Review Article

HYDROGEN BOND ENERGIES IN FORMATION OF WATER MOLECULE CLUSTERS

ABSTRACT

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, theoretical analyzes. New effects of water are also being described.

In 1984, 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 measuring 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:

$$\theta = \mathrm{arcos}(-1-bE) \qquad (1)$$

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

Keywords : water, hydrohen 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, theoretical analyzes. New effects of water are also being described.

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It has also been found that the wetting angle changes discretely as the water droplet evaporates. 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 [1, 2], far-infrared [3], vibration-rotation-tunneling (VRT) [4], neutron diffraction [5], SCC-DFTB Method [6, 7], NES [8]. An earlier authors' study has estimated that at (E = -0.1387 eV) (λ = 8.95 μm) ($\tilde{\nu}$ = 1117 cm-1) a water cluster of approx. 21 water molecules is formed in catholyte water [9]. Based on this, a cluster model was proposedwith 20 water molecules in a dodecahedral structure with diameter of the circumscribed sphereequal to 0.822 nm.

This result corresponds to our result by applying the Antonov effect to "discrete" evaporation of a water drop. Studies have been performed on clusters of 6, 21 and 22 water molecules using the SCC-DFTB method [7]. Analyzes for clusters of n = 6-20 water molecules are available in a number of publications [10, 11, 12]. Cases of n = 1-6 have been described in [13].

It has also been found that at n = 20 about 25% of water molecules are structured with this number [14].

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 with the following parameters was used for the study: pH = 9.30, oxidation reduction potential (ORP) = - 450 mV.

The wetting angle θ was measured with a specially designed apparatus which is described in detail in [8, 9, 15, 16]. Measured wetting angles of water droplets during their evaporating from a hard 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 is 10 minutes. The measurements were performed at 20^{o} C.

From the obtained values for 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^{o} C.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the wetting angle on the sequential number of the corresponding measurement. This angle decreased from 74^{o} to 10^{o}, and the dependence has a step character.

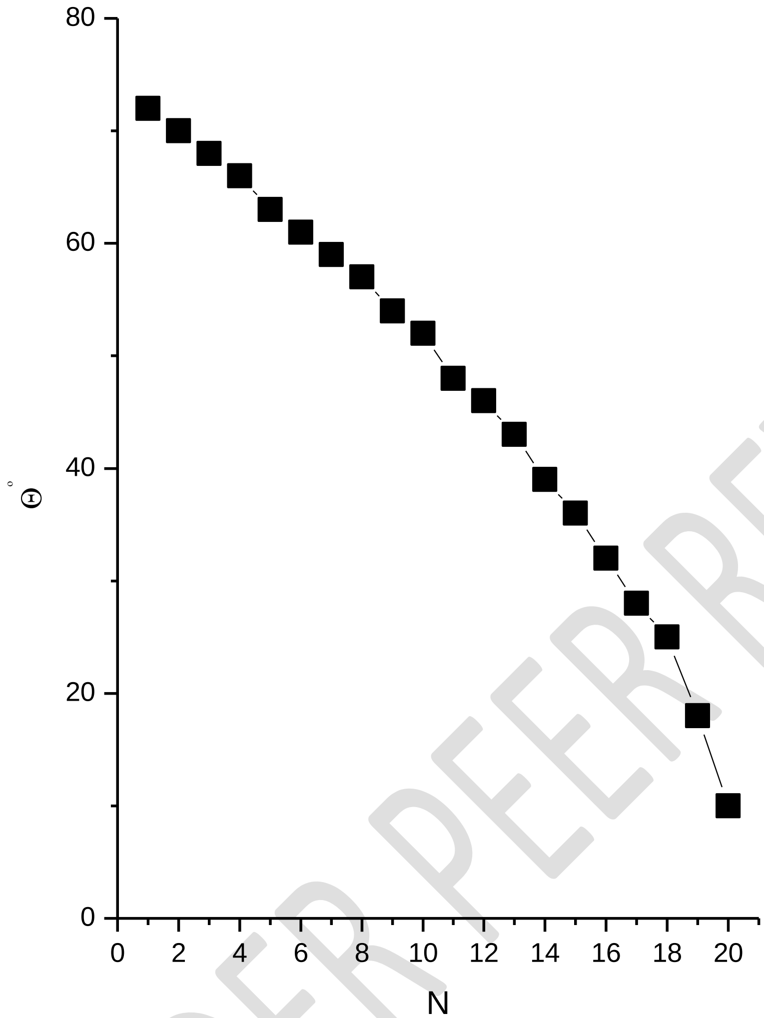

Figure 1. Dependence of the wetting angle θ on the sequential number of the corresponding measurement.

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

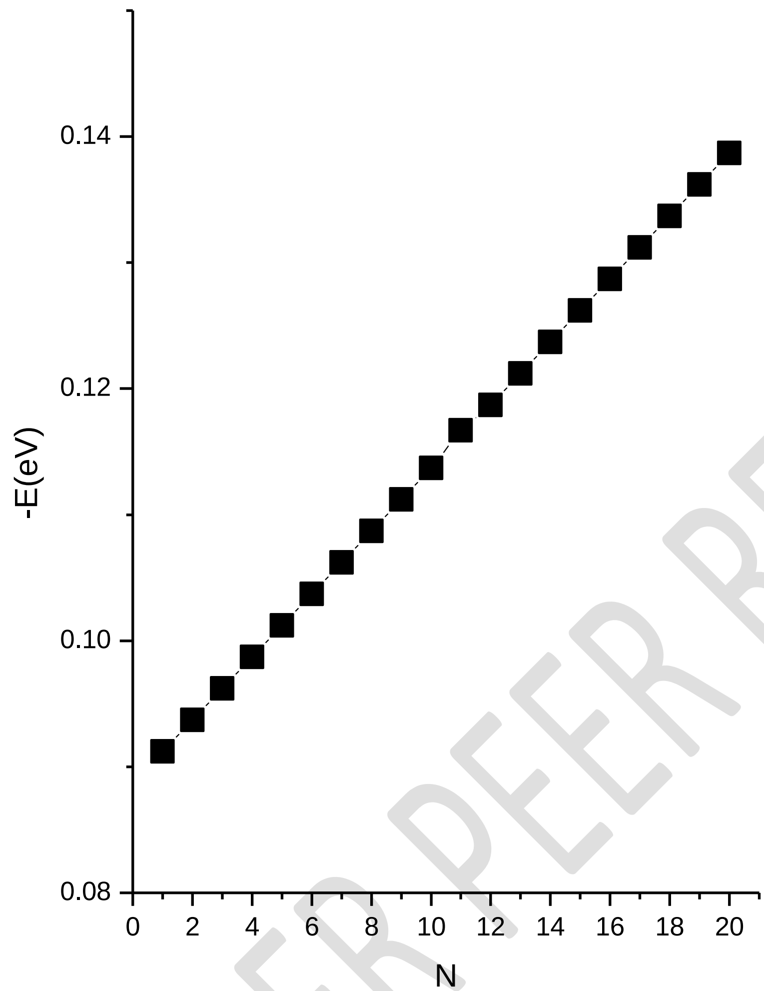

Figure 2. Dependence of the average energy of the hydrogen bonds E on the sequential number of the corresponding measurement.

As can be seen from the figure, the average energy of the hydrogen bonds increases from 0.0912 to 0.1387 eV. Its dependence on the wetting angle is shown in Figure 3.

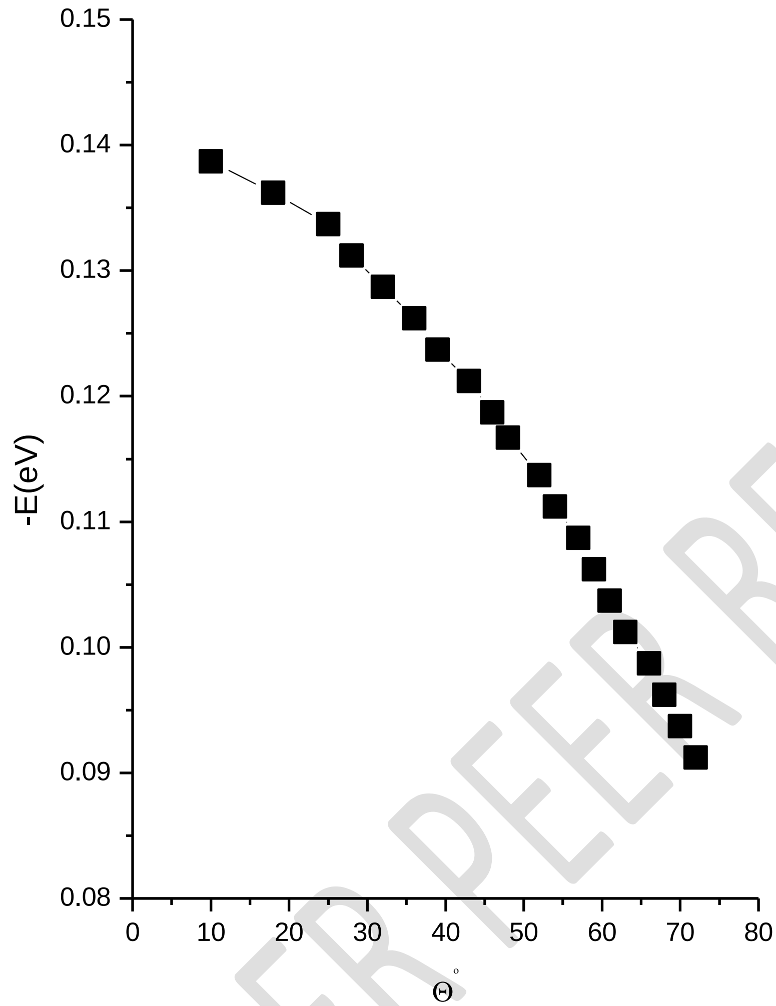

Figure 3. Average energy of the hydrogen bond depending on the wetting angle θ.

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 Fig.1. The wetting angle decreases with greater valuesas evaporation of water from the drop advances. However, the energy of the hydrogen bonds E increases linearly, as can be seen from 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.

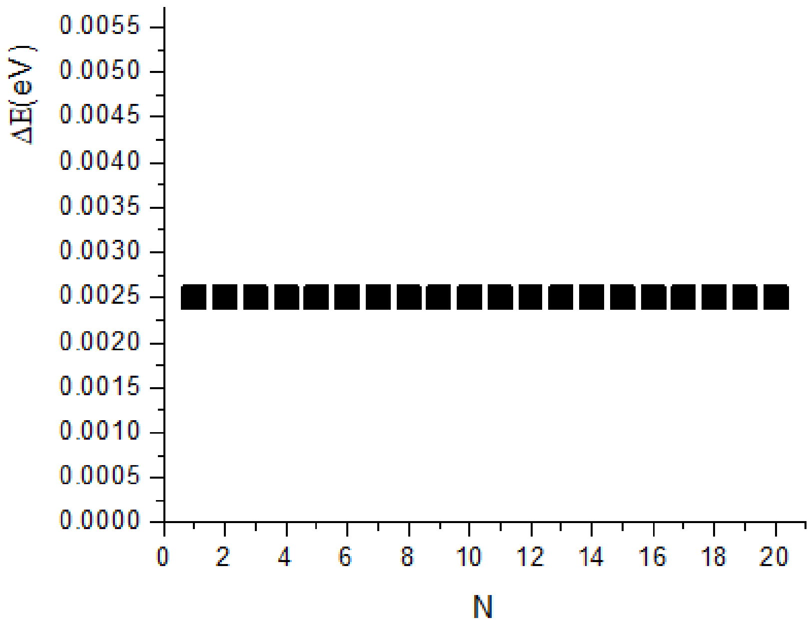

Figure 4. Dependence of ΔE on N.

As can be seen from Figure 4, ΔE is a constant value during the whole process of evaporation of the water drop. 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 the water drop causes the disintegration of these clusters, each step will correspond to the loss of a single water molecule. Then the average energy of the hydrogen bondsin the system will decrease with the value of the energy of the bond that was 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 we divide the corresponding values by 0.0025 and thenby 2, because each hydrogen bond is associated with two water molecules, we obtain numbers that correspond in order of magnitude concerning the numbers of molecules that form particular clusters in bulk water.

Therefore, we can assume 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 the water drop 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 measuring the wetting angle when water droplets evaporate from the surface of different materials. When the droplets evaporate, disintegration of the water clusters begins by separating 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.

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