more complex than predicted from simple theory of clathrate solutions [17], or by simple rules of classical size-structure dependence. As shown by spectroscopic methods, carbon dioxide [18], oxygen [19], nitrogen and carbon monoxide [20] can form hydrates of type II from vapour-deposited amorphous solid water. X-ray studies give similar results with respect to the natural air-hydrate in Greenland Dye-3 deep ice core [21]. It seems likely, however, that some of the structure II hydrates undergo the II - I phase transitions at high-pressure conditions [22]. There are many subtle structural features of clathrate hydrates, and related structures like e.g. semiclathrates, which are a subject of interest in advanced studies which employ solid state NMR [27]. In addition to guest order-disorder phenomena, rather common in clathrate compounds, hydrates show proton disordering around host water oxygen atoms. These systems are dynamic at room temperature, freeze down to rather complex static patterns at lower temperatures [23]. It has been found by neutron diffraction study of the structure II clathrate hydrate of xenon/carbon tetrachloride (3.5 : 8 : 136) that the  $\text{D}_2\text{O}$  molecules are disordered at 13 K and 100 K in 6 H-bonded orientations [24]. It has recently been demonstrated that polar guest molecules may alter the rearrangement process in a defect-bearing solid clathrate hydrate network [25]. It was found that the rearrangement dynamics in a clathrate hydrate encaging polar guests follows a different mechanism from that proposed for Bjerrum for crystalline ices.

## Hydrophobic hydration

**Methane hydrate.** The apparently most important clathrate hydrate at present is methane hydrate since its potential as an energy source is becoming widely recognized, as well as hazards associated with conceivable gas eruption on clathrate decomposition [26]. However, it is not unlikely that clathrate hydration plays a more substantial role, at least for the biosphere, in formation and stabilization of biological supramolecular systems. For example it has been shown that the behavior of protein-containing reversed micelles may be significantly modified when the species are subjected to clathrate hydrate formation conditions [27]. It was shown that clathrate hydrates of methane can form in protein-containing reversed micellar systems; their effect is to reduce the water content in the micelles. This observation has possible important implications since it has been known that, e.g., enzyme activity is dependent on water content.

**Semiclathrate structures.** A series of novel semi-clathrate structures of water have recently been found. In semiclathrates the water intermolecular structure contains some deviations from a four-connected, three-dimensional polyhedral network. Typically, as found e.g. in the structure of the 7.25-hydrate of tert-butylamine [28], the guest species are not only enclathrated but also participate in the hydrogen bonding. Another possibility is to replace some water molecules of the host framework with hydroxyl [29] or fluoride ion. In such a way the host water connectivity is subjected to significant modification and also adopts an ionic character. Tetramethylammonium hydroxide has been reported to form solid hydrates  ${}^{39}\text{Me}_4\text{NOH}\cdot n\text{H}_2\text{O}$  with, at least, eight different structures ( $n = 2, 4, 5, 7.5$  and  $10$ , at some compositions polymorphism has been observed); tert-butylamine has been reported to form as many as seven different solid hydrates [28].

It would be conceivable to include a metal cation into small cavities present in such semiclathrate lattices having an anionic nature. As clearly demonstrated [30] cesium ions can be enclathrated in small decahedral cavities; the Cs...O distances of 3.43 and 3.53 Å to two non-related by symmetry oxygen atoms (two sets of eight atoms each form the cavity) being evidence for a good fit.

Another series of recently reported structures of this type is based upon cavity architectures in which the network formed by host water molecules is more or less distorted from the regular shape. This is the case of 1,10-diaza-18-crown-6 hydrate. Rather characteristic for these systems is that more than one hydrate is formed under slightly different experimental conditions. The next example shown represents a somewhat more open structure in which guest cations (methylammonium) are arranged, together with 18-crown-6 receptor molecules, parallel channels to the water framework which assumes an open channel structure presumably able to transport simple ions or small molecules through the crystal along the  $z$  axis. The tetra- $n$ -propylammonium fluoride complexed with 18-crown-6 and hydrated [31] shows a layered structure in which the three-dimensional intermolecular bonding between water molecules is preserved only partially, i.e. within the layer formed by  $\text{H}_2\text{O}$  molecules.

When going from the cage structures to the layered one, fewer and fewer intermolecular water-water hydrogen bonds are seen and, at last, one can hardly identify any “host” or “guest” component in the structure. By inspection of the structures given in these Figures, and of the corresponding phase diagrams, of these systems, it may be concluded that the type of structure of the host-guest associates is strongly dependent upon the composition of the solution phase from which the solid crystallizes. If, for example, a layered structure is obtained for which less host material is necessary when compared to the cage type, then at higher guest concentrations in solution the crystallization of layered compounds is observed.

Hydrophobic and hydrophilic hydration do co-exist and cooperate. Bonding *via* hydrophobic hydration is an important contribution, in terms of attractive interactions, to overall stability of intermolecular compounds.

When the internal crown ether receptor site is blocked by complexation of anoty complexation of another species, (e.g. by an aminoacid or peptide moiety), then water-crown hydrogen bonding is no longer feasible. Regardless, high hydration of the complexes is possible as has been shown recently [32].

The examples shown above are intended as simple model illustrations of structural situations which may play, and presumably do, important role in biochemical systems. The structures which are most stable at given conditions and environment are the ones which represent the function of the system. Water is a predominant component in biosphere and its interactions with any other components are of major importance. What is taken as granted is that water is a hydrophilic molecule. It is, of course, true statement. However, this truth is incomplete. Water may, as shown on selected examples above, behave as a combination of hydrophilic and hydrophobic molecule. If hydrophilic functions (hydrogen bonds) are saturated by forming sufficient bonding to the surrounding hydrophilic species (other water molecules, e.g.), what remains is hydrophobic interactions geometrically situated in between the tetrahedrally arranged hydrogen bonds. These interactions are not negligible, in many cases these are the structure determining factor. This phenomenon is of great importance in biochemistry. There are many protein structures in which hydrophobic hydration, i.e. hydration without hydrogen bonds between water and the second component, plays decisive role and it may well be referred to smaller blocks of protein structures. Many details still await complete discovery but the role of ‘hydrophobic water’ in chemists’ understanding of structure and function of biological systems is growing.

## Conclusions

Hydrophobic hydration is the concept derived in the 1950s from thermodynamic studies from which it became clear that, in addition to hydrogen bonding, water has some extra ability to bind, without hydrophilic interactions, molecular species which are routinely considered hydrophobic. The outcome, e.g. in the form of stable compounds of water and hydrocarbons, is impressive. This binding is based upon structure effects, namely on aggregation of water molecules around a 'structure-directing agent' (as named by silica chemists) or 'template' (commonly used by organic synthetic chemists) or, simply, guest component. This is a typical collective phenomenon, not easily corresponding to the classical tools of chemists who prefer to rationalize interactions in terms of bonds between specified atoms. Hydrate solids are often non-stoichiometric, phenomenon which is certainly unknown in molecular chemistry while rather common in solid state sciences.

Hydrophobic hydration is a common phenomenon and is important from different viewpoints. Directly as a source of special type of material, which may be of practical importance. Also, indirectly, as a means of facilitating synthesis of organic and/or inorganic substances either in nature (as illustrated above on the example of porous silica materials) or in the laboratory.

Ecological aspects of hydrophobic hydration are manifold. Climate change due to stabilization /destabilization of huge deposits of natural gas in the form of 'soft' hydrate material seem the most important on large time scale whilst geohazards and resource of energy are important also on the short time scale. Common occurrence of hydrophobic hydrates on earth is a firm basis for further research of these complex systems, so important for biological life on our planet.

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