Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Water Structure: Unstable Aggregations of Stable Clusters: Letters to the Editor

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To cite this Article Pollak, M. E.(1971) 'Water Structure: Unstable Aggregations of Stable Clusters: Letters to the Editor', Journal of Macromolecular Science, Part A, 5: 4, 809 — 814

To link to this Article: DOI: 10.1080/00222337108061061

URL: http://dx.doi.org/10.1080/00222337108061061

J. MACROMOL. SCI.–CHEM., A5(4), pp. 809-814, July, 1971

LETTER TO THE EDITOR

Water Structure: Unstable Aggregations of Stable Clusters

SUMMARY

A precise atomic description of a highly stable tetrahedrally hydrogen bonded decameric water cluster containing OH . . . OH . . . OH rings demonstrates "cluster aggregation," a phenomenon postulated in Erlander's structural model of water.

INTRODUCTION

The increased size and stability of a water cluster at a cellulose acetate or silica glass interface is presumably the result of an interaction involving hydrogen bonding with certain hydrophilic polar groups in the surface of the solid [1]. Cope [2] obtained evidence for two types of ordered water in rat muscle and brain by means of NMR line broadening techniques. Simultaneously, Hazelwood et al. [3] reported similar evidence for two types of ordered water in skeletal muscle.

Compared to ordinary liquid water, water of tissues is believed to have increased organization. There is evidence that small ions are less soluble in water of cells than in liquid water. Using steady-state NMR analysis of water, Hazelwood et al. [3] have found evidence for at least two fractions of muscle water with different degrees of structure, but both with significantly more structure than ordinary liquid water. The minor fraction (approximately 8% of total water) is believed to have an extremely high degree of structure.

Recently, Derjagin of the Soviet Academy of Sciences disclosed during a lecture at the Polytechnic Institute of Brooklyn that he has successfully prepared anomalous water having a molecular weight of 180 amu.

Derjagin's preparation of anomalous water [4] was accomplished using capillaries of borosilicate glass with diameters of 1 to 10 μ. It has been suggested that the glass surface of the tubes in which the substance is made may act as a catalytic template for the formation of initial "anomalous water seed units."

Some properties of anomalous water that have been reported are: 1) molecular weight of 180 amu is observed for vapor and liquid forms; 2) the substance can be distilled; 3) water of differing "degrees of anomaly" can be prepared [5]; 4) the density of liquid anomalous water is about 1.4 at room temperature; 5) in the liquid state, anomalous water is observed to coexist with ordinary water under certain conditions; 6) the liquid is birefringent; 7) formation of "liquid threads" is often observed during preparation; 8) Derjagin and Lippincott [6] have reported the curious ability of anomalous water to creep up the walls of the capillary tube in which it is contained; 9) solid anomalous water has an amorphous structure.

DESCRIPTION OF THE ANOMALOUS WATER CLUSTER

Erlander [7] presented a "stable cluster" model for water which assumed that below 60°C stable water clusters form unstable cluster aggregates. He later extended his model to include an explanation for the "anomalous water" discovered and described by Derjagin. The 180 amu water cluster, which is in accord with Derjagin's observations, must be capable of distillation and existence in frozen equilibrium with ordinary liquid water. An atomic structural model for such a highly stable tetrahedrally hydrogen bonded water cluster capable of forming cluster aggregates can now be proposed. (Figure 1 is a perspective drawing of the proposed 180 amu cluster; Table 1 gives a numbering scheme for the atoms.)

Each oxygen atom may be regarded as situated at the center of a regular tetrahedron, two corners of which are occupied by covalently attached hydrogen atoms. The oxygen will act as an acceptor of hydrogen bonds in the neighborhood of the other two corners. Oxygens 10, 14, 16, 18, 4, 8, and 6 are coplanar. Hydrogens 19, 29, 33, 17, 25, 5, 15, and 13 are coplanar. The decamer contains five six-atom rings (2, 3, 8, 15, 6, 9; 2, 3, 8, 13, 4, 7; 10, 21, 12, 27, 14, 19; 4, 5, 16, 29, 14, 25; 16, 33, 18, 39, 20, 31) and one ten-atom ring (2, 7, 4, 25, 14, 19, 10, 17, 6, 9). Part of the high stability of the cluster can be ascribed to the abundance of six-membered rings comprised of alternating oxygen and hydrogen atoms.

To justify the fact that precisely ten ordinary water molecules form a stable cluster, examine those oxygen atoms in Fig. 1 that are available to

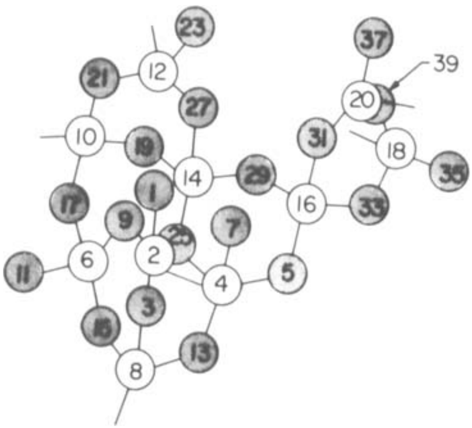

Fig. 1. An anomalous water molecule of molecular weight 180 amu.

participate in further hydrogen bonding, namely, numbers 8, 10, 12, 18, and 20. (Oxygens 2, 4, 6, 14, and 16 are saturated with hydrogen bonds.) Oxygen number 8 might very well form a weak ordinary strength hydrogen bond with an ambient ordinary water molecule. However, there is no reason to expect that oxygen number 8 would easily form another hydrogen bond as strong as the one it is participating in with hydrogen 3 of Molecule I.

Oxygens 10 and 12, along with oxygens 18 and 20, have become part of six-membered rings (asymmetric cyclic water trimers). In the case of 10 and 12, oxygen 12 has assumed an orientation so that the bond to hydrogen 23 is cis (with respect to ring 10, 21, 12, 27, 14, 19) to a possible extra hydrogen bond oxygen 10 might wish to participate in. That is to say, 10 is oriented to form any new hydrogen bond trans to any new hydrogen bond 12 might be tempted to form.

In the case of 18 and 20, 20 has chosen an orientation so that 18 must similarly form any additional hydrogen bonds trans to an additional hydrogen bond of 20 with respect to the ring 16, 31, 20, 39, 18, 33. In the former case, hydrogen 23 is the culprit; in the latter situation 37 and 35 make formation of additional strong hydrogen bonds unlikely. Thus,

Table 1. Labels for Atoms. Hydrogens are labeled with odd numbers and oxygens are labeled with even numbers.

Ordinary water molecule number	Oxygen number	Hydrogen numbers
I	2	1,3
II	4	5,7
III	6	9,11
IV	8	13,15
V	10	17,19
VI	12	21,23
VII	14	25,27
VIII	16	29,31
IX	18	33,35
X	.20	37,39

oxygens 8, 10, 12, 18, and 20 probably do occasionally form weaker hydrogen bonds to ordinary water molecules, but they cannot form lattices which are anywhere near as stable as those present throughout the 180 amu water cluster.

The fact that some hydrogens of the cluster, e.g., 11, 23, 35, and 37, do not ensnare oxygens of ordinary water molecules into additional strong hydrogen bonding is justified when one considers that the seed anomalous water unit was initially formed only with help from the surface of the glass capillary tubing. This sort of aid is apparently not very likely to be extended in the case of hydrogens 11, 23, 35, or 37.

Del Bene and Pople [8] in a letter concerning the intermolecular energies of small water polymers indicated that an asymmetric cyclic water trimer has a binding energy as great as that of three separate hydrogen bonds, in spite of the strain or distortion energy involved. They calculated that a cyclic water trimer of C_3 symmetry is somewhat less stable. The stability of small isolated water polymers was great enough to suggest a "significant role in the structure of liquid water."

MECHANISM OF FORMATION

The mechanism of cluster formation is: 1) a cyclic trimer of C_3 symmetry containing oxygens 14, 16, and 4 is formed by surface catalysis so that the ring is parallel to the surface; 2) three additional six-atom rings which are asymmetric cyclic trimers are formed perpendicular to the plan of the catalytic surface; 3) water molecule number III is the tenth ordinary water molecule to become part of the cluster. Oxygen 6 (of Molecule III) takes an asymmetric position bridging two of the three asymmetric cyclic trimer rings so that the fifth six-atom ring (2, 3, 8, 15, 6, 9) is formed.

Cluster aggregation, evidenced by the formation of "liquid threads," occurs when the 180 amu clusters are "hooked" together, i.e., oxygens 10 and 12 of one decamer hydrogen bonding with hydrogens 35 and 37 of another decamer. Cluster aggregates in anomalous water would take the form of long strands. Erlander [7] correctly predicted: "The organizational pattern of these cluster aggregates of super water must make it virtually impossible to link one cluster aggregate to another."

However, Erlander also tells us: "These stable clusters are crystalline structures and hence involve hydrogen bonding between all water molecules in a specific cluster. This hydrogen bonding contrasts with the Pauling model [9] of a clathrate-water structure surrounding non-hydrogen-bonded water molecules."

If an ordinary ambient water molecule were to find itself in the "basket-like" area at the left of Fig. 1, a casual observer might indeed conclude that he was looking at a clathrate-water structure surrounding a nonhydrogen-bonded water molecule.

Further, the model presented here would be expected to yield an unstable cluster aggregate since clusters are held together by highly distorted eight-atom rings, such as 37, 20, 39, 18, 35, 10′, 21′, 12′ (primes refer to atom numbering in the adjacent decamer cluster).

CONCLUSIONS

The determination of the molecular weight of the anomalous water observed by Derjagin represents the first experimental observation of a water cluster capable of forming cluster aggregates. In fact, the "liquid threads" are the first experimental observations of cluster aggregates. Perhaps the 180 amu cluster exists to some small extent in ordinary water. It is too early to know. However, the existence of anomalous water provides some experimental evidence of a water cluster stable enough not to be labelled "flickering."

There are, of course, many who are continuing to attempt explanations of anomalous water in terms of impurities. They will be most interested in the recent work of Middlehurst and Fisher [10] who claim that it is possible to produce a form of polywater without the presence of a surface containing –Si–O groups.

Added in proof: W. C. McCabe, S. Subramanian, and H. F. Fisher, *J. Phys. Chem.*, **74**, 4360(1970) provide spectroscopic data further supporting a flickering cluster liquid water model containing "extensively doubly H-bonded three-dimensional network molecules of water."

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Accepted by editor September 1, 1970
Received for publication October 12, 1970