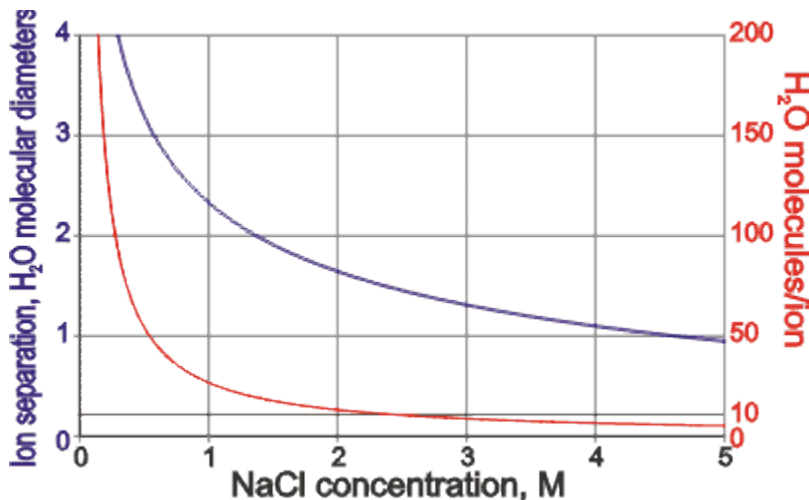


Ion Hydration and Aqueous Solutions of Salts

- ▼ Methods for determining ion hydration
- ▼ Water clustering around ions
- ▼ Sulfate and other large anions

Methods for determining ion hydration

A great deal of information exists concerning the hydration of ions. Much of this concerns the number of molecules of water that are bound to the ions and their distribution. Unfortunately the data is not clear cut, with different methods measuring different aspects of the ionic hydration and, hence, producing different figures. Also, the bound water reduces with increased temperature and concentration, and varies with the nature of the counter-ions and any other solutes present. The main methods chosen are IR [895], NMR [781], molecular dynamics, use of colligative properties and x-ray and neutron diffraction [1062]; other methods include X-ray spectroscopy [1125], ultraacoustics [1288], Raman spectroscopy [1313] and gel exclusion chromatography [1124]. Of these methods, only molecular dynamics and IR give dynamic information whereas most methods give time-averaged data. Water molecules are most affected when they lie closest to the ions and the structuring of the water away from the ions is little changed from its natural state. Water molecules around small cations are highly polarized due equally to the cation and the other cation-surrounding but not mutually hydrogen-bonded water molecules [1439]. This polarization causes strengthening in their donor hydrogen bonding; for example, the hydrogen bond energies of $\text{Zn}^{2+}(\text{H}_2\text{O})_5\text{HO}-\text{H}\cdots\text{OH}_2$, $\text{ZnCl}^+(\text{H}_2\text{O})_4\text{HO}-\text{H}\cdots\text{OH}_2$, $\text{ZnCl}_2(\text{H}_2\text{O})_3\text{HO}-\text{H}\cdots\text{OH}_2$ are 426%, 277% and 23% respectively stronger than the $\text{HO}-\text{H}\cdots\text{OH}$ hydrogen bond [1906]. Although the information that is available mostly concerns the local clustering of water around the ions, the formation of much larger domain structures [407] with diameters ~ 100 nm [1148] have also been found.



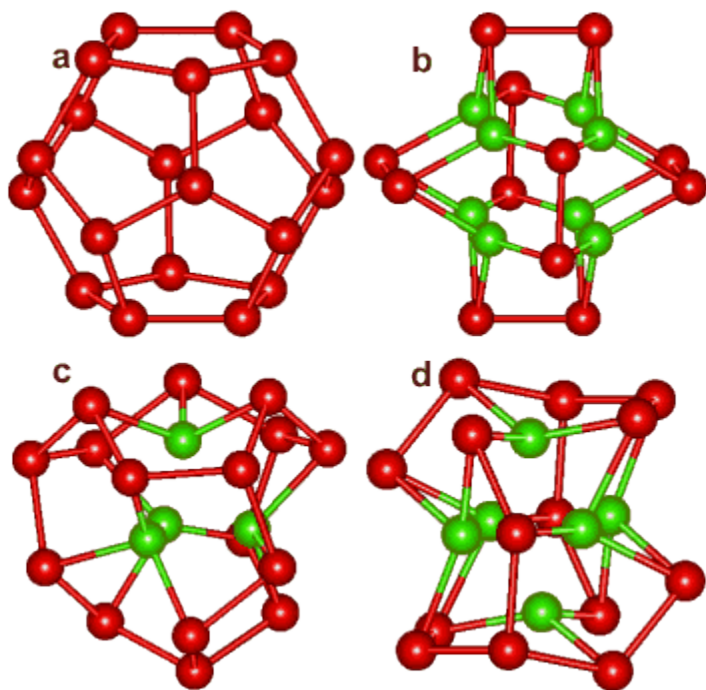
Often, concentrated solutions are used to examine salt hydration to reduce the signal from 'bulk' water. Clearly, such solutions only lead to descriptions of the hydrated state in such concentrated solutions and cannot be used to establish the hydration states in more commonly encountered dilute solution. Sometimes the solution may be so concentrated that there is no 'bulk' water present and all water molecules are interacting with one or more ions [1559]. As an example seen left, the

number of water molecules associated with each ion in 5 M NaCl solutions is less than five per ion when the separation of the ions is less than one H₂O molecular diameter.

The dominant forces on ions, and polar molecules, in aqueous solution are short range chemical interactions involving the spare outer electrons on the water molecules with cations, and positively charged atoms, and hydrogen bonds donated from water molecules with anions [1190] and negatively charged atoms. Both processes involve effective partial charge transfer from the ion, or charged atom, to water.^f The resulting interactions with water are quite different with the anion-hydrogen bond interactions being enthalpically much greater than cation-lone pair electron interactions for the same size ions due to the closer approach of the atoms [1418]. Longer-range electric fields (> 3 nm), due to the ionic charges are weak relative to water-water hydrogen bonding [1190]. The solvation energy of monovalent cations and anions are well modelled by a continuum model that includes electrostatic, dispersion, and cavity contributions showing that the water molecules outside these influences has little net effect difference from bulk water [2010].

The presence of ions causes localized water clusters to be stabilized over their state in the bulk of the solution as they reduce the hydrogen bonding exchanges, and proton mobility [1919], of the affected water molecules. Using statistical mechanics, it has been shown that the affect on the clustering extends out to 3-4 hydration shells ($\sim(\text{H}_2\text{O})_{130}$) in the case of weakly hydrated ions and 7-9 shells ($\sim(\text{H}_2\text{O})_{400}$) in the case of strongly hydrated cations, but retaining good hydrogen bonding [1915]. This theoretical result is in agreement with the experimental ensemble infrared photodissociation (IRPD) spectra in the hydrogen stretch region ($\sim 2800\text{-}3800\text{ cm}^{-1}$) for aqueous nanodrops containing approximately 250 water molecules (equivalent to those in an ES or CS structure) and SO_4^{2-} , I^- , Na^+ , Ca^{2+} , or La^{3+} [1917]. Much of the inner clustering may be understood in terms of the puckered dodecahedra (see below right, also described elsewhere).

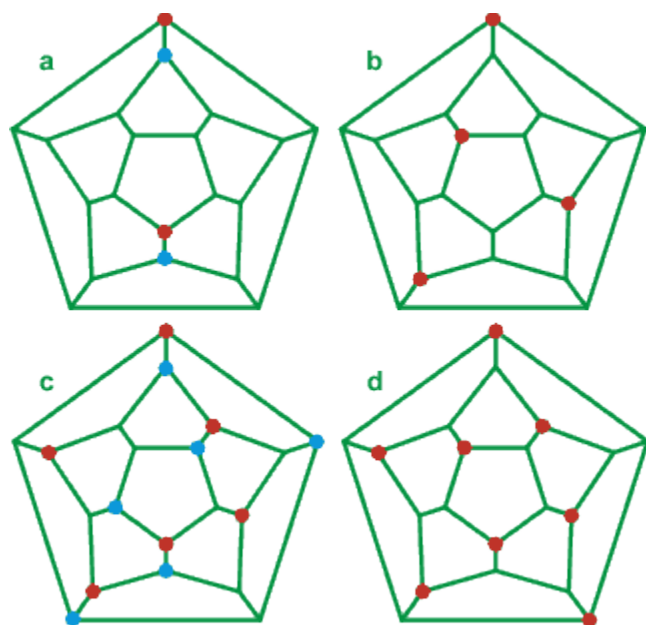
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Water clustering around ions

Infrared photodissociation spectroscopy (IRPD) and blackbody infrared radiative dissociation (BIRD) support the importance of $(\text{H}_2\text{O})_{20}$ water clathrates (a) surrounding monovalent cations [2017]. A tetrahedral cavity (c) in a puckered water dodecahedron may be used by H_3O^+ and NH_4^+ to form magic number cluster ions. The octahedral cavity (d) could be occupied by any of the many monatomic cations and anions that are normally found in contact with six water molecules in their (inner) hydration shell (for example, Na^+ , K^+ , Cs^+ , Ca^{2+} , Cl^- , Br^-), whilst allowing a fully hydrogen-bonded second shell. Such a structure for $\text{Na}^+(\text{H}_2\text{O})_{20}$ has been obtained using the AM1 semi-empirical model [323]. Similarly the cubic cavity (b) could be occupied by triply charged lanthanoid or actinoid ions that have a coordination number of eight (see also the connectivity maps below). Such clathrate hydration around K^+ and Cl^- in dilute KCl solutions agrees with the ~ 45 molecules of water found by X-ray phase analysis [1161]. In agreement with this idea, recent terahertz (THz) spectroscopy of solvated alkali halide salts at around 85 cm^{-1} (2.5 THz) shows the ions rattle around within the water network [1649]. Assuming icosahedral clustering, water molecules around ions shows that only the inner two cluster layers (~ 40 molecules) are strongly affected with the effect of different amounts of puckering (caused by higher charge density and smaller ions) disappearing by about 0.68 nm and a cavity size of 0.45 nm having no effect on the water coordinates. This is in close agreement with such length scales discovered by quasichemical theory [2008].

In the case of chloride, the $\text{O-H}\cdots\text{Cl}^-$ distance (0.37 nm) is only slightly less than the normal clathrate size (0.39 nm), with the bond strength about 1 kJ mol^{-1} weaker, so allowing water's easy large angle orientational jumps [1366], consistent with reversible puckering, such that there are flickering changes in the closest water molecules.



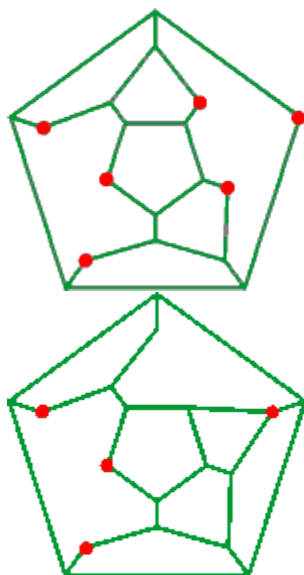
Shown opposite are the connectivity maps of the dodecahedra showing the collapsed positions (red or blue circles) for 2 (a), 4 (b), 6 (c) and 8 (d) molecules. Alternative structures may be formed from all of these connectivity maps by rotation and reflection. In these cases, the dodecahedral cluster, comprising the inner hydration shell and its hydrogen bonded linking water (often termed the 'second' hydration shell) would contain hydrogen bonding defects where water molecules are associated through hydrogen bonding or lone pair electrostatics to the central ions, reducing the water-water hydrogen bonding. Given that the total hydration in the first and second shells is the

same, there may be smooth transitions between different coordination preferences resulting in the intermediate 'mean' primary hydration noted with several ions.^a

Different ions, even with the same inner hydration level, may hold their water molecules more tightly or more loosely giving varying degrees of dynamic puckering. Hence, they would cause different degrees of hydrogen bonding in their surroundings, as shown by the various properties of kosmotropic and chaotropic ions. This has been proven by the free -O-H stretch of surface water molecules in ion containing ES-sized nanodrops ($\sim(\text{H}_2\text{O})_{250}$) of water, where Ca^{2+} and SO_4^{2-} show distinct differences from Na^+ and I^- [1967].

In all these puckered clusters there is an opposing balance between the ion-water interactions and first shell second shell water interactions. When the water-water interactions are weakened by, for example raised temperature, then the ions will hold the water molecules more tightly and the ion-water distance contracts [1126]. Where the water molecules are only weakly held to the central ion, the water molecules expand away from the central ion with temperature [1126].

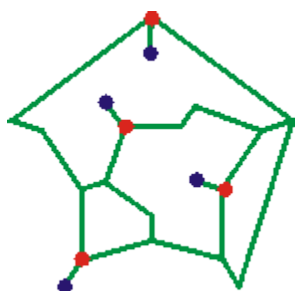
A further possibility with dodecahedral clustering is that the two opposite positions from the water dodecahedra may come together and be replaced by a single ion (see (e) in the connectivity map above); giving that ion an inner shell of six water molecules and a second shell of 12 water molecules. Such an arrangement has been found around Mg^{2+} ions [253, 378].



The $\text{Mg}^{2+}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$, $\text{Al}^{3+}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$, $\text{Zn}^{2+}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$ and $\text{Be}^{2+}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$, clusters with two hydrogen bonds leading from each of the six inner coordination sphere (shown as red circles) gave the connectivity opposite top [378] as minimum energy structures. Together with the $\text{Li}^+(\text{H}_2\text{O})_4(\text{H}_2\text{O})_9(\text{H}_2\text{O})_5$ and $\text{Na}^+(\text{H}_2\text{O})_4(\text{H}_2\text{O})_9(\text{H}_2\text{O})_5$ clusters, similarly calculated [378] and shown opposite bottom, these clusters can be seen to show much similarity to structure (d) above. The dipoles of the inner water molecules are oriented towards the ion so preventing the formation of a complete dodecahedral water cluster. Hydrogen bonding between the second sphere water molecules was shown to be particularly important. An identical arrangement (to opposite top) has been found in the $\text{Ti}^{3+}(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{12}$ cluster and used for other hydrated transition metal clusters [332].

An interesting possibility that fits with a recent ionic model [314] is that the experimentally-determined second hydration shell water may consist of all the water molecules that are doubly-

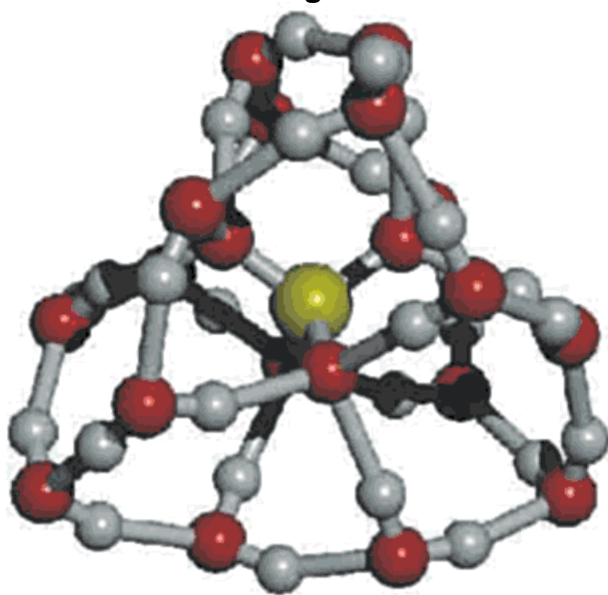
hydrogen bonded directly to any two of the primary hydration water molecules in the puckered dodecahedral model (above). This would result in tetrahedrally (4), octahedrally (6) and cubic (8) coordinated primary hydration water molecules having 0, 6 and 12 secondary hydration water molecules respectively. Examples (from [314]) of this primary and secondary hydration are Li^+ (tetrahedral, 4.68 primary, 0 secondary), Ca^{2+} (octahedral, 6.10 primary, 5.29 secondary) and Ho^{3+} (as a typical lanthanide, cubic, 8.00 primary, 10.67 secondary). The Li^+ ion has somewhat strange behavior out of series with the other alkali metal ions, which may be due to it holding on particularly strongly to one of its inner sphere water molecules [1214], and/or it forming short alternating linear clusters with the anions [1324].



A highly stable solvated electron has been identified inside a tetrahedrally collapsed dodecahedral $(\text{H}_2\text{O})_{20}$ structure, $e^-(\text{H}_2\text{O})_{20}$ (cluster **c**, as above, with four inwardly pointing H-atoms) [734]. Others have found the preferred hydrated electron structure is $e^-(\text{H}_2\text{O})_{16}$ [695] with four water molecules in the inner shell only linking through a weak network to the rest of the cluster (here the electron is shown as blue circles and the inner shell water as red circles).^d

Hydroxide ion hydration may also involve such $(\text{H}_2\text{O})_{20}$ clusters as it is found that liquid water in its solutions undergoes a great change in structuring when the concentration of OH^- rises above the ratio of one OH^- to 20 H_2O [1229]. [[Back to Top ▲](#)]

Sulfate and other large anions



Ions such as sulfate [156]^e and ZnBr_4^{2-} [178] form a hydration shell from small rings of hydrogen bonded water. Such a shell may consist of a symmetrical dodecahedral arrangement of 16 water

molecules where each sulfate oxygen (or ZnBr_4^{2-} bromine) is hydrogen bonded to three water molecules; these water molecules forming small looped chains of 2 (6 occurrences per $\text{SO}_4^{2-}(\text{H}_2\text{O})_{16}$) or 3 (12 occurrences per $\text{SO}_4^{2-}(\text{H}_2\text{O})_{16}$) molecules from one sulfate oxygen to another. Bisulfate (HSO_4^-), the main ion in dilute sulfuric acid (~ 0.1 M), may also be hydrated similarly as $\text{HSO}_4^-(\text{H}_2\text{O})_{16}$. It should be noted, however, that sulfuric acid has many hydration shells and is not completely hydrated, as judged by the heat of mixing, until over 500,000 molecules of water are added to each molecule of H_2SO_4 [947]

Although this clustering is not indicated from gas phase kinetic studies [646], support comes from photoemission spectroscopy where there is an obvious change in properties beyond $n=16$ for $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters [298], and from FTIR [1072].

Interactive Jmol structures are given.

Similar clustering may occur around PO_4^{3-} where the surrounding $(\text{H}_2\text{O})_n$ cluster has $n=15\pm 3$ as shown by neutron scattering [544] and $n\approx 16$, with consistent geometric parameters, by molecular dynamics simulation [668].^b

Such a cluster can form the central part of an icosahedral water cluster ($\text{SO}_4^{2-}(\text{H}_2\text{O})_{276}$) possessing just four defects^c. One of the puzzles associated with this ability to interact with a water dodecahedron is the very different aqueous properties of sulfate (SO_4^{2-}) and perchlorate (ClO_4^-) ions. These ions are at opposite ends of the Hofmeister series but have similar geometry; tetrahedral with perchlorate Cl–O bond lengths only a few hundredths of an angstrom shorter than sulfate S–O bond lengths. Explanation comes from the experimental partial molar volumes at infinite dilution [233]; that of perchlorate has been found to be twice that of sulfate, in agreement with perchlorate ions being found in expanded clathrate-like water dodecahedra whilst sulfate is found in collapsed puckered water dodecahedra. The difference is due to the inability of the perchlorate oxygen atoms to successfully form sufficiently strong hydrogen bonds, so allowing it to sit within a complete dodecahedral water clathrate shell, a factor due to its approximately four-fold more diffuse surface charge (which scales with the absolute charge squared [529]) and borne out by its lack of perturbation of the O–H vibrational spectra and lower water cluster sorption [306]. In support, a recent FTIR-ATR study showed ClO_4^- ions to be more disruptive of water's hydrogen bonding than SO_4^{2-} ions [862]; see also their relative kosmotropic/chaotropic effects.

The anomalously high solubility of CO_2 compared to CO [166] may also be explained by its residence as part of such hydrogen-bonded clusters. [[Back to Top](#) ▲]

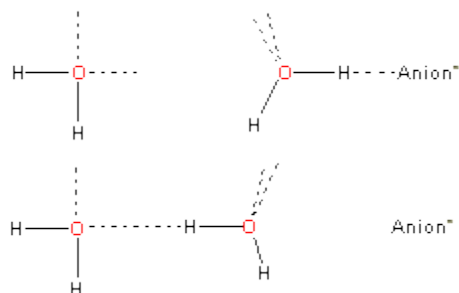
Footnotes

^a Some workers report that K^+ and Cs^+ may have a coordination number of between 6 - 8. With a coordination shell of eight, K^+ could sit in a cubic hole similar to that used by the K^+ selectivity filter in K^+ channels, where coordination shifts between six and eight to allow transport [267]. Chaotropic ions, such as these, bind water less strongly than water-water interactions. Therefore, it is unsurprising that water molecules readily detach from these ions. However, the same molecules usually return within less than a picosecond [586]. Such behavior is consistent with these ions residing within a rapidly fluctuating and puckering dodecahedral cluster. [Back]

^b When the anion charge is reduced through HPO_4^{2-} and H_2PO_4^- the hydration shell increases to 20 H_2O [668], in line with clathrate formation. [Back]

^c Cluster defects are water molecules, (labeled b-type previously) within the icosahedral cluster structure, with only 3 rather than 4 hydrogen bonds as the fourth site cannot accept/donate

a hydrogen bond from/to either (a) a water molecule already possessing 4 hydrogen bonds; that is, the fourth site has the arrangement



rather than

or (b) a bound atom that already possesses 3 hydrogen bonds such as the oxygen atoms in SO_4^{2-} . [Back]

^d The cavity model for solvated electrons is currently disputed by a study that gives increased $\text{H}_2\text{O} - \text{H}_2\text{O}$ attraction when within the excess electron's influence [1704]. Any such additional attraction would cause stronger H_2O clustering. However, another recent study describes the excess electron residing in a cavity [1841]. [Back]

^e It has been reported that sulfuric acid (H_2SO_4) in concentrated aqueous solution acts as though it is a tribasic H_4SO_5 acid [1936]. [Back]

^f Transfer of electrons through the hydrogen bonds between anions (e.g. Cl^-) and H_2O may not be equal between the neighboring H_2O molecules, leading to unequal but flickering changes in the bond lengths. [Back]

Source:<http://www1.lsbu.ac.uk/water/ions.html>