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Formation of clusters in water and their distribution according to the number of water molecules

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Measurements of average energies of hydrogen bonds in water droplets evaporating from a hard surface were analyzed with a mathematical model based on a Gaussian distribution of the number of water molecule clusters with the same energy of hydrogen bonds and the same number of water molecules. The model was derived from results of previous research showing that in bulk water, clusters are formed due to hydrogen bonds, having different numbers of water molecules; as the number of water molecules in the clusters increases, the average energy of the hydrogen bonds also increases; with the evaporation of water droplets, the average energy of hydrogen bonds increases. Thus, in bulk water, at the beginning of evaporation, the maximum number of clusters must have average hydrogen bonds energy of (-E) = 0.1162 eV and contain 12-13 water molecules.

Keywords: water, hydrogen bonds, energy, clusters, Gaussian distribution

INTRODUCTION

There is ongoing research on the number of molecules in water clusters. In 2021, four of the authors showed a cluster of 20 H_2O molecules with a size of 0.822 nm [1]. The work was based on Antonov's method of measuring the wetting angle during evaporation of water droplets [2-4]. The method is based on a physical effect where, the wetting angle θ decreases discreetly to 0, while the diameter of the base area changes slightly [2, 5, 6].

Luck views the water like consisting of O-H···O groups [5]. Most of them are bonded by energy of the connection (-E) and the remaining are free (E=0). It is accepted that E has a negative value.

This is called model of the two states of Luck [6-9]. Each water molecule has two hydroxyl groups. The number of O-H···O groups in a certain volume of water is twice as big as the number of the molecules in it.

Part of hydrogen bonds is restructuring in the vicinity of the spherical part of the drop surface and as a result one obtains the dependence between the surface tension δ and the hydrogen bond energy [10-12]:

$$\delta = -kTI\ln[\ 1+\alpha/[\exp(-\beta E)+\alpha] \quad (1)$$

Here k is the Boltzman constant, β=1/kT, T – the absolute temperature, E – the hydrogen bond energy, α is the ratio of two subvolumes of the phase space related to structuring and restructuring of hydrogen bonds, α =28±8 and I=5.03. 10^{18} m^{-2} is density of water molecules at the hydrophobic surface layer.

The values of E and α are fixed by a comparison with experiment. Expression (1) explains fraction C of the actual surface tension γ, i.e. δ = Cγ [12]. According to [10, 12] the contribution of non-hydrogen bond interaction amounts to 20% of the true value of γ and C=4/5.

Consider the Helmholtz free surface energy F=γΣ where Σ is the spherical part of the drop's surface [10].

At the instant of mechanical equilibrium, F should be minimal, i.e. dF=0=d(γΣ) [10]

$$0= \gamma\Sigma- \gamma_0\Sigma_0 \quad (2)$$

The process of evaporation of water drops is at constant temperature 20°C in a hermetic camera [2].

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The expressions for Σ0 and Σ are as follows [10]:

$$\Sigma = \pi D^2/2(1+\cos\theta);\ \Sigma_0 = \pi D^2/2(1+\cos\theta_0) \quad (3)$$

$$-E/kT = C\gamma/IkT \quad (4)$$

$$E = C\gamma o(1+\cos\theta)/I(1+\cos\theta_0) \quad (5)$$

During the process, the wetting angle changes in discrete steps and characterizes the average energy of hydrogen bonds as follows:

$$\theta = \arccos(-1+bE), \text{ where } b = I(1+\cos\theta_0)/C\gamma o \quad (6)$$

where θ is the wetting angle, E is the average energy of hydrogen bonds, b is a temperature-dependent parameter [13-18]. The development of the method is Non-equilibrium energy spectrum (NES) and Differential non-equilibrium spectrum (DNES) [1, 15, 19, 20]. They are used for research of natural waters and plants [9, 21, 22]. Molecular dynamics simulation is applied to research the wetting behavior of water droplets on the surface of sandstone under different salinities. The system equilibrium configuration was used for the study of its components interaction. The number of hydrogen bonds was calculated [23].

The average weight reduction values of the investigated drops of deionized water during their evaporation and 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 [24].

Table 1 illustrates 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.

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

Wetting angle, (°) 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

Another previous study of ours has shown that the discrete changes in hydrogen bonds energy of water clusters have the same value and are based on formation of clusters with different numbers of water molecules [25]. There are researches of clusters with different numbers of water molecules according to the energy of hydrogen bonds among water molecules.

Infrared spectroscopy studies have detected the following clusters: $H^+(H_2O)_{22}$ [26] and $(H_2O)_n$, n=6-22 [27]. In addition, the total interaction energy has been represented by five terms; repulsive, charge–charge, intramolecular relaxation, polarization, and hydrogen bonding with three models for n = 6-20 [28]. Water clusters have also been described with the density functional theory (DFT) for n=2-20 [29].

Extensive *ab initio* calculations with 6-31G(d, p) and 6-311++G(2d, 2p) base sets were used for modeling of possible structures of water clusters $(H_2O)_n$ for n=8-20. The most stable clusters were found in tetramer and pentamer rings. For n = 8, 12, 16 and 20, the derived clusters were cuboid. For n=10 and 15, they were merged into pentamer structures [30]. It has also been found that, for n=20, about 25% of water molecules are structured in such clusters [31].

In general, our previous research on water structure, cluster formation and hydrogen bonds energy leads to the following conclusions [1, 17]:

1. In water, clusters are formed due to hydrogen bonds, having different numbers of water molecules.
2. As the number of water molecules in the clusters increases, the average energy of the hydrogen bonds also increases.
3. With the evaporation of water droplets, the average energy of hydrogen bonds increases.

In this research, the control samples were with deionized water and samples were initially treated with a patented filter EVOdrop [32, 33].

The aim of the present work was to answer the question about what determines the number of water molecules in clusters and about the distribution of clusters in water according to the number of water molecules. In addition, it had to clarify how this distribution changes during evaporation of water droplets from a hard surface.

MATERIALS AND METHODS

The wetting angle θ was measured with a specially designed apparatus which is described in detail in [2-4]. Evaporation of deionized water drops was performed in a hermetic chamber with a stable temperature of 22°C [2, 10]. The drops were placed on BoPET (biaxially-oriented polyethylene terephthalate) foil with 350 μm thickness. Deionized water was initially treated with a patented filter EVOdrop [32, 33].

In order to determine the numbers of water molecules in clusters, as well as the distribution of clusters in bulk water according to these numbers our previous model was used with the following assumptions.

1. The number of clusters of a particular type in bulk water (with equal numbers of water molecules) is related to their average energy of hydrogen bonds.

2. The distribution of the numbers of particular types of clusters is Gaussian.

3. The number of water molecules in clusters (determining their different types) varies from 3 to 22.

To find the distribution of clusters according to the average energy of the hydrogen bond in them, we use the Gaussian function in the following formula:

$$y = [\ 1/s\sqrt{2\pi}\ ] .\exp[-\ (x-x_s)^2/2s^2\ ], \qquad (7)$$

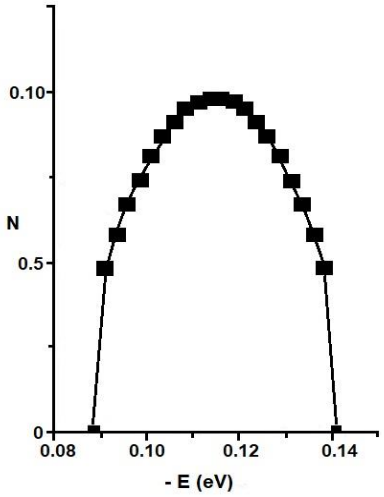
where x is the average energy of hydrogen bonds in a particular group of clusters, y is the number of clusters with the same energy of hydrogen bonds and the same number of water molecules, x_s is the average energy of hydrogen bonds for all groups and s is the standard deviation.

RESULTS AND DISCUSSION

The average values of hydrogen bonds energy in water droplets during their evaporation from a BoPET surface, measured with Antonov's method, and the numbers of water molecules are presented in Table 2. The number of order is signed with No. The value (-E) in eV is the energy of hydrogen bonds among water molecules. No(n) stands for the number n of water molecules at order No.

These values stand for x in Eq. (2). As it has been pointed out, the energy (-E) changes stepwise and its increment is always the same and equal to 0.0025 eV [1, 3, 10]. Table 1 also shows the numbers of water molecules that can contribute to these average hydrogen bond energies.

Figure 1. Distribution of the number of clusters with equal energy of hydrogen bonds, on the average energy of hydrogen bonds



Four energy ranges were considered for cluster formation with particular numbers of water molecules according to the average energy of hydrogen bonds (-E):

Range 1: from 0.0912 to 0.1387 eV;
Range 2: from 0.1062 to 0.1387 eV;
Range 3: from 0.1212 to 0.1387 eV;
Range 4: from 0.1312 to 0.1387 eV.

For each range, the values of y were calculated according to eq. (7).

Fig. 1 represents the distribution of the number of clusters with equal energy of hydrogen bonds (-E) in the measurement range from 0.0912 to 0.1387 eV.

The distribution of the number of clusters with equal numbers of water molecules, on the number of water molecules in them is shown in Fig. 2.

Table 2. Average values of hydrogen bonds energy in water droplets during their evaporation from a BoPET surface

No	-E (eV)	n	No	-E (eV)	n	No	-E (eV)	n
1.	0.0912	3	8.	0.1087	10	15.	0.1262	17
2.	0.0937	4	9.	0.1112	11	16.	0.1287	18
3.	0.0962	5	10.	0.1137	12	17.	0.1312	19
4.	0.0987	6	11.	0.1162	13	18.	0.1337	20
5.	0.1012	7	12.	0.1187	14	19.	0.1362	21
6.	0.1037	8	13.	0.1212	15	20.	0.1387	22
7.	0.1062	9	14.	0.1237	16			

*No - number of order; n - number of water molecules

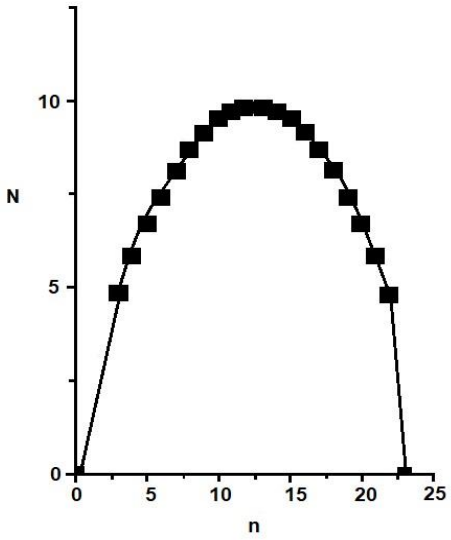


Figure 2. Distribution of the number of clusters with equal numbers of water molecules, on the number of water molecules in them.

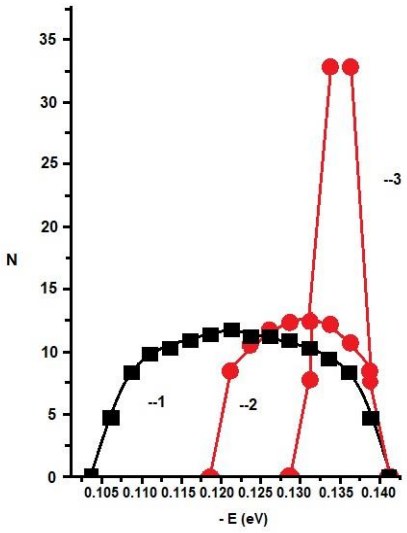


Figure 3. Distribution of the number of clusters with equal hydrogen bonds energy (-E), on the average hydrogen bonds energy in the corresponding ranges. Curve 1 – Range 2 (average hydrogen bonds energy from 0.1062 to 0.1387 eV), Curve 2 – Range 3 (average hydrogen bonds energy from 0.1212 to 0.1387 eV), Curve 3 – Range 4 (average hydrogen bonds energy from 0.1312 to 0.1387 eV).

If the Gaussian distribution takes place the maximum number of clusters must have average hydrogen bonds energy (-E) of 0.1137 eV or (λ=10.91 μm; $\tilde{\nu}$=917 cm^{-1}). The research shows that $\tilde{\nu}$ =917 for the hydrogen-bonded molecules [34]. Assuming that the first type of clusters contains three water molecules and all the rest have one more molecule compared to the previous type as shown in [24], then the next type of clusters will have four molecules, etc. These values are presented in Table 1 and, consequently, the maximum number of clusters have to contain 12-13 water molecules.

The results for the other three ranges are shown in Fig. 3.

As expected, the maxima of these curves are shifted towards higher hydrogen bonds energy (-E). For Range 2, the maximum is at 0.1212 eV or (λ=10.23 μm; $\tilde{\nu}$=978 cm^{-1}), for Range 3 it is at 0.1287 eV or (λ=9.63 μm; $\tilde{\nu}$=1038 cm^{-1}) and for Range 4 it is at 0.1362 eV or (λ= 9.10 μm; $\tilde{\nu}$=1099 cm^{-1}). The same dependence on the number of water molecules is shown in Fig. 4.

It should be pointed out that, during experiments in 2020 with EVOdrop filtration of tap water, local (-E) maxima were measured at 0.1112; 0.1212; 0.1287; 0.1362; 0.1387 eV [33].

During evaporation of droplets, clusters with increasing numbers of water molecules are present. The clusters that are maximum in number in the different ranges have the following composition: Range 2 – 15, Range 3 – 18 and Range 4 – 21 water molecules.

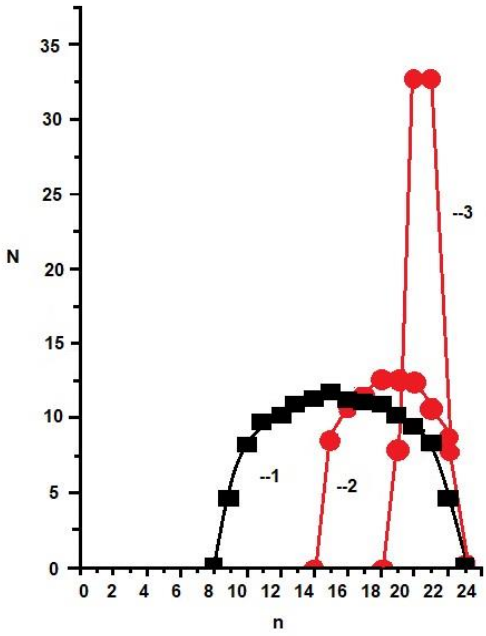


Figure 4. Distribution of the number of clusters with equal numbers of water molecules, on the number of water molecules in the different ranges. Curve 1 – Range 2 (average hydrogen bonds energy (-E) from 0.1062 to 0.1387 eV), Curve 2 – Range 3 (average hydrogen bonds energy from 0.1212 to 0.1387 eV), Curve 3 – Range 4 (average hydrogen bonds energy (-E) from 0.1312 to 0.1387 eV).

Table 3 illustrates the mean values, standard deviations and maximal numbers of water molecules in clusters.

Table 3. Mean values, standard deviations and maximal numbers of water molecules in clusters.

Range of (-E) [eV]	$\bar{x}$ [eV]	S	n_{max}
0.0912 - 0.1412	0.115	0.0148	11
0.1037 - 0.1412	0.1225	0.01045	15
0.1187 - 0.1412	0.1299	0.00612	18
0.1287 - 0.1412	0.1349	0.00321	21

*****Range of (-E) - energy of hydrogen bonds [eV]; $\bar{x}$ [eV] - mean value; S - standard deviation; n_{max} - maximum number of water molecules in clusters.

CONCLUSION

The obtained results show that the structure of water filtered with patented filter EVOdrop has a complex character that could be influenced by external conditions. In the normal state, clusters with different numbers of water molecules are formed in the water. Since the average energy of hydrogen bonds depends on the numbers of water molecules in the clusters, the numbers of clusters with the same numbers of water molecules can vary. Under the assumption that these numbers have Gaussian distribution, different numbers of clusters with equal hydrogen bonds energy are prevalent in water filtered with patented filter EVOdrop.

Under normal conditions, temperature and pressure, the results show that a maximum of 11 water molecules are present in water. During evaporation, the maximum number of clusters changes and those with larger numbers of water molecules prevail. If the types of the predominant clusters have different numbers of water molecules, they may cause different chemical and biological effects which must be taken into account.

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