Forschung, Wissenschaft

Structural Considerations about Liquid Water and Aqueous Solutions *

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Abstract

A quasi-continuum model for liquid water has been developed which is characterized by long range order structural effects. A solute is considered as a structure regulating center, as the hydrogen bonds in its immediate environment are shorter than in the more remote areas. In "pure" water the role of mobile holes, which are partly occupied by dissolved gases, such as N_2, O_2 and CO_2, is emphasized.

1. Introduction

In the absence of direct experimental information about the structure of liquid water, various models have been developed, while efforts to verify or to invalidate any of these hypotheses are hampered by lack of a general theory of the liquid state [1]. In its absence considerations of the structure of liquid water have been based mainly on two approaches, neither of them rigorous. One of them consists in formulating a model by the methods of statistical mechanics, which usually involve massive approximations [1, 2]. The second is to deduce aspects of the liquid structure from the macroscopic properties of water.

"Structural order" in liquid water is regarded as due to the presence of hydrogen bonded clusters, which have a very limited half life period [3] in the order of magnitude of 10^{-11} s. A distinction is made according to the differences in relaxation times. The so-called "I-structure" (instantaneous structure) refers to a time interval short compared to the period of oscillation τ_v, which is roughly 10^{-13} s in ice. No experimental technique is available to obtain information on this structure. The so-called "V-structure" (vibrationally averaged structure) is ascribed to the features observed in a time interval longer than the period of oscillation, but shorter than the half-life time (displacement time) of the clusters [1]. The "D-structure" (diffusionally averaged structure) is applied to a time interval long compared to the displacement time of approximately 10^{-11} s. Most of the experimental information, for example the thermodynamic properties of water, its volume, heat capacity, compressibility, X-ray pat-, tern or NMR-data are characteristic of the D-structure [1], to which we shall refer in this article, whenever the therm "structure" is used.

A distinction is made between the "two-state models" or "mixture models" [4] and the "continuum models" [4]. All of them are intuitive and heuristic and none of them has a firm physical foundation [5]. They differ from each other by virtue of the assertion that the separate contributions to any property from the several species are in principle measurable [6]. If this assertion is abandoned the differences between the models boil down to semantic niceties [6]. Both features must be present in the actual liquid which is more complex than any of the simple models proposed. In this sense, the controversy reflects more the limitation of the ways in which we describe water. It should disappear as better models are developed [6].

It is a common feature of "two-state models" that they require at least two distinctively different species of water, namely a bulky species, the so-called clusters [2] representing a framework of hydrogen bonded units as well as a dense species, such as monomeric (vapour-like) water molecules.

Frank and *Wen* [3] apply the term "mixture" to a model involving a hydrogen bond forming and breaking equilibrium. They postulate that the formation of the bonded structure in liquid water is a cooperative process in which "flickering clusters" [7] of varying extent form, relax and reform in a temporal sequence and in a spatial pattern determined by the energy fluctuations which are constantly taking place [8].

The so-called continuum models, namely the distorted hydrogen bond model of *Pople* [9] and the closely related random-network of *Bernal* [10] avoid the presence of monomers in equilibrium, as they are characterized by a long range order in liquid water. The structure of water is very sensitive to any disturbance: hydrogen bonds are readily formed and broken, external fields lead to changes in charge distribution and the protons are highly mobile, leading to polarization effects by shifts of nuclear charges, the polarizabilities being about by two orders of magnitude larger than usual bond polarizabilities [11, 12]. The ion-water interactions based on a dipole model for the outer solvation sphere has been calculated by more than one order of magnitude greater when the polarizabilities of the dipoles are taken into consideration [13].

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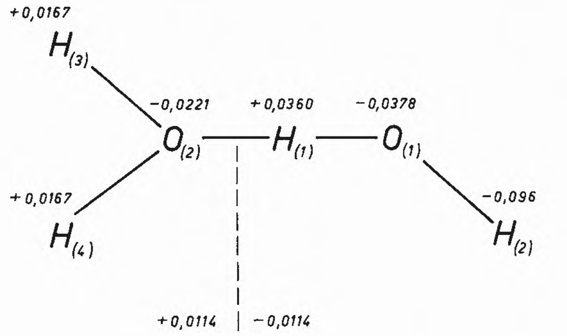
2. Hydrogen-Bonding

It is a common feature of all of the models to account for the association between water molecules through hydrogen bonding. The shortcomings of the electrostatic interpretation of hydrogen bonding have been summarized as follows [14]: No relationship exists between dipole moment of the donor molecule and the strength of the hydrogen bond, the nuclei are found at much smaller distances than would be expected from the consideration of the Van der Waals radii, and the characteristic changes in IR- and NMR-spectra due to hydrogen bond formation cannot be explained by the electrostatic theory.

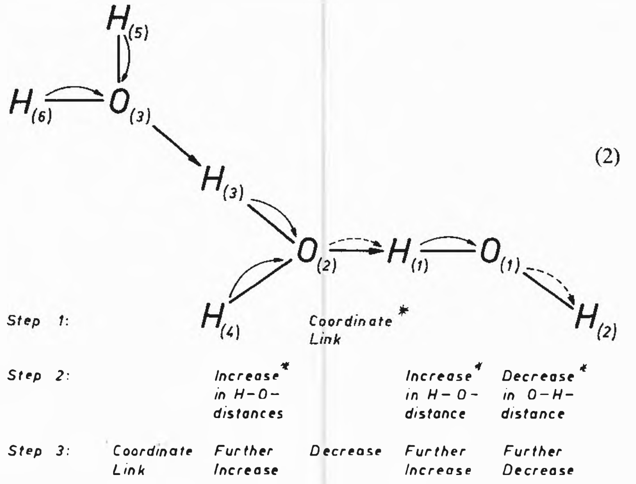
On the other hand the treatment of the delocalization of the electrons has been successful in a semiquantitative way by means of LCAO-MO-methods. Numerous structural questions involved in hydrogen bonding have been solved by these as well as by other semiquantitative theoretical approaches, such as by *Coulson* [15] and *Sokolov* [16] (VB-theory), as well as by *Bratoz* [17] (charge transfer theory). For the dimerization of water molecules the following changes in charge densities have been obtained by an accurate ab initio SCF calculation [18]:



(1)

According to the first bond variation rule of the extended donor-acceptor concept [19, 20] the H–O bonds adjacent to the new intermolecular bond are lengthened and the negative fractional charges at both oxygen atoms are increased, as is also evidenced by the observed increase in basic properties in going from gaseous water to the liquid phase [19, 21]. At the hydrogen atoms $H_{(1)}$, $H_{(3)}$ and $H_{(4)}$ the fractional positive charges are increased, which is reflected in their greater acidities as compared to those in a monomeric water molecule. On the other hand the terminal H-atom $H_{(2)}$ of the acceptor unit is increased in negative fractional charge and hence its acidity is decreased, as is the bond length $O_{(1)}-H_{(2)}$.

The process of association of three molecules has been described in the following way [20, 22]: Nucleophilic attack of a water molecule (oxygen atom $O_{(2)}$ at hydrogen atom $H_{(1)}$ of another water molecule) induces increase in polarity of the adjacent bonds and hence increases both the acidities of the hydrogen atoms $H_{(3)}$ and $H_{(4)}$, and the base strength of oxygen atom $O_{(1)}$. Donor-Acceptor interactions between hydrogen atom $H_{(3)}$ (or $H_{(4)}$) and the oxygen atom $O_{(3)}$ of another water molecule will increase both the acidities of the terminal hydrogen atoms $H_{(5)}$ and $H_{(6)}$ and further increase the base strength of oxygen $O_{(1)}$. With increasing association, e. g. increasing number of hydrogen bonded water molecules, the effects are increased although to lesser extents. The result is a structure containing a variety of different hydrogen bond lengths.



(2)

* The arrows indicate the direction of the induced electron shifts: a full bent arrow denotes increase and a dotted bent arrow decrease in bond distance.

While the OH-distance in gaseous water is 95.8 pm, it is greater in ice, namely 99 pm. For the liquid phase the values are less accurately known and they should be expected even slightly greater than in ice due to the higher density of the liquid.

Due to the cooperative effects between the water molecules the mean energy ΔE of the hydrogen bonds is increased with increasing number of associated molecules [14, 20]. Even more significant is the energy $\Delta E_{(n-1)\rightarrow n}$ for addition of the "last" solvent molecule, which is always higher than ΔE and it reflects the increasing basicities of the terminal oxygen atoms and the changes in acidities of the terminal hydrogen atoms respectively.

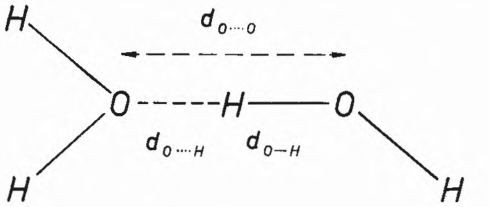
Table 1: Mean hydrogen bond energies [kJ/bond] for linear chains of H_2O molecules as a function of the number of H_2O molecules

Number of H_2O molecules	E[kJ/bond]*	$E_{(n-1)\rightarrow n}$[kJ/bond]
2	36.33	36.33
3	40.30	44.32
4	42.35	46.50
5	43.65	47.46
6	44.40	47.88
7	45.11	48.13
8	45.95	48.30

* Due to the semiempirical LCAO-MO method used the calculated hydrogen bond energies are somewhat too large.

Calculations for units with tetrahedral geometry which represents a more realistic model for the structure of liquid water, show similar trends, altough the effects appear somewhat smaller [14].

Measurement of the individual bond distances in liquid water is not possible. It has been shown, however, that in crystalline hydrates an inverse relationship exists between the "intermolecular" O·····O distance and the intramolecular H–O distance [23] (fig. 1), e. g. the stronger the interaction, the more symmetrical becomes the hydrogen bond.



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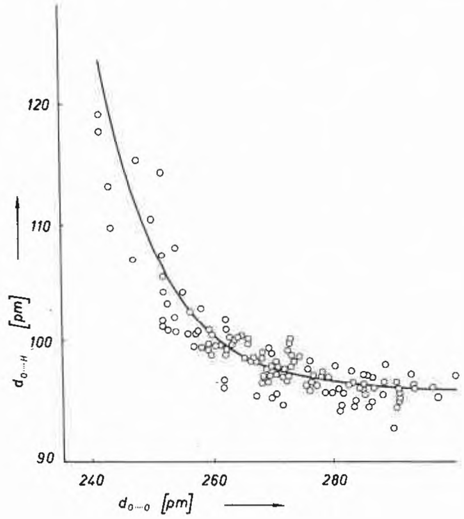


Fig. 1: Relationship between intermolecular O····· O distances and intramolecular O–H distances in crystalline hydrates (*Lundgren* and *Olovsson* [23]).

Water and aqueous solutions are characterized by a continuous absorption in the IR-spectra, which are altered by the nature and by the concentration of the solutes present [24]. In pure water three bands are observed with maxima at 3420 cm^{-1} (stretching vibration), 1645 cm^{-1} (scissor vibration) and at 705 cm^{-1} (torsional vibration) [24]. This shows the simultaneous presence of differently polarized hydrogen bonds in the liquid indicating a continuous array of structural units of slightly different energies. Apart from different internuclear distances—or rather associated with it—are different orientation effects as evidenced by a wide distribution in bond angles. The most probable value for the deviation of hydrogen bonds from linearity [24, 25] is not in the region between 0° and 5°, but rather in that between 5° and 10° with deviations up to 70° (fig. 2). Deviation from linearity are greater the longer the O·····O distance [26] (fig. 3) [27]. Linearity of hydrogen bonds in many-atomic molecules and in crystals appears rather the exception than the rule [27]!

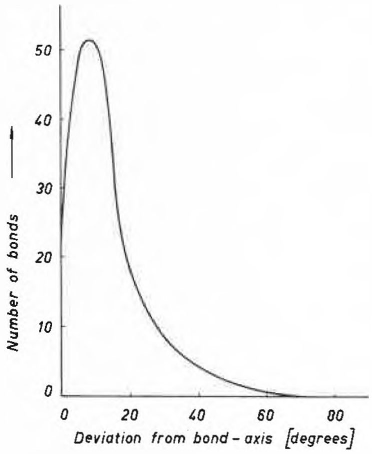


Fig. 2: Deviation of hydrogen bonds from linearity in crystalline hydrates (*Ferraris* and *Franchini-Angela* [27]).

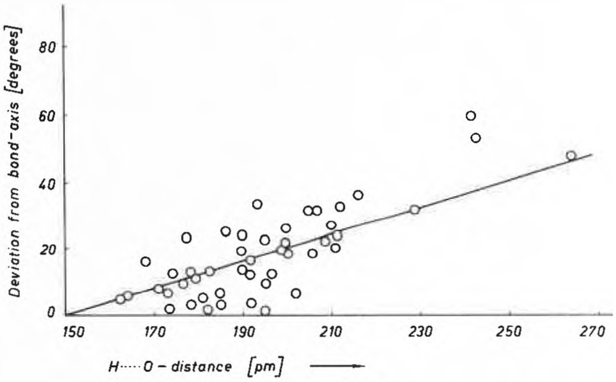


Fig. 3: Relationship between H ····· O distance of deviation of hydrogen bonds from linearity (*Ferraris* and *Franchini-Angela* [27]).

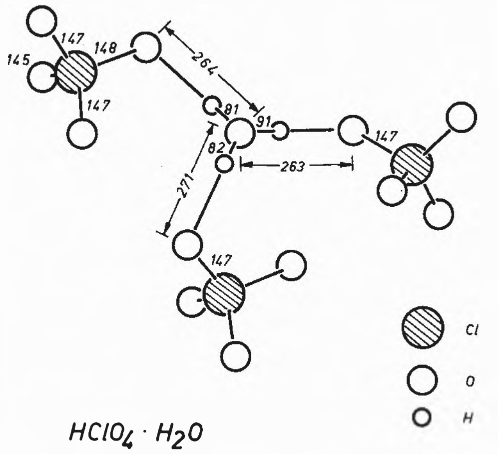
The terms "structure makers" and "structure breakers" are widely applied, although their usefulness has been questioned [28]. Indeed as will be shown later, their effects on the water structure are not vastly different, as in the immediate environment of any solute the hydrogen bonds are found shorter than within the bulk water structure.

3. Hydration Structures

3.1. Hydration Structures of Structure Breakers

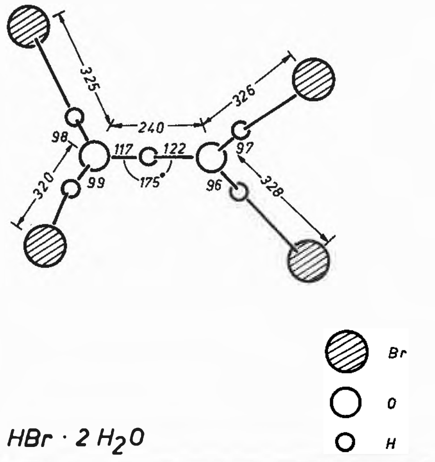
A large number of hydrates of strong acids has been studied in the solid state by diffraction methods, and detailed information on internuclear distances and bond angles in hydrated proton complexes in such crystals is available [23]. The results show that changes in the environment are reflected in changes both in internuclear distances within a certain structural framework and in changes in bond angles: While in the gaseous water molecule the H–O–H-bond angle is 104°, in acid hydrates bond angles have been found to vary from 98° to 133° with an average of 109°.

Bond lengths and bond angles within the hydrated hydrogen ion are highly influenced by the number of water molecules attached as well as by the nature of the counter ion. In solid hydrates H_3O^+ and $H_5O_2^+$ complexes have been structurally characterized. The structure of the H_3O^+ is symmetrical as long as all three H-bonds are coordinated to the same group [29]. In $HClO_4 \cdot H_2O$ each H_3O^+ is coordinated to three perchlorate groups with an average O · · · · · O distance of 266 pm. The $H_5O_2^+$-ion has been found in many crystals containing more than two water molecules for each proton [30]. In such cases the $H_5O_2^+$-ion is often bonded to extra water molecules with considerably longer (up to 17 pm) $H_2OHOH_2^+ \cdot\cdot\cdot\cdot\cdot OH_2$ bonds.



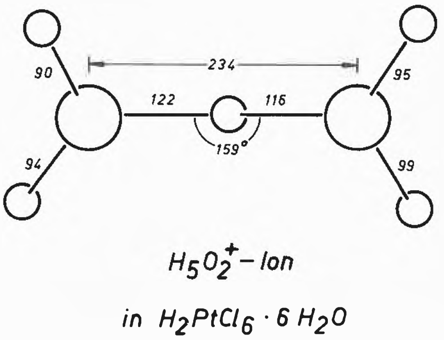
(4)

Deviations from the symmetric O–H–O structure in the $H_5O_2^+$-ion are due to asymmetrical environments. In crystalline HBr. 2 H_2O the four Br–O distances are not equal [31]. The neutron diffraction analysis [32] shows the bond length relationships in accordance with the bond lengths variation rules [20]. The site with long Br · · · · · O-distances of 324 and 326 pm provides a H–O distance of 97 pm and an adjacent O · · · · · H (bridge) distance of 122 pm. The stronger interaction on the other site with shorter Br · · · · · O distances of 320 pm and 325 pm increases the H–O distance to 99 pm and 98 pm respectively and decreases the O · · · · · H (bridge) distance to 117 pm. The central proton has the greatest vibrational amplitude along the bond axis, which indicates a broad and shallow potential minimum of the bridging bond, which cannot be clearly distinguished from a symmetric double minimum potential. In both cases the position of the bridging proton may be smeared.



(5)

The situation is analogous for the $H_5O_2^+$ unit in $H_2PtCl_6 \cdot 6\ H_2O$ [33]. The site with long H–O distances of 99 and 95 pm induces a short O–H (bridge) distance of 116 pm, while at the site of the shorter H–O distances of 94 and 90 pm the O–H (bridge) distance is 122 pm. An analogous situation is found in picrylsulfonic acid tetrahydrate $C_6H_2(NO_2)_3SO_3H . 4\,H_2O$ [34].

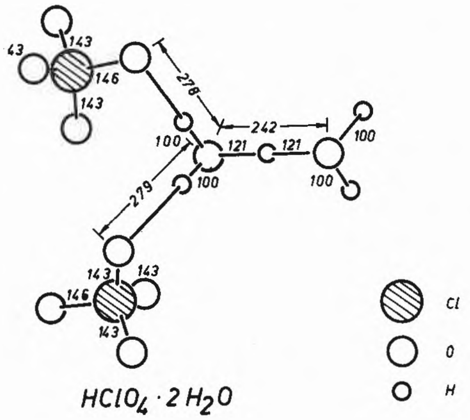


(6)

The $H_5O_2^+$ with an average O · · · · · O distance to the neighbouring oxygen atom of 270 pm is a stronger acceptor than a normal water molecule, where the O · · · · · O distance is 276 pm, but weaker than the H_3O^+-ion, where the corresponding distance is 257 pm. Accordingly the terminal OH distances are 101 pm, 98 pm and 95.8 pm for H_3O^+, $H_5O_2^+$ and H_2O respectively [23].

The effect of the counter ion may be remarkable: When one of the three perchlorate anions in $HClO_4 \cdot H_2O$ (formula 4) is replaced by a water molecule, the O · · · · · O distance of the oxygen atom of the water molecule will be shortened from 266 to 242 pm, while the distances to the oxygen atoms of the remaining two perchlorate groups are lengthened from 266 to 278 pm [30]. This is due to the stronger donor function of the oxygen atom in the water molecule as compared to that of the perchlorate ion. The O (water)· · · · · O (water) hydrogen bond is symmetrical and due to the symmetrical environment it represents the ideal case of an H_5O_2-ion with O–H distances of 121 pm. The effect of the replacement of the second perchlorate group by a water molecule to give an $H_7O_3^+$-ion, weakens the interaction with the first water molecule and strengthens that with the remaining perchlorate ion.

The O(water) · · · · · O(water) distances are found to be 248 pm and the O(water) · · · · · O(perchlorate) distance 265 pm [23]. The induced effects are well pronounced throughout the whole molecule, in that the stronger coordination by one water molecule is reflected even in remarkable lengthening of the peripheric Cl–O bonds within the perchlorate groups:



(7)

Hydrated proton species with the general formula $H_7O_3^+$ have been found either as isolated complexes or H-bonded to other water molecules [23]. In the latter case the $H_7O_3^+ \cdots\cdots HOH$ bond lengths are at least 22 pm longer than the H-bonds within the cation. The internal structure can be very asymmetric, however, and in some cases it is a matter of definition whether the formulation should be $H_3O^+ \cdot 2\ H_2O$ or $H_5O_2^+ \cdot H_2O$.

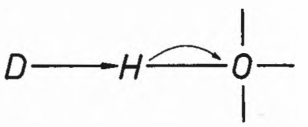
The ion $H_9O_4^+$ has so far been found in three compounds; in no case is the ion isolated, but is H-bonded to water molecules or to other hydrated proton complexes [23]. In all of the species the $O \cdots\cdots O$ distances are shorter than in water, where it is 276 pm. This distance is reduced in $HCl \cdot 3^1/_2 H_2O$ to 243 pm [35] and in $HClO_4 \cdot 3\ H_2O$ two of the four independent H-bonds between the water molecules are 248 and 254 pm respectively [36]. The distances found depend on the number of water molecules present and on the nature of the counter ion. The inverse relationship between the O–H distance as a function of the $O \cdots\cdots O$ distance has been represented in fig. 1.

The classical Eigen-type $H_9O_4^+$-ion is represented by a central H_3O^+ part which is pyramidically surrounded by three water molecules at an average $O \cdots\cdots O$ distance of 257 pm and an average $O \cdots\cdots O \cdots\cdots O$ bond angle of 111° [23]. The H-bond distances and angles within the individual complexes deviate in some cases quite considerably due to the crystallographic environment of water molecules surrounding the H_3O^+. The $O \cdots\cdots O$ distance within the $H_9O_4^+$ unit is increased by increasing coordination of the terminal oxygen atoms. For example in $HClO_4 \cdot 3^1/_2 H_2O$ the $O \cdots\cdots O$ distance towards a three coordinate oxygen atom is 248 pm and hence shorter than that towards a tetrahedrally coordinated oxygen atom (268 pm) [37].

The largest protonated unit structurally characterized is the $H_{13}O_6^+$-ion which has a high symmetry 2/m (C_{2h}), symmetrically surrounded by chloride ions [38]. The central O–H–O hydrogen bond lies across a center of symmetry with the $O \cdots\cdots O$ distance of 239 pm, which is among the shortest such distances yet observed. A difference electron density map supports the expectation of a symmetric hydrogen bond with its potential function represented by a curve with a single minimum [39].

3.2. Structure Breakers in Solution

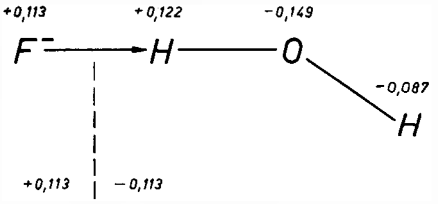
The role of donor-acceptor interactions for neutral solutes can be seen from the relationship between the H-bond energy and the donor strength of the solute molecules [40]. The frequency shift of the OH-stretching vibration increases as the donor number of the donor molecule *D* increases in the series: nitromethane < nitrobenzene < acetonitrile < ethylacetate < acetone < dioxane < diethylether < dimethylformamide < pyridine:



(8)

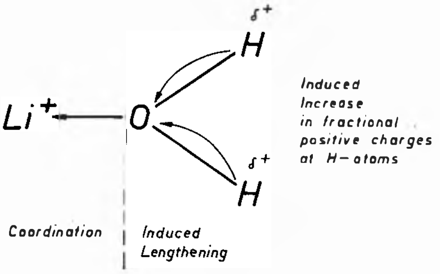
The effects of outer-sphere solvation for hydrated cations and anions have been formulated as follows [41]: Outer-sphere coordination leads to an increase in bond energy in the inner coordination sphere due to the cooperative effects between the water molecules. The electronic changes involved in the formation of a molecular adduct due to a charge transfer from donor to acceptor and to polarization effects, lead to an increase in electron density at the donor atom and to a decrease in electron density at the acceptor atom [42]. For example the calculated changes in net charges for the interaction of a water molecule as donor and a chlorine molecule as acceptor are low, while the gain in negative fractional charge at the terminal chlorine atom $Cl_{(2)}$ is considerably greater [43]. This is due to the "spill over-effect" [42] at the acceptor atom $Cl_{(1)}$ which is increased in positive fractional charge although it has gained originally electron density by the donor-acceptor interaction. Within the donor molecule electron changes are induced which result in a "pile-up" [42] of electron density at the donor atom by attracting electronic charges from other parts of the molecule, e. g. in a water molecule from the hydrogen atoms.

For a hydrated atomic anion, such as the fluoride ion, there is no possibility for compensating the loss of negative fractional charge due to a donor-acceptor interaction. Hence the fluoride ion is reduced in fractional negative charge by coordination of water molecules, while at the bridging hydrogen atom of the coordinated water molecule the positive fractional charge and at the oxygen atom the fractional negative charge is increased. Semiempirical calculations for the tetrahydrated fluoride ion gave the following results [44]: Reduction in fractional negative charge at the F^--ion to -0.887 electron by withdrawal of 0.113 electron, decrease in fractional positive charge at each of the bridging H-atoms by 0.122 electron and gain in negative fractional charge of 0.149 electron at each of the adjacent oxygen atoms [44].



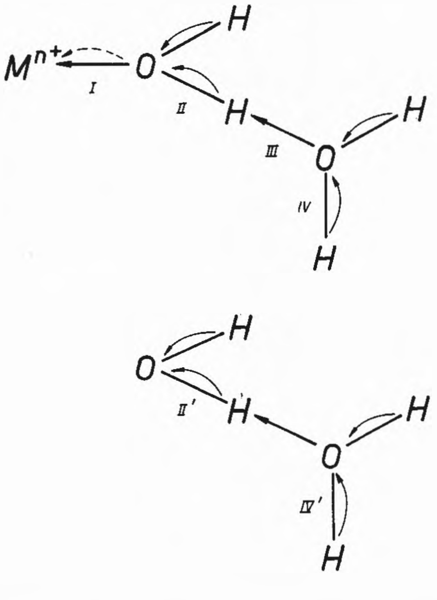
(9)

In the tetrahydrated lithium ion the fractional positive charge at the coordination center is lower than in Li^+. The increase in acidities of the terminal hydrogen atoms has been known for a long time and it is found in agreement with the first bond length variation rule [20, 45]:



(10)

The coordination of outer-sphere hydration layers involves additional charge transfer toward the metal ion, thus shortening the metal-ion-oxygen distance [41]. By addition of water to $LiCl \cdot 3\,H_2O$ the strain on the structure is lowered and the Li-O distance is considerably decreased. The cooperative effects between the hydration layers are considered responsible for the arrangement in a particular solution. Bond (II) becomes longer than bond (II′), bond (IV) longer than (IV′), bond (IV) is not as long as (II).



(11)

In concentrated salt solutions (> 1 M) the ions are so close together that the water structures around the ions become considerably distorted [46]. In a LiF solution the lithium ion has been calculated to contain four water molecules in its first coordination shell [46], in a lithium chloride solution the coordination number for water is five [46] and in a lithium bromide solution six [47]. Hence the coordination number for water molecules is decreased as they are partly displaced by increasing donor properties of the competing anion.

3.3 Hydration Structures of Structure Makers

With a few exceptions the structural feature common to clathrate hydrates is the pentagonal dodecahedron of water molecules. As an $H_{40}O_{20}$ unit of water structure, each vertex is the site of an oxygen atom and each edge an O−H · · · · · O hydrogen bond. Of the 40 hydrogen atoms, 30 are located in the edges [48]. As there is no direct evidence concerning the positions of the hydrogen atoms, the geometry is described only in terms of the oxygen atoms, which lie at the vertices of the polyhedra. With small distortions the pentagonal dodecahedron occurs in the crystal structures of clathrates with other polyhedra, so that together they satisfy the requirements for a periodic lattice. Depending on the pattern of association of the pentagonal dodecahedra various groups can be distinguished [48], e. g. (a) vertex linking in three dimensions (b) face sharing in two dimensions with vertex linking in the third (c) face sharing in three dimensions and (d) face sharing within limited groups of pentagonal dodecahedra with vertex linking between the groups. In the gas hydrates no distortions of the first lattice by reason of the presence of the guests is observed. The re-orientation of molecules encaged in clathrate hydrates are thought to be controlled mainly by cage geometry [49]. Clathrates are potentially nonstoichiometric compounds since all the voids need not necessarily be occupied in order to form a stable crystalline material. However, in the cationic hydrates the host lattice may be severly distorted.

The size and shape of the holes provided for the solute molecules appear to be adaptable to the spatial requirements of the solute particles. For instance the tri-n-butylsulfonium cations are paired in irregular cavities formed of infinite sheets of face-sharing pentagonal dodecahedra separated by hydrogen-bonded water structure which cannot be described in terms of the polyhedra observed in any other clathrate structure [50]. The sulfonium ions are oriented «back to back» with a S−S distance of 349 pm corresponding to a Van der Waals distance, the S-atoms almost completely shielded by alkyl groups from the water environment. The water cage which encloses these two cations is formed of 96 water molecules hydrogen bonded into 48 pentagons, 10 hexagons and two quadrilaterals. In order to attempt a description in terms of known clathrate structures, polyhedra with additional very irregular faces have to be used. The resulting polyhedra ara quite unsymmetrical and permit no rational description in terms of a symmetrical arrangement on a geometrical basis. The fluoride ions are part of the water network. There are 92 hydrogen bond distances in one unit cell of the water framework ranging from 269 to 290 pm. All of the hydrogen atoms available in the unit cell are hydrogen bonded. It has been suggested that the great utilization of the protons for the hydrogen bonding may be a significant energetic factor offsetting the unsymmetrical and distorted bonding of the more irregular clathration cavities. It has been shown that the O · · · · · O distances of the water framework enclosing a cavity will be shorter for unoccupied than for occupied holes [49, 51]. *King* [52] has shown that there is no inherent direct limitation on the size of polyhedra in clathrate-water networks. The clathrate structures and hence the holes are stable, although there are no chemical bonds involved between the water host and the guest molecules [53], with an exceptional degree of rotational mobility for the guest molecules.

Two types of solid gas hydrate structures may be distinguished [54]. Structure I contains 46 water molecules in the unit cell with a lattice constant of 1200 pm, which contains six big holes up to 590 pm diameter and two small holes. The smaller cavities are located at the vertices and the center of the unit cell; each of them are formed by a pentagonal dodecahedral array of 20 water molecules. These cavities may remain unoccupied. The remaining six water molecules in the unit cell form bridges between these dodecahedra in such a way that a second type of cavity is formed. Structure II has a unit cell of 1730 pm lattice constant containing 136 water molecules, 20 great holes of 590 to 690 pm diameter as well as 8 smaller holes. The ideal composition is $M \cdot 17H_2O$. The small holes remain usually empty, but they may be occupied by small molecules, such as nitrogen, oxygen or carbon dioxide molecules ("mixed hydrates").

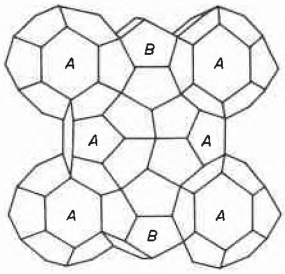


Fig. 4: Gas hydrate structure type I, A: tetrakaidecahedron, B: pentagonal dodecahedron (*Jeffrey* and *McMullan* [48]).

The presence of such gas molecules increases the thermal stabilities and the melting point up to 15 °C [55] due to their stabilizing effect they have been termed "Hilfsgase" (auxiliary gases) [55, 56]. While carbon tetrachloride does not give a clathrate, it is stabilizied in air under a pressure of 2 atm. Likewise iodine gives a hydrate if an oxygen pressure of 330 atm. has been applied, the hydrate being stable up to 8 °C [57]. Most hydrate crystals evolve air on melting indicating that a proportion of the pentagonal dodecahedra are so occupied giving a stoichiometry which is sensitive to the experimental conditions of crystallization. When chloroform-ice water has been shaken in air, N_2 and O_2 are evolved on gentle warming. While the composition of the hydrate is following only slowly the change in pressure of the auxiliary gas, the decomposition temperature corresponding to the pressure is very soon reached. It is therefore the composition within the surface area which is responsible for the decomposition temperature. The composition of the clathrate depends also on the pressure of the gas.

The effect of air on the properties of the structure II-clathrate hydrate of tetrahydrofuran has been studied by *Gough* and *Davidson* [58]. If the air present in the solution at atmospheric pressure and at 4 °C is entirely taken into the small cages of the hydrate, the hydrate density is increased by 0.000034 g/cm^3 and the volume change of melting reduced only by 0.013 cm^3/mol. On warming a frozen sample of THF. 16.79 H_2O, the bulk was found to melt at 4.45 °C, followed by evolution of bubbles which only completely disappeared at 5 °C, while the melting point of an air-free sample lies at 4.4 °C.

3.4. Structure Makers in Solution

The structural aspects in solutions of clathrates appear also similar to those in the crystalline compounds. A study of the alkyl proton resonances of symmetrical tetraalkylammonium ions [59] showed that the infinite dilution values, which are much higher in water than in acetonitrile, appear to be the result of the collective properties of the water structure with a relatively stable configuration of the water molecules around the non-polar alkyl chains. This is also evidenced by the temperature dependence of the proton chemical shift, which is decreased by increase in temperature: increased thermal motion causes progressive destruction of the enhanced water structure around the hydrophobic chains. The different protons of the alkyl groups are not equally effected by changes in temperature and in concentration with greater shifts of the inner CH_2-group protons. This suggests that the positive charge of the nitrogen atom is distributed over the neighboured methylene groups in accordance with quantum mechanical requirements [60]. At low concentrations the slight changes in δ show a weak increase for Et_4NBr, nearly constant values for Pr_4NBr and even a slight decrease for Pr_4NF and Bu_4NBr. In this range cation-cation interactions are dominant. Whereas in solutions so concentrated that there is not enough water available for the required structural arrangement which provides holes for the pairs of tetraalkylammonium ions, cation-anion interactions become inevitable. $\Delta\delta$ values for the fluoride remain well below those of the bromide, which in view of the greater effective polarizing power of a gaseous fluoride ion as compared to that of the bromide ion, is interpretable by a considerably stronger solvation of the fluoride ion incorporated within the aqueous framework similar to that in the corresponding clathrate hydrate. Hence it is much easier for the bromide ion to interact with the cation. An important finding is the effect of the amount of dissolved air on the surface tension of aqueous solutions [61]. A change with time was found to depend strongly on the inital quantity of air dissolved in the water sample. Surface tension is related to the structural differences of the interfacial region relative to the bulk. Hence a change in surface tension will be related to structural changes in the surface film and these reflect the changes in the bulk water molecular organization. In analogy to the effects on crystal surfaces [20, 62] the bond distances within the surface area are expected shorter than within a greater distance from the surface area. It is therefore not convenient to adhere to a rigid concept of an interfacial region structure consisting of a uniform type of molecular organization [63], but to assume rather the existence of collective structures in the presence of structure maker solutes [61] with polarizations of the H-bonds of the water network induced by gas molecules being even greater than those induced by structure breaking ions, as the hydrogen bond polarizabilities are increased by decreasing field strength [24].

4. Long Range Structural Effects

It is usually anticipated that the rearrangement of water molecules around a solute is restricted to a limited number of water molecules [64]. There is, however, good reason for assuming a greater number of water molecules involved in the hydration structures than is usually thought [20]:

1) A recent experimental study on hydration of the lithium ion reveals that after incorporation of 90 water molecules the properties of the water molecules are still slightly different from those in pure water [65]. The results of micelle formation with polyethylene oxide derivatives indicate hydration numbers up to 200 and hence a long-range distribution of the water structure [66]. From the partition coefficient of p-cresol between cyclohexane/water a hydration number of 90 has been found for a 0.1 M Na_2SO_4 solution [66]. In a 1 M $Al_2(SO_4)_3$ solution nearly all of the water molecules are engaged in the hydration structure, while a hydration number of 130 has been attributed to its 0.05 solution [67].

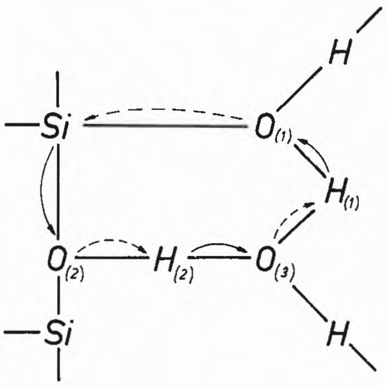
2) Calculations on an oversimplified model for the structures of successive water molecules arranged in a hypothetical chain commencing from an alkali metal ion gave the following results [68]: With increasing number of water molecules, which should simulate the number of hydration layers surrounding the cation, the inner-sphere metal-oxygen bond distance is decreased. A limiting bond energy appears to be attained only after addition of six layers of water molecules.

3) *Drost-Hansen* [63] emphasizes that structural elements may be induced in water by the presence of certain solutes. Evidence for particularly long-range structural stabilization has been inferred from the rheological properties of an aqueous solution of the copper salt of cetylphenyl ether sulfonic acid which retains elastic properties in a 0.002% solution [69]. This solution has a solute concentration of approximately 2.10^{-6}mol/liter and it contains about 20 million water molecules for one solute molecule. Hence the approximate mean separation between solute molecules is of the order of 250 water layers.

4) *Hammes* and *Schimmel* [70] have shown from an ultrasonic study of polyethylene glycol in aqueous solution that the relaxation process may be attributed to a cooperative process in the local hydration structures, in which considerable amounts of water appear to be involved.

5) A formal analogy exists between this concept and the structural features observed for the growth of successive SiO_2-layers on a aluminosilicate surface. *Weiss* [71] has shown that the information contained at the surface of an aluminosilicate structure, as determined by the LEED-method is transmitted to further layers of silicon dioxide which are allowed to grow on the surface. The remarkable result of this study is that the original information is not completely lost before the formation of 20 molecular layers. As the polarizabilities of hydrogen bonds in water are considerably greater than that of a normal bond [24] the number of molecular water layers should be correspondingly greater.

6) A highly concentrated solution containing silicic acid and various ions [72] is formed when water is condensed in capillary tubes of silica of 2 to 4 μm in diameter [73], which was originally thought to be "polywater". When the diameter of the capillary tube is increased, the dissolution process does not set in.
The donor-acceptor interpretation is as follows [20]: The interactions between a silicon surface atom and an oxygen atom $O_{(1)}$ of the water surface lead to lengthening of both the $Si{-}O_{(2)}$ and the $O_{(1)}{-}H_{(1)}$ bonds. The increased electron density at $O_{(2)}$ allows a strong interaction with $H_{(2)}$ of another water molecule with subsequent further lengthening of $Si{-}O_{(2)}$ and lengthening of $H_{(2)}{-}O_{(3)}$. In the simplified model $O_{(3)}$ interacts with $H_{(1)}$, initiating further cooperative effects, e. g. shortening of $O_{(1)}{-}Si$, further lengthening of $Si{-}O_{(2)}$, shortening of $O_{(2)}{-}H_{(2)}$, lengthening of $H_{(2)}{-}O_{(3)}$, shortening of $O_{(3)}{-}H_{(1)}$ and lengthening of $H_{(1)}{-}O_{(1)}$. In this way the electronic cycle may be repeated with final heterolysis of $Si{-}O_{(2)}$, $H_{(2)}{-}O_{(3)}$ and $H_{(1)}{-}O_{(1)}$. The electronic effects are however, transmitted throughout the liquid water structure and hence the changes in bond length in the water surface layer remain small. In a capillary tube of 2 μm radius the number of water layers from surface to surface is approximately 14800.



(12)

From the minimum radius of the capillary tube required for the formation of the concentrated solution, the number of water layers which are structurally and chemically effected by the silica surface is estimated to be 7.400!

Unfortunately minor structural differences within the hydration structure are beyond the accuracy of measurement. The possible drastic effects of extremely small differences in structural parameters can be seen by comparing the different effects of H_2O and D_2O on most organisms [74]: normal water, which contains only small amount mainly of DHO, is a "conditio sine qua non" for all biological systems, while D_2O is a retarder. The intermolecular forces in liquid D_2O are greater than in normal liquid water, as can be seen from comparing the melting points (+ 3.8°C for heavy water), the heats of melting (5.99 $kJ \cdot mol^{-1}$ for H_2O and 6.32 $kJ \cdot mol^{-1}$ for D_2O) and the lower solubilities of amino acids in D_2O [63]. Many differences in physiological action are known, but the differences in bond lengths are too small to be traced unambiguously by the experimental methods available. In the solid state there is no difference between OH- and OD-distances each being 101 pm [75]. In the liquid phase the O·····O distances are found to be equal both in normal and in heavy water [76]. In the gas phase the OH-distance is 96.9 pm and the OD-distance 96.4 pm [77]. Likewise there are no measurable differences in dielectric constant, dipole moment or surface tension. However, a very careful investigation revealed slight differences in structural parameters of H_3O^+ and D_3O^+ [78, 79].

Likewise the effects of added salts both on IR- and NMR-spectra are small [80] in contrast to the large effects on the solubilities of organic compounds in water.

5. Conclusions for Liquid Water

In the previous sections it has been concluded that in solutions of either structure making or of structure breaking solutes highly specific structural features are induced the effects of which are propagated through a large number of water molecules, suggesting that there are no defined ranges of interactions. In principle there are no clear-cut border lines between solvation sphere structure and completely undisturbed solvent structure. Instead, the structural rearrangements due to a solute particle are such that small gradual differences will be found in each of the solvation layers, yielding a complicated, flexible and highly organized "pseudomacromolecule". Even slight changes in the chemical composition of the solution will be reflected in structural changes throughout the liquid phase [20].

At this point it is important to note that a water structure consisting exclusively of water molecules, is purely hypothetical. All of the water models which have been proposed ignore the fact that "pure liquid water" is incapable of existence: Even in highly purified water both hydrated hydrogen ions and hydrated hydroxyl ions are present at equilibrium. One of such ions is expected within a cube formed from edges each of them occupied by 820 water molecules. In addition to these ions normal water contains CO_2 which is partly present as hydrogen and hydrogen carbonate ions. In adopting the concept of long range order (section 4) appreciable structural effects should be expected according to the presence of these ions [20].

A second important effect is due to the fact that water if saturated by air, constitutes at 0°C a $1.25 \cdot 10^{-3}$ molar solution of oxygen, nitrogen and carbon dioxide. This corresponds to approximately 44.000 water molecules for one solute molecule and for a spherical hydration shell to approximately 18 layers of water molecules around each gas molecule. The gas molecules may be expected to occupy holes in the liquid just as they do in the crystalline clathrate hydrates which can be obtained from the solutions. In addition to the occupied holes a number of vacant holes is expected to be present in liquid water in analogy to the structural features of clathrate hydrates.

We may therefore consider liquid water as a highly differentiated, highly organized and rather flexible "pseudomacromolecule" containing both ions and a number of mobile holes. The holes are partly occupied by the constituent molecules of air and partly vacant. To some extent this description correspounds to that provided by the flickering cluster model, as the boundaries connecting the contacts between the clusters surround unoccupied areas, which are mobile as the clusters change their relative positions.

The boundaries between the "individual" clusters have not been defined structurally and the individuality of a cluster cannot be maintained at the areas where they have come in immediate contact with each other. Since each cluster will always have several of such contacts at the same time, it can never represent a completely isolated entity. The situation may be better represented by the quasi-continuum model containing holes, not necessarily spherical, although their stability is expected greatest in this arrangement. The holes are considered as rather mobile in a quasi-continuum which is subject to continous structural changes related to the relative positions of the holes at any given

The structural pattern becomes more uniform and more specific as the number of structure-regulating centers is decreased, e. g. the greater their mean distances. At the same time the maximum O·····O distances are also increased. According to fig. 1 the O–H bond length is decreased as the O·····O distance is increased and hence the symmetry of the O·····H–O bonds is decreased by increasing dilution. The peak areas in this diagram represent the regions, which are neglected in any short-range order treatment!

There seems to be a relation between bond lengths and relaxation times. For a dissociative mechanism the rate of exchange is a function of the bond strength [41]. We should therefore expect the signal for the relaxation times becoming sharper the more dilute the solution and broadening as the concentration is increased. *Barthel* [82] has shown that this is actually found to be the case. The spectrum of expected life times corresponds at least in a qualitative way to the hydrogen bond length spectrum: the greater the number of structure regulating centers, the broader the bond length spectrum, the smaller the maximum bond lengths. This is paralleled by a broadening of the relaxation times spectrum and a decrease in the relaxation times. Thus each solution is characterized individually both by structural and by dynamic properties.

The high mobilities of the structure regulating centers in the liquid request continuous changes in their relative positions and in that way structural fluctuations are effectuated. We suggest therefore to regard liquid water and each of its solutions as a highly differentiated "pseudo-macromolecule" consisting of consecutive arrays of inderdependent structural units which provide a fluctuating collective pattern. This pattern is changed by any change in composition and hence for a given solute it depends on its concentration not only in more concentrated, but even in extremely dilute solutions, such as normally purified water.

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