__Review Article__

HYDROGEN BOND ENERGIES IN FORMATION OF WATER MOLECULE CLUSTERS

ABSTRACT

During the last decades, the interest in water structure has increased as an important theoretical and practical problem, connected with different industrial and biological applications. Theoretically, the mechanisms of water molecules cluster formation have been of special interest. It has been assumed that aggregation of water molecules depends on the energy of hydrogen bonds. The character of this process was investigated in the present study. The approach was based on measurements of the wetting angle θ of water droplets at different energy levels during their evaporation. Taking into account previous findings that θ depends on the average energy of hydrogen bonds between water molecules, it was assumed that the size of water clusters is related to the value of θ, measured at different energy levels. This assumption was confirmed by the obtained experimental results.

Keywords: water, hydrogen bonds, water clusters, energy.

INTRODUCTION

The interest in elucidating the structure of water has especially increased in connection with studies of hydrophobic boundary surfaces and in processes with practical application such as electrolysis, structuring of organic molecular crystals, non-polar media and theoretical analyses. New effects of water are also being described.

The wetting angle, also known as contact angle, quantitatively describes how liquids wet solid surfaces. In terms of geometry, it is the angle formed at the intersection point of the three phase boundaries between a liquid, solid and air. The wetting angle is a common predictor of the qualities and behavior of solid surfaces after physical or chemical treatment.

In 1983, Antonov showed that, during evaporation of water droplets on different surfaces, the wetting angle is related with the average energy of the hydrogen bonds. For this purpose, he and co-authors designed specialized equipment for real time measurements of this angle with sufficient accuracy. So, the relation between the wetting angle and the average energy of the hydrogen bonds during droplet evaporation can be expressed as follows:

$$\theta = \arccos(-1-bE) \qquad (1)$$

where θ is the wetting angle, E is the average energy of the hydrogen bonds, b is a temperature-dependent parameter (1, 2, 3).

It has also been found that the wetting angle changes discretely as water droplets evaporate. The shape of these curves depends on the composition of investigated water and other liquids, and this has opened up new possibilities for studying biochemical and biological effects.

Studies have shown that clusters with different numbers of water molecules are formed on the basis of hydrogen bonds in bulk water.

The following spectral methods have been generally used to study water clusters - H-NMR (4, 5), far-infrared (6), vibration-rotation-tunneling (VRT) (7), neutron diffraction (8), SCC-DFTB Method (9, 10), NES (11, 12). An earlier authors' study has estimated that, at (E = -0.1387 eV) (λ = 8.95 µm) ($\tilde{v}$ = 1117 cm^{-1}), water clusters of approx. 21 water molecules are formed in catholyte water (13). Based on this, a cluster model was proposed with 20 water molecules in a dodecahedral structure with diameter of the circumscribed sphere equal to 0.822 nm.

This result corresponds to our result by applying the Antonov effect to "discrete" evaporation of water drops. Analyses for clusters of n = 6-20 water molecules are available in a number of publications (14, 15, 16). Cases of n = 1-6 have been described in (17).

It has also been found that at n = 20 about 25% of water molecules are structured with this number (18).

The question arises to what extent the discrete change in the wetting angle during evaporation of water droplets depends on the formation of clusters with different numbers of water molecules. This is the purpose of the present study.

MATHERIALS AND METHODS

Electrochemically activated catholyte water (19, 20) with the following parameters was used for the study: pH = 9.30, oxidation reduction potental (ORP) = - 450 mV.

The wetting angle θ was measured with a specially designed apparatus which is described in detail in (11, 12, 21). Measured wetting angles of 10 water droplets during their evaporation from a solid surface varied from 74 to 0 deg. The measurements were sequential and N denotes the number of measurements taken from the initial value of θ_0 to 0. The time interval for each reading was 10minutes. From the obtained values of θ, the average energy of the hydrogen bonds E in eV was calculated according to the formula:

$$E = \gamma^o (1+\cos\theta)/\tau(1+\cos\theta_o) \qquad (2)$$

where θ is the wetting angle, E is the energy of the hydrogen bonds.

The expression $\tau (1+\cos\theta_0) / \gamma^o$ is equal to 14.33 eV at 20° C.

Evaporation of water drops was performed in a hermetic chamber with stable temperature of 20° C (19). The drops were placed on BoPET (biaxially-oriented polyethylene terephthalate) foil with 350 µm thicknesses.

RESULTS AND DISCUSSION

The average weight reduction values of the investigated water drops during their evaporation and to the corresponding values of the wetting angle are shown in Table 1. The average initial height of the droplets was h_i=2.30 mm and their average final height was h_f=0.26 mm. The layering structure of water has a periodicity of 0.30 ± 0.03 nm (20).

Table 1. Average weight reduction values of water drops during their evaporation and the corresponding values of the wetting angle

Wetting angle (º) θ	Weight mg
74	48.0
66	37.9
58	29.0
50	21.3
42	14.8
34	9.4
26	5.3
18	2.4
10	0.6

Figure 1 shows the dependence of the wetting angle on the sequential number of the corresponding measurement. This angle decreased from 74 deg to 10 deg and the dependence had a step character.
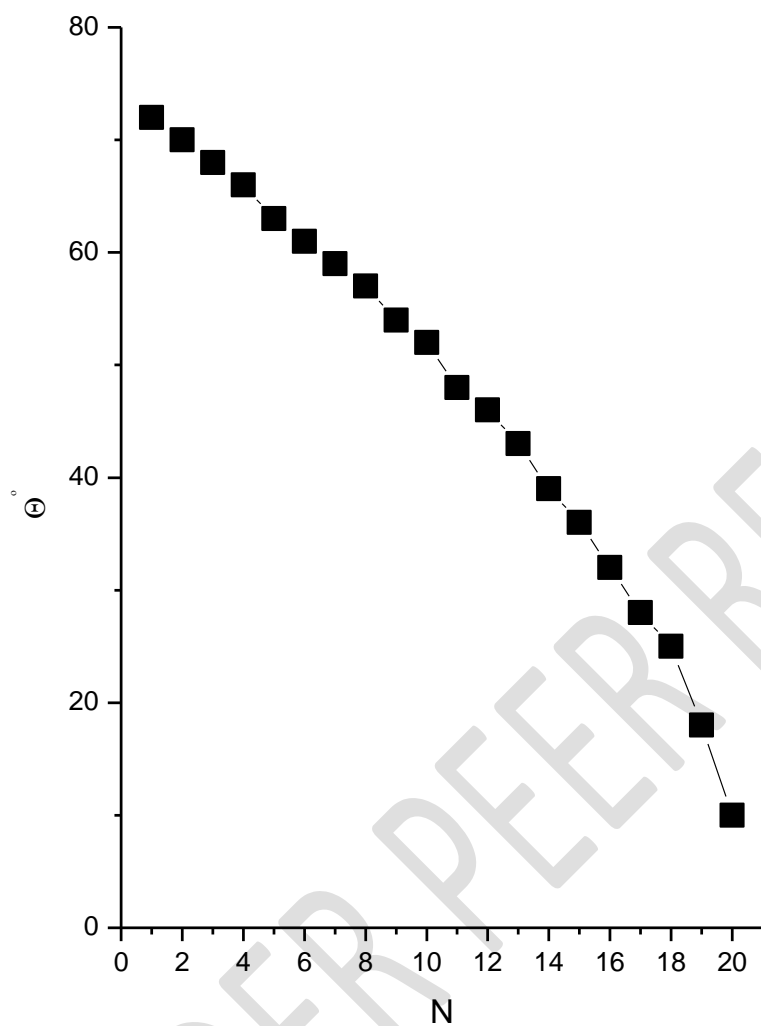
Figure 1. Dependence of the wetting angle θ on the sequential number of the corresponding measurement.

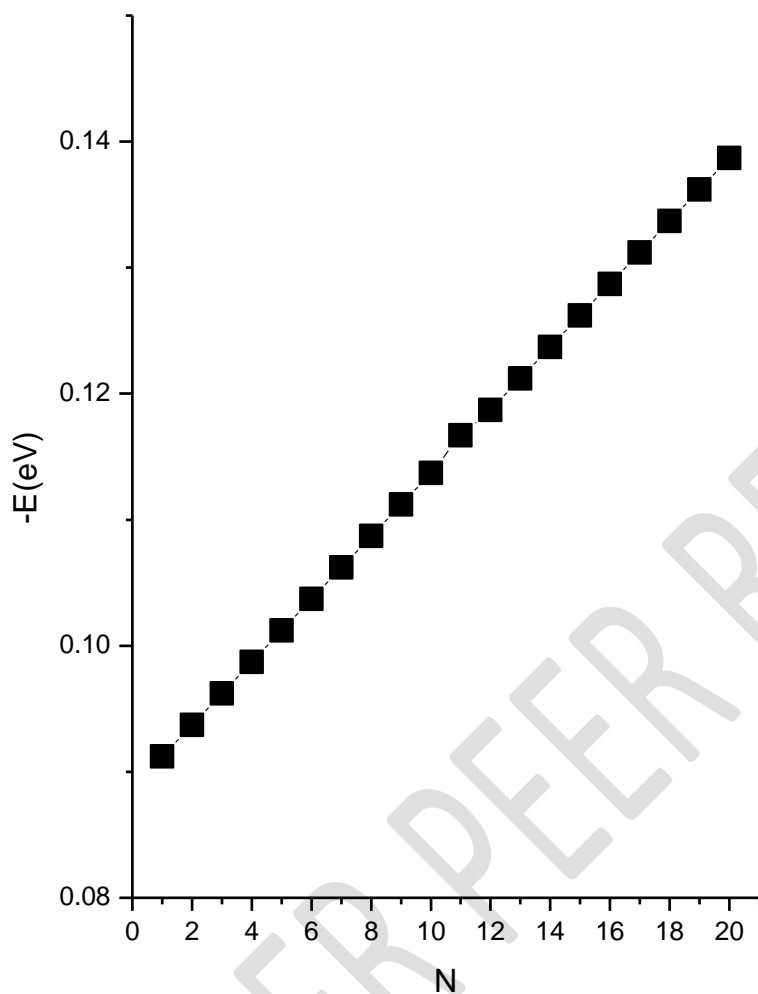Figure 2 shows the change in the average energy of the hydrogen bonds calculated with formula (2).

Figure 2. Dependence of the average energy of hydrogen bonds E on the sequential number of the corresponding measurement.

As it can be seen from the above figure, the average energy (-E) of the hydrogen bonds increases from 0.0912 to 0.1387 eV. Its dependence on the wetting angle is shown in Figure 3.
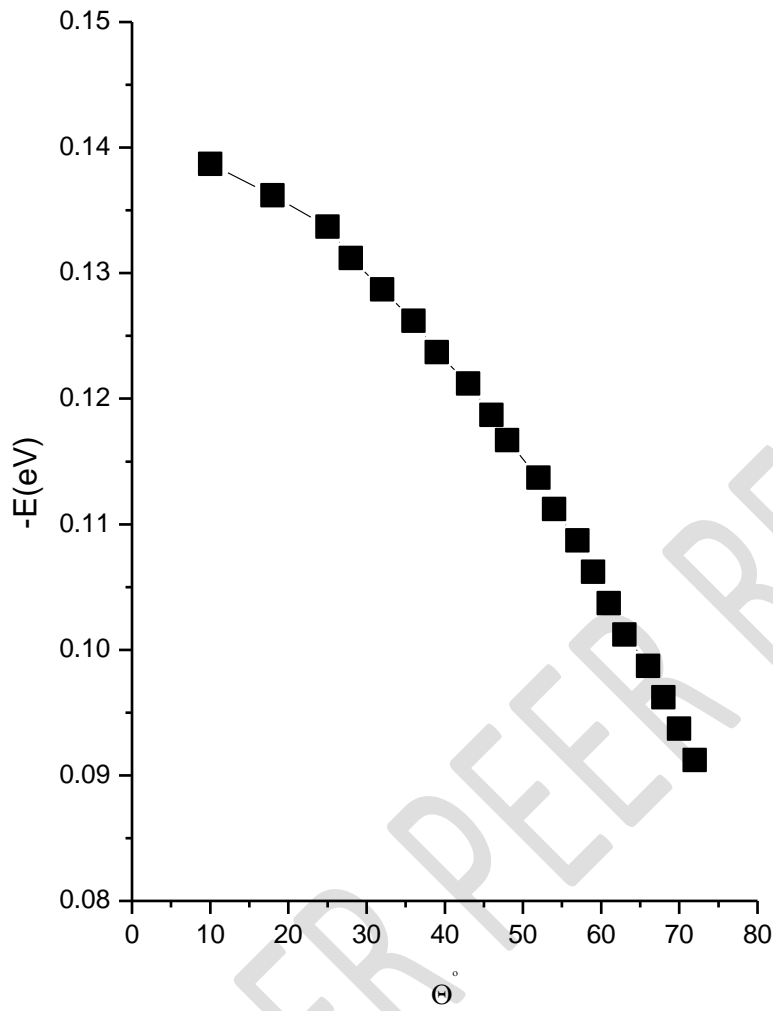
Figure 3. Dependence of the average energy of hydrogen bonds on the wetting angle θ.

It illustrates that the smaller the wetting angle, the higher the average hydrogen bonds energy is. From the point of view of the physical process, when the water evaporates from the drop, the energy of the hydrogen bonds increases. The dependence of the wetting angle is not linear, as can be seen from Figure 1. The wetting angle decreases with greater values as evaporation of water from the drop advances. However, the energy of the hydrogen bonds E increases linearly, as shown in Figure 2. Therefore, the energy of the hydrogen bonds increases stepwise, but with a constant value. Figure 4 shows the difference at each step of the change of E.
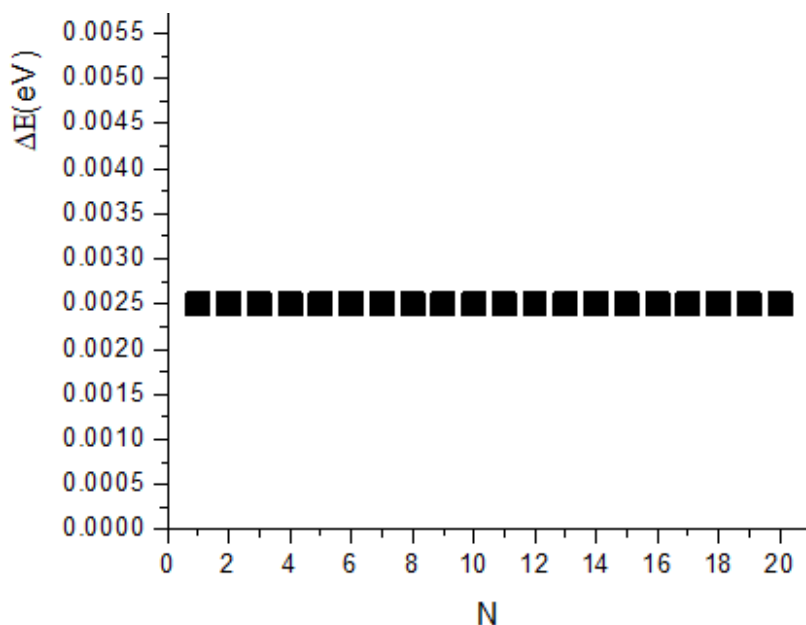
Figure 4. Dependence of ΔE on N.

As can be seen from Figure 4, ΔE is a constant value during the whole process of evaporation of water drops. Then the question arises about what determines this constancy in the magnitude of ΔE. As it was pointed above, clusters of different numbers of water molecules form in bulk water. They also determine the amount of average energy of the hydrogen bonds. If the evaporation of water from water drops causes disintegration of these clusters, each step will correspond to the loss of a single water molecule. Then the average energy of the hydrogen bonds in the system will decrease with the value of the energy of the bond that had been associated with this water molecule in the cluster.

If this release energy is equal to 0.0025 eV, as can be seen from Figure 4, then this will also determine the step in the change of E, which is calculated from the wetting angle θ. This fact makes it possible to calculate the number of water molecules involved in the formation of clusters for each energy presented in Figure 2. If the corresponding values are divided by 0.0025 and thenby 2, because each hydrogen bond is associated with two water molecules, numbers are obtained that correspond in order of magnitudeto the numbers of molecules that form particular clusters in bulk water.

Therefore, it can be assumed that the stepwise nature of the change in the energy of the hydrogen bonds is due to the disintegration of the existing clusters in bulk water. This determines the nature of the change and the wetting angle of water drops during evaporation.

CONCLULISION

Clusters of different numbers of water molecules are formed in water on the basis of hydrogen bonds. This results in different values of the average energy of the hydrogen bonds, proved by measurements of the wetting angle during water droplets evaporation from surfaces of different materials. When droplets evaporate, disintegration of water clusters takes place through separation of water molecules from them.

This changes the average energy of the hydrogen bonds and causes its stepwise change. On this basis, the abrupt changes in the wetting angle during evaporation of water droplets can be explained. Clusters can be formed in water, composed of more than 20 water molecules and with a high average hydrogen bonds energy.

COMPETING INTERESTS
Authors have declared that no competing interests exist.

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