

Structuring of water clusters depending on the energy of hydrogen bonds in electrochemically activated waters Anolyte and Catholyte

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Experiments with alkaline (Catholyte), acidic (Anolyte) components of electrolyzed water, and control sample were carried out using NES and DNES methods. Clusters of different energy of hydrogen bonds were obtained. They were modeled with dodecahedral structures consisting of 20 water molecules having a diameter of circumscribed spheres equal to 0.822 nm. Lower number of clusters and increased average number of molecules per cluster in Catholyte and Anolyte compared to control water points to their better structuring. Higher average energy of hydrogen bonds in Catholyte and lower energy in Anolyte than that in control water, points to increased/decreased energy density, respectively, which could be related to different physiological effects. Thus, a new point of view to the processes of electrochemically activated water and its physiological action is suggested.

Keywords: Anolyte, Catholyte, NES, DNES, hydrogen bonds, clusters

INTRODUCTION

It is well known that energetic influence on a water solution causes alterations of its physicochemical properties, intermolecular forces and formation of configurations of different numbers of molecules [1, 2]. Thus, new properties of water could be obtained. These changes, together with the underlying physicochemical processes, have been studied during the last decades. Different hypotheses about the water structure have been launched assuming the existence of clusters and numbers of molecules in specific configuration [3-10]. For experimental proof different methods, such as far-infrared (FIR) [11], vibration-rotation-tunneling (VRT)[12], EXAFS- and X-ray spectroscopy [13], ¹H-NMR [14], neutron diffraction [15] and SCC-DFTB method [16] have been used.

However, to the best of our knowledge, there is no satisfactory description of the processes taking place during the electrolysis of water with a semipermeable membrane, leading to different properties of the obtained fractions, Catholyte at the cathode chamber, and Anolyte at the anode one. Their physiological effects as anti-oxidation, immune system stimulation, tissue regeneration of the Catholyte; anti-bacterial, anti-viral, anti-fungal, anti-inflammatory action of the Anolyte, have been confirmed by many researchers [17-23]. In this respect very interesting is the question about the

structure of Catholyte and Anolyte, i.e. formation of clusters, distribution of molecules according to the energy of hydrogen bonds and, as a result, energy redistribution between the two fractions. For this the methods NES (Non-equilibrium Energy Spectrum) and DNES (Differential Non-equilibrium Energy Spectrum) developed by Antonov [24] for the evaluation of molecule distribution depending on the energy of hydrogen bonds seem to be promising [25].

The methods are based on a unique physical effect where, during drop evaporation the wetting angle θ decreases discreetly to 0, while the diameter of the drop base area changes slightly.

Measurements of this angle at regular time intervals allows for determination of the distribution function $f(\theta)$ of the number of water molecules according to the energy of hydrogen bonds. $f(\theta)$ is called *water state spectrum* [24, 25]. Subsequently, the average energy $E(\theta)$ of hydrogen bonds in the sample can be derived for every measured value of the wetting angle θ . Derivation is based on Luck's model [26] according to which water is composed of O-H...O groups. The greater part of these groups contribute to hydrogen bond energy ($-E$), while the rest are not bound ($E=0$). The shape of $E(\theta)$ function also depends on external influencing factors. Its measurement unit is reciprocal electronvolt (eV^{-1}).

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Some results concerning the measurement of hydrogen bonds energy spectrum have already been published by the authors [27]. The present work is a continuation of the analysis of energy redistribution between Catholyte and Anolyte on the basis of data from [27].

MATERIALS AND METHODS

Water samples

Catholyte and Anolyte samples of water were produced in an electrolytic cell consisting of cathode and anode with a semipermeable membrane between them (Fig. 1). The membrane separates the water fractions: an alkaline one (Catholyte) and an acidic one (Anolyte) [17]. When direct electric current passes through both water-filled chambers, electrons from the cathode, as well as those extracted from water at the anode cause a series of redox reactions on the surface of both electrodes, and induce changes in the water structure, resulting in high pH and negative ORP values of the Catholyte, and low pH and positive ORP values of the Anolyte. It is worth noting that the mechanism of such changes is still not clear, but in any case it relates to the redistribution of electrical charges, i.e. energy. For comparison a control sample of non-processed water is used.

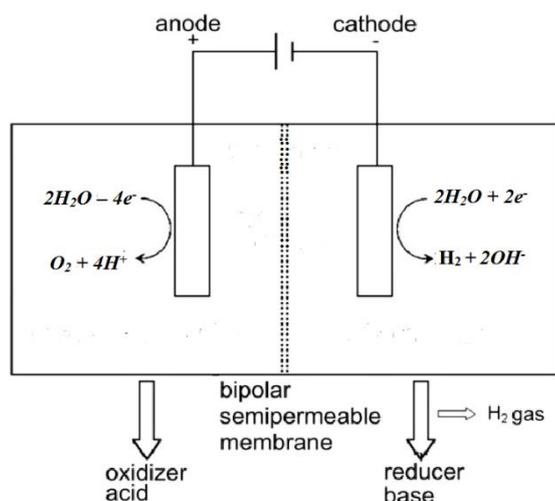


Figure 1. Electrolyzer scheme

NES and DNES spectral analysis

This study assumes a model of water molecule structuring based on average hydrogen bonds energy in the interval (-0.0912 eV to -0.1387 eV).

Measurements were performed with the optical device invented by Antonov for NES and DNES spectral analysis [24]. Water drops were evaporated in a hermetic camera, on a glass plate covered with transparent mylar foil.

The device characteristics are:

1. Monochromatic filter: wave length $\lambda = 580 \pm 7$ nm (yellow color in the visible spectrum);
2. Wetting angle of water drops: from 72.3° to 0° ;
3. Temperature range: $(+22 - 24^\circ \text{C})$;
4. Energy range of hydrogen bonds: $E = -0.08 - -0.1387$ eV (corresponding to $\lambda = 8.9 - 13.8$ μm).

Characteristics of NES and DNES water state spectra

The energy ($E_{H...O}$) of hydrogen O...H-bonds between H_2O molecules in water is measured in eV. The $f(\theta)$ function is called *energy distribution spectrum*. It is characterized by the non-equilibrium process of water droplets evaporation.

Figure 2 shows the operating principle of the method for measurement of wetting angle of liquid drops on a hard surface.

The relation between $f(\theta)$ and the energy of hydrogen bonds between water molecules $f(E)$ is expressed as follows:

$$f(E) = \frac{14.33f(\theta)}{[1-(1+bE)^2]^2} \quad (1)$$

where b depends on the number of water molecules at the surface layer of water per unit area, on the water surface tension and on the initial contact angle of the drop.

The water state spectrum is obtained from the non-equilibrium process of evaporation of water drops and, due to this, the term Non-equilibrium spectrum of water (NES) is used [24]. The evaluated measurement error for E is ± 0.0011 eV.

The difference:

$$\Delta E(\theta) = E(\theta)_{\text{sample}} - E(\theta)_{\text{control sample}} \quad (2)$$

is called Differential Non-equilibrium Energy Spectrum (DNES) [2, 24].

DNES is a measure of the alteration of water structure as a result of a certain influencing factor. The combined effect of all other influencing factors besides the examined one is the same for the control and the sample, that is why it is canceled out.

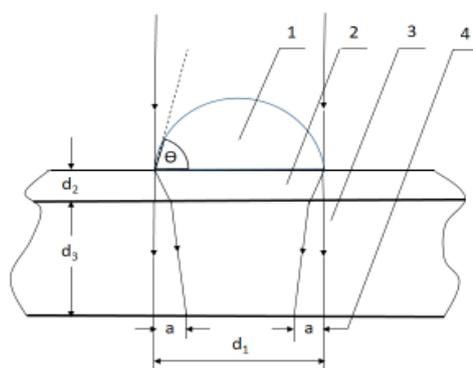


Figure 2. Operating principle of the method for measurement of wetting angle of liquid drops on a hard surface: 1 – drop, 2 – thin maylar foil, 3 – glass plate, 4 – refraction ring width. The wetting angle θ is a function of a and d_1 .

Electrical measurements

A HANNA Instruments HI221 meter equipped with Sensorex sensors was used for measurement of oxidation reduction potential (ORP) in mV, and pH. Its measurement ranges are: pH: (2.00 – 16.00 ± 0.01); ORP: ($\pm 699.9 \pm 0.01$ – $\pm 2000 \pm 0.1$) mV.

RESULTS AND DISCUSSION

Water samples

Following parameters were measured for the three samples of water: pH = 9.5, ORP = -400 mV for the Catholyte; pH = 3.5, ORP = +800 mV for the Anolyte, and pH = 7.2, ORP = +260 mV for the control sample (Table 2).

Results with NES and DNES methods for Catholyte, Anolyte and the control

The average energy ($\Delta E_{H...O}$) of hydrogen H...O-bonds between individual H₂O molecules was calculated for Catholyte, Anolyte and the control by NES- and DNES-methods. The result for Catholyte in the NES-spectrum is $E = -0.1251$ eV, for Anolyte it is $E = -0.1144$ eV and for control water $E = -0.1191$ eV. Calculations of $\Delta E_{H...O}$ for Catholyte with the DNES method lead to (-0.0060 eV), and to (+0.0047 eV) for the Anolyte (Table 1). These results point to restructuring among individual H₂O molecules with a significant increase of local extrema in Catholyte and Anolyte spectra (Table 2).

Characteristics of water molecules and hydrogen bonds

Water, as a weak electrolyte, dissociates into the hydrogen cations H⁺ and hydroxide anion OH⁻. Splitting up of the H–OH bond is accompanied by formation of new disordered bonds between

“fragments” of the initial molecules, leading to formation of areas with density fluctuations different from those in aqueous solutions.

The water molecule has a size of 0.27 nm. Hydrogen bond length is 1.5-2.6 Å or 0.24-0.26 nm [28]. The covalent bond length is 0.096 nm. Hydrogen bond strength between two water molecules is 5-6 kcal/mol or 0.22-0.26 eV [29].

In spectral analysis using NES and DNES methods, the working range is from (-0.0912) to (-0.1387) eV. The outermost layer of water drops evaporates at hydrogen bonds energy of -0.0912 eV. The last water molecules evaporate at hydrogen bonds energy of -0.1387 eV.

We adopted Saykally’s [4] model according to which the total number of available hydrogen bonds is maximum for 100 water molecules (Fig. 3).

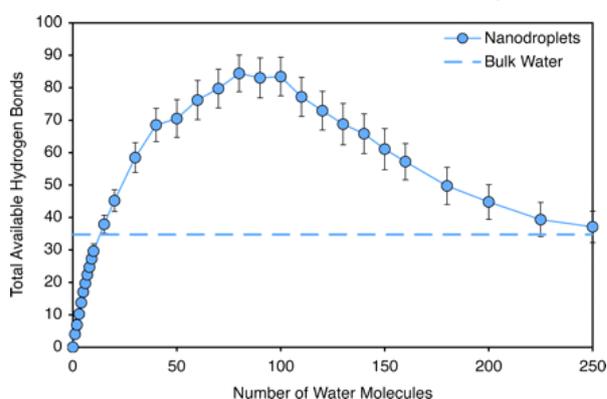


Figure 3. Saykally’s model of total available hydrogen bond numbers

Table 1 shows the distribution of numbers of water molecules according to the energy of hydrogen bonds per each 100 water molecules in the bulk volume of Anolyte, Catholyte and control water (data for Catholyte and Anolyte are taken from Table 2

[27]). These distributions are due to the spatial arrangement of H₂O molecules with equal energies of hydrogen bonds. This is a feasible mathematical model for explaining the behavior of Anolyte and Catholyte, by showing how their H₂O molecules are grouped in clusters.

In particular, at hydrogen bonds energy $E = -0.1387$ eV, we estimated that the biggest stable clusters can consist of 21 water molecules for Catholyte and of 22 water molecules for Anolyte at $E = -0.1212$ eV. Their hydrogen bonds were measured last during evaporation of water according to the wetting angle. Such preliminary considerations lead to a realistic model of stable clusters with 20 water molecules in both cases, arranged in dodecahedral structures shown in Fig. 4.

Their size can be estimated using the diameter of circumscribed spheres, provided that nuclei of oxygen atoms are located at dodecahedron vertices.

It should be pointed out that, according to Ignatov [30, 31], the local maximum at -0.1212 eV in Anolyte is related to anti-inflammatory effects, while the local maximum -0.1387 eV in Catholyte is related to inhibition of tumor cells development on molecular level [2, 23].

Measured values of pH and ORP, as well as derived values of cluster numbers and average energy of hydrogen bonds for Catholyte, Anolyte and control water are shown in Table 2.

Table 1. Values of pH, ORP, number of clusters and average energy of hydrogen bonds for Catholyte, Anolyte and control water.

Parameter	Catholyte	Anolyte	Control water
pH	9.5	3.5	6.7
ORP	- 400 mV	+ 800 mV	+170 mV
Number of clusters	11	11	15
Average number of molecules per cluster	9	9	6.7
Average energy of hydrogen bonds $\langle E \rangle$	-0.1251 (eV)	+0.1144 (eV)	-0.1191(eV)

Table 2. Distribution of numbers of water molecules according to the energy of hydrogen bonds

-E(eV)	Catholyte	Anolyte	Control water	-E(eV)	Catholyte	Anolyte	Control water
0.0912	0	0	0	0.1162	9	7	8
0.0937	0	15	9	0.1187	0	7	7
0.0962	0	0	5	0.1212	9	22	0
0.0987	0	11	0	0.1237	0	7	7
0.1012	0	0	6	0.1262	9	0	0
0.1037	9	0	8	0.1287	9	4	5
0.1062	4	0	0	0.1312	13	4	9
0.1087	4	15	11	0.1337	0	0	7
0.1112	4	0	6	0.1362	9	4	3
0.1137	0	0	7	0.1387	21	4	2

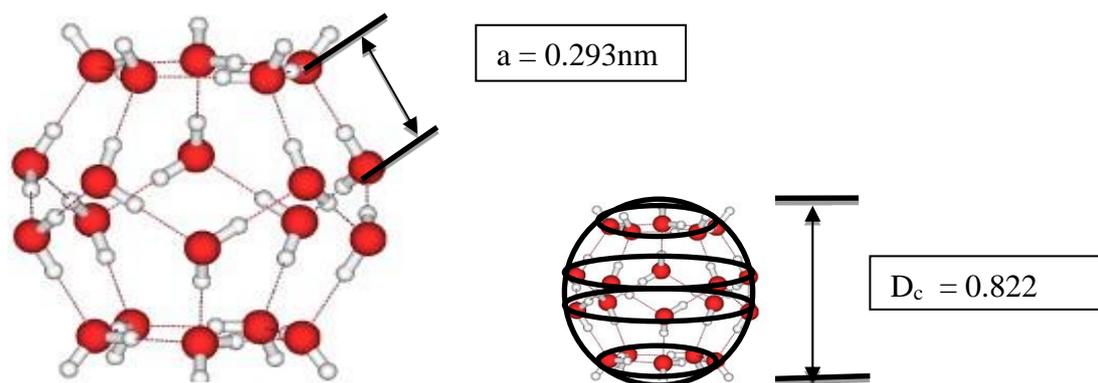


Figure 4. Dodecahedral cluster structure with 20 water molecules and the diameter of its circumscribed sphere

Average energy $\langle E \rangle$ of hydrogen bonds is calculated as:

$$\langle E \rangle = - \frac{1}{n} \sum_i^k n_i E_i$$

where n is the total number of molecules according to the adopted model, k is the number of clusters, n_i is the number of molecules in the i -th cluster, and E_i is the energy of hydrogen bonds corresponding to the i -th cluster.

DISCUSSION

The obtained data show a decreased number of clusters and an increased number of molecules per cluster in Catholyte and Anolyte solutions compared to control water, i.e. Catholyte and Anolyte are better structured. However, it is interesting to note that despite of this the average energy of the Anolyte is lower than the energy of the control sample which means that clusters in Anolyte are predominantly formed in the lower part of the energy spectrum, while the clusters of non-processed water are more spread. The increased average energy of Catholyte could be related to its stimulating immune system effect and inhibition of tumor growth due to energy adding, while the decreased energy of Anolyte could be connected to its biocidal effect due to energy sucking out. Also, many researchers from different countries have registered quite interesting and inexplicable Catholyte effects in stock-breeding and plant-growing, consisting in faster growing of plants and animals without additional nutrition, and increased production from them. Also, it was noticed that drying up flowers started refreshing in Catholyte. Possible explanation could be related to the higher energy in the Catholyte.

Increased pH and decreased ORP values of Catholyte compared to Anolyte do not affect cluster numbers and average number of molecules per

cluster in both fractions, but relate to the changes in average energy of hydrogen bonds. It is interesting to investigate this relationship at different values of pH and ORP which could be a subject of a future work. This may elucidate their inexplicable behavior in different periods of time. While in Catholyte they change rapidly and reach the values of the non-processed water in a couple of days, in Anolyte they remain quite stable during a few months regardless of the preservation conditions (decrease of less than 10% after half a year).

Information about the number of clusters and molecules could help to better understand the effect of nascent hydrogen and oxygen stabilization in electrochemically activated water – Catholyte and Anolyte, respectively. This process could relate to generation of clusters with a specific number of molecules in a specific configuration. Promising results about the nascent hydrogen in Catholyte have already been obtained [32]. However, to be fully verified, such a hypothesis requires further investigations.

CONCLUSIONS

The evaluation of hydrogen bonds energy of electrochemically activated fractions of water – Catholyte and Anolyte, and a sample of non-processed water, was carried out using the methods NES and DNES. The obtained spectra of energies allowed estimation of the possible number of clusters and the number of molecules in them. Also, the AVERAGE energy of each of the three samples was calculated.

The energetic position of the clusters with the maximal number of molecules corresponds to already establish physiological effects of Catholyte and Anolyte, respectively. This allows connecting these effects to the changed cluster structure and

redistributed energy between both fractions, which gives a new point of view on the processes of electrochemical activation of water and its useful effects.

An idea of adding/extracting energy to/from living things seems to be working, since some phenomena could be easily explained on its base.

The obtained results could be used for further investigation of the processes of electrochemical activation of water that are still quite unclear, including the stability of nascent hydrogen and oxygen in it [32].

REFERENCES

1. P. Gramatikov, A. Antonov, M. Gramatikova, *Fresenius Journal of Analytical Chemistry*, **343** (1), 134 (1992).
2. A. Yu, P. Carlson, G. Pollack, *The European Physical Journal Special Topics*, **223**, 947 (2014).
3. A. V. Nemuhin, *Russian Chemical Journal*, **40**(2), 48 (1996).
4. J. Smith, C. Cappa, K. Wilson, R. Cohen, P. Geisler, R. Saykally, *PNAS*, **102** (40), 14171 (2005).
5. O. Loboda, V. Goncharuk, *Chemical Physics Letters*, **484** (4-6), 144 (2010).
6. F. Keutsch, R. Saykally, *PNAS*, **98** (19), 10530 (2011).
7. M. Chaplin. The water molecule, Liquid water, hydrogen bonds and water networks, in: *Water the Forgotten Biological Molecule*, D. Le Brihan, H. Fukuyama (eds.), Pan Stanford Publishing Pte. Ltd, Singapore, 2011, p. 3.
8. I. Ignatov, O. V. Mosin, *Journal of Mathematical Theory and Modeling*, **3** (11), 72 (2013).
9. L. Shu, L. Jegatheesan, V. Jegatheesan, C. Q. Li, *Fluid Phase Equilibria*, **511** (2020).
10. I. Ignatov, G. Gluhchev, S. Karadzhov, I. Yaneva, N. Valcheva, G. Dinkov, T. Popova, T. Petrova, D. Mehandjiev, I. Akszjonovich, *Physical Science International Journal*, **24** (1), 46 (2020).
11. K. Liu, R. Fellers, M. Viant, R. McLaughlin, M. Brown, R. Saykally, *Review of Scientific Instruments*, **67** (2), (1998).
12. K. Liu, J. Cruzan, R. Saykally, *Science*, **271** (5251), 929 (1996).
13. P. D'Angelo, A. Zitolo, G. Aquilanti, V. Migliorati, *The Journal of Physical Chemistry B*, **117** (41), 12516 (2013).
14. V. Turov, T. Krupskaya, V. Barvinchenko, N. Lipkovska, M. Kartel, L. Suvorova, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **499**, 97 (2016).
15. K. Yoshida, S. Ishuda, T. Yamaguchi, *Molecular Physics*, **117** (22), 3297 (2019).
16. T. Choi, K. Jordan, *The Journal of Physical Chemistry B*, **114** (20), 6932 (2010).
17. V. F. Prilutsky, V. M. Bakhir, *All Russian Scientific Research and Experimental Institute of Medical Engineering (VNIIMT)*, *UDK 621.357*: **541.13** (1997).
18. M. Henry, J. Chambron, *Water*, **5**(4), 2094 (2013)
19. C.-N. Cha, E.-K. Park, J.-Y. Jung, C.-Y. Yoo, S. Kim. H.-J. Lee, *Korean Journal of Veterinary Service*, **39** (2), 117 (2016).
20. S. Shirahata, T. Hamasaki, K. Teruya, *Trends in Food Science and Technology*, **23**, 124 (2012).
21. G. Gluhchev, I. Ignatov, S. Karadzhov, G. Miloshev, N. Ivanov, O. V. Mosin, *European Journal of Molecular Biotechnology*, **7**(1), 12 (2015).
22. T. P. Popova, T. Petrova, S. Karadzhov, *Int. J. Curr. Microbiol. Appl. Sci.*, **5** (1), 624 (2016).
23. R. Toshkova, E. Zvetkova, I. Ignatov, G. Gluhchev, *Bulgarian Journal of Public Health*, **11** (3), 60 (2019).
24. A. Antonov, Research of the non-equilibrium processes in the area in allocated systems, Dissertation thesis for degree "Doctor of physical sciences", Blagoevgrad, 1995.
25. S. Todorov, A. Damianova, I. Sivriev, A. Antonov, T. Galabova, *Comptes Rendus de l'Academie Bulgare des Sciences*, **61** (5251), 857 (2008).
26. W. Luck, D. Schioberg, U. Siemann, *J. Chem. Soc., Faraday*, **76**, 136 (1980).
27. I. Ignatov, G. Gluhchev, S. Karadzhov, I. Yaneva, N. Valcheva, G. Dinkov, T. Popova, T. Petrova, D. Mehandjiev, I. Akszjonovich, *Physical Science International Journal*, **24** (1), 46 (2020).
28. Sh. Zhou, L. Wang, *Chemical Science*, **33** (2019).
29. B. E. Rocher-Casterline, L. C. Ch'ng, A. K. Mollner, H. Reisler, *Journal of Chemical Physics*, **115**, 6903 (2011).
30. I. Ignatov, S. Karadzhov, A. Atanasov, E. Ivanova, O. V. Mosin, *Journal of Health, Medicine and Nursing*, **8**, 1 (2014).
31. I. Ignatov, S. Karadzhov, G. Gluhchev, I. Yakimov, *Bulgarian Journal of Public Health*, **10** (4), 63 (2018).
32. P. Vassileva, D. Voykova, I. Ignatov, S. Karadzhov, G. Gluhchev, N. Ivanov, D. Mehandjiev, *Journal of Medicine, Physiology and Biophysics*, **52**, 7 (2019).