EARTH SCIENCES

STRUCTURING OF WATER MOLECULES ON ORGANIC COMPOUNDS AND OTHER SUBSTANCES. COPING OF THE RESULTING WATER CLUSTERS BY BULK WATER

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Abstract

A very small amount of water molecules in an organic solvent (0.02 % in acetonitrile) can form clusters of different sizes on contact with dissolved organic molecules. Bulk water added to such wet solvent will then copy and reproduce these clusters and acquire different hydrolytic activities depending on the size of the copied organic molecules. For example, if wet commercial acetonitrile contains 0.3 % sugar, then bulk water added to it will hydrolyze triethyl phosphite substantially slower than in the same acetonitrile without sugar. The size of clusters in wet acetonitrile can also vary within wide limits upon contact with various substances. For example, after contact of wet acetonitrile with copper or silver, the added bulk water reacts with triethyl phosphite up to 500 times slower, depending on the time of contact with these metals and intensity of the solar influence. On the contrary, after contact of wet acetonitrile with aluminum or molybdenum this reaction accelerates.

Keywords: water, clusters, copying, hydrolysis, solar influence.

Introduction

Water possesses unique properties owing to the ability of its molecules to form hydrogen bonds with each other. In the bulk phase all water molecules form a common continuous three-dimensional network of hydrogen bonds in which every molecule has tetrahedral bonding directions. [1,2] However, on mixing water with organic solvents, for example, with acetonitrile, this network disintegrates with the formation of clusters $(H_2O)_n$ rather than single water molecules. The size of clusters may vary from a few water molecules to several hundred. [3] Small clusters are much more chemically reactive than large ones as they contain a lot of free –OH groups which are not involved in the network of hydrogen bonds. [1,2,4-6]

We have recently found that even a very small amount of water molecules in an organic solvent (0.02 % in acetonitrile) form clusters the size of which constantly changes under the influence of the Sun. Bulk water, added to such wet acetonitrile, copies and reproduces these original clusters and depending on their size acquires different hydrolytic activity, as it can consist of a larger number of small active clusters or a smaller number of large passive clusters. For this reason, the rate of hydrolysis of triethyl phosphite with the same amount of added water strongly depends on the intensity of the solar influence and on where wet acetonitrile was located before mixing it with water - outdoors, inside buildings or underground. [7] The dependence on the solar influence makes this reaction in wet acetonitrile very dynamic. Its rate can change up to 200 times during the year and 11-year solar cycle and exhibits diurnal variations depending on the position of the Sun in the sky. [8,9] Figure 1 shows two annual rate variations in 2015 and 2019, in the middle and end of the 24th solar cycle, respectively.

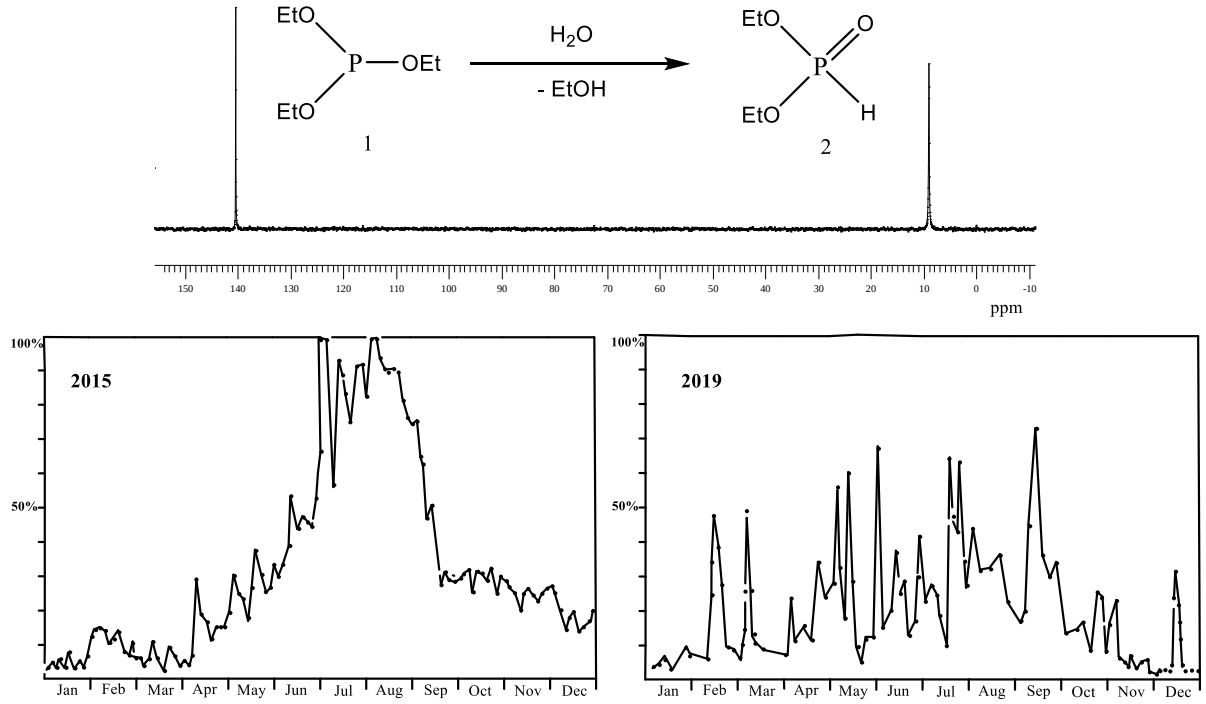

***Fig. 1**. Annual changes in the rate of hydrolysis of triethyl phosphite **1** into diethyl phosphonate **2** in acetonitrile in the middle and end of the 24th 11-year solar cycle. The reaction rate can be accurately measured using ^{31}P-NMR spectroscopy.*

The influence of the Sun on the size of water clusters in wet acetonitrile and their copying by bulk water is confirmed by the fact that in thoroughly dried acetonitrile, in which there are no clusters for copying, the reaction of added bulk water with triethyl phosphite is not sensitive to variations in solar influence.

Further research of this phenomenon showed that different factors can influence the structuring of water clusters.

Results and discussion

We have found that structuring of a very small amount of water molecules (0.02 %) in acetonitrile depends not only on the intensity of solar influence. Water clusters of different sizes are also formed on contact of wet acetonitrile with organic compounds. Bulk water added thereafter will copy and reproduce these initial clusters and acquire different hydrolytic activities depending on the size of copied organic molecules. This was confirmed using sugar, the molecule of which is rather large ($C_{12}H_{22}O_{11}$). In wet acetonitrile, containing 0.3 % sugar, the reaction of triethyl phosphite with bulk water proceeds up to 4 times slower than in the same experiment without sugar. (Fig. 2) The extent of this slowdown depends on the intensity of solar influence. The structuring of water clusters upon contact with sugar and their copying by bulk water is clearly manifested during periods of low solar influence, when water clusters are stable. During periods of high solar exposure, large clusters are quickly destroyed, and the rate of hydrolysis increases greatly and can be the same in the presence of sugar and without it. Therefore, this phenomenon depends also on geographic latitude, time of year and position of the Sun in the sky.

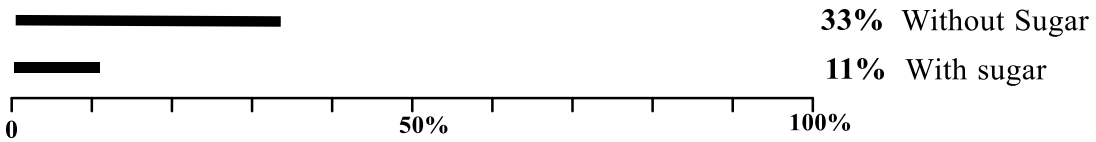

***Fig. 2.** Hydrolysis rate of $(EtO)_3P$ in CH_3CN, containing 0.3 % sugar compared with the control reaction without sugar. Reaction time 22h in January 2023.*

The structuring of water molecules and the formation of clusters are very sensitive to contacts not only with organic molecules, but also with other various materials and their surfaces. We have found that when in contact with various metals, water clusters in wet acetonitrile can either disintegrate into smaller active clusters or combine into very large passive clusters. After copying and reproducing these clusters with bulk water, the rate of hydrolysis of triethyl phosphite in it will be very different.

For example, if aluminum or molybdenum is placed in acetonitrile containing 0.02% water, the existing water clusters will reduce their size and the added bulk water after copying them will become more hydrolytically active. In contrast, after contact of wet acetonitrile with copper, silver or iron, all water clusters will combine into very large inactive clusters. The size of clusters can increase by a factor of about 100 and their concentration in the solvent will proportionally decrease. The degree of clusters enlargement depends on the contact area with metals and on the contact time.

For example, if 3 copper wires with the diameter of 1 mm are placed in 0.5 ml of acetonitrile in a 5 mm-NMR-tube for 20 minutes, then bulk water added after this will react with triethyl phosphite up to 50 times slower than in the same experiment in which acetonitrile had no contact with copper. (Fig. 3) And if copper was in acetonitrile a couple of days, then the reaction can slow down up to 500 times. With silver and iron, the slowdown is somewhat less, although still large.

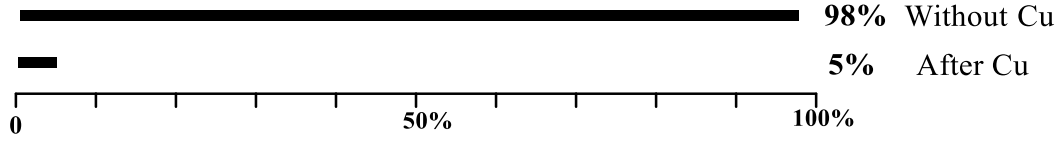

Fig. 3. *Hydrolysis rate of $(EtO)_3P$ in CH_3CN, which was in contact with copper for 20 min, compared with the control reaction without copper. Reaction time 0.5h at noon in July 2020.*

The fact that the metal acts only on water clusters is confirmed by the lack of influence of copper, silver, or iron on thoroughly dried acetonitrile. Further evidence is that after metal exposure ceases, the large integrated clusters gradually break down into smaller clusters and the reactivity of the added water increases again. This process of cluster decomposition is greatly accelerated by ultraviolet and X-ray irradiation.

Thus, by changing the size of a small number of initial clusters in acetonitrile, one can control the size and chemical reactivity of the clusters reproduced by bulk water after its addition.

The structuring of water molecules and the formation of clusters of different sizes also occurs upon contact with the surfaces of different materials. For example, if a 1.8 % solution of water in acetonitrile is drawn into a dry Pasteur pipette for 1 minute before adding triethyl phosphite, then the hydrolysis accelerates, and if such a pipette was just made from molten glass, the hydrolysis slows down noticeably.

Influence of the Sun

Solar radiation destroys water clusters, that is why due to annual changes in solar influence, the structuring of water molecules upon contact with sugar and metals and the copying of the resulting clusters with bulk water was stably recorded in winter with weak solar exposure and was less stable in summer. Our experiments were conducted in Kiev and in Bremen, at 50º and 53º North latitude. Near the equator the solar influence is greater and less variable throughout the year. For this reason, large water clusters there should be less stable, and the coping process less pronounced.

Influence of salts

In the presence of salts, the self-organization of water molecules and formation of larger water clusters are substantially facilitated. [8] Therefore, even small amount of salts dissolved in water noticeably slows down the hydrolysis of triethyl phosphite. All presented results were obtained using fresh water from the Dnieper and Weser.

Materials and methods

Structuring of water molecules upon contact with sugar. Powdered sugar (1,2 mg) was added to commercial acetonitrile (400 mg) in 5 mm-NMR-tube. In 30 minutes, water (7 mg) was added, and the solution was briefly stirred by shaking. After 2 minutes triethyl phosphite (25 mg) was added, and the reaction mixture was briefly stirred by shaking.

Structuring of water molecules upon contact with metals. 3 Copper, silver or iron wires of 1 mm diameter were inserted into 5 mm-NMR-tube containing commercial acetonitrile (400 mg). The time of contact with the metals varied from several minutes to several days. After removing the metals, bulk water (7 mg) was added to acetonitrile and the solution was briefly mixed by shaking. After 2 minutes triethyl phosphite (25 mg) was added, and the reaction mixture was briefly stirred by shaking. Depending on the intensity of solar influence, the reaction can be completed in 30 minutes, but can last 2 weeks.

When preparing reaction solutions and during the reaction, NMR tubes should be protected from light with cardboard screens and located in the same direction in space. [9] The degree of conversion was determined by measuring the integral intensities of the signals of triethyl phosphite (at 140 ppm) and diethyl phosphonate (9 ppm) in ^{31}P-NMR spectra.

The commercial acetonitrile used contained ≤0.02 % water. Water was taken from the Dnieper and Weser. NMR-tubes used should be checked for identity by the reaction of triethyl phosphite with bulk water added to commercial acetonitrile. They should only be washed with acetonitrile and should not come into contact with other substances.

Conclusions

Water molecules are structured differently and form clusters of different sizes upon contact with organic compounds or other substances. Bulk water added after that can copy the formed clusters, reproduce them in large quantities and acquire different hydrolytic activities depending on the size of the copied clusters. Solar radiation destroys water clusters, so their copying by bulk water occurs only during periods of weak solar influence when water clusters are stable. The obtained results shed light on the 'water memory' phenomenon and explain the instability of its experimental reproducibility. [10,11,12]

Competing interest

There are no conflicts to declare.

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