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## Articles and Statements

# Water Electrolysis-Processes in Catholyte and Anolyte Results with Differential Non-Equilibrium Water Spectrum

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## Abstract

A two stage model of the physicochemical processes at the electrolysis of pure water is proposed. The presence of nascent hydrogen in the catholyte and nascent oxygen in the anolyte during the first stage explains the antioxidant properties of the catholyte and the strong biocidal action of the anolyte. In the second stage the nascent hydrogen and oxygen are combined into hydrogen and oxygen molecules, respectively. The comparison between their average energies with the average energy of the control sample of water shows an increase in the average energy of the catholyte and decrease in the average energy of the anolyte. This indicates that some changes in the structure of the activated water have occurred.

There are results with method of Differential Non-equilibrium Water Spectrum (DNES) for alteration of energy of hydrogen bonds in catholyte and anolyte according control sample of water.

**Keywords:** electrochemically activated water (ECAW), catholyte, anolyte, nascent hydrogen, nascent oxygen, water spectrum DNES, energy of hydrogen bonds.

## 1. Introduction

Water is the main factor of the life on our planet. Even more, according to one of the coauthors of this paper the life has started in the warm thermal springs on the earth (Ignatov, Mosin, 2010). Water regulates the vital processes in the living things actively participating in the metabolism and their adaptation to the environment. That's why every change of its composition and structure influences the live matter either aiding its development and stability or on contrary provoking its destruction. It seems strange that despite such enormous importance scientists from different countries have seriously started paying attention and investigating the unusual properties of the water put to different kind of influence only in the last decades. In this direction a great attention was paid to its electrochemical activation (Bakhir, 1999; Kloss, 1988; Petrushenko, Lobyshev, 2004; Prilutsky, Bakhir, 1997; Zenin, 1999). Notwithstanding the easy description of the chemical processes the explanation of the obtained properties of the alkaline (catholyte) and acidic (anolyte) water solutions are still not fully convincing (Ball, 2008). Even more, in the majority of the existing descriptions and experiments NaCl has been used which gives a satisfactory

\* Corresponding author E-mail addresses: mbioph@dir.bg (I. Ignatov) explanation of the biocidal properties of the anolyte but does not work in case of pure water which obtains same properties. The explanation probably relates not only to the chemical changes in the water composition but also to the changes of its structure.

The main questions that researchers have to answer are as follows.

1. What physical and chemical changes occur in the water during its electrolysis?

This question should be investigated in two aspects:

a) pure water is processed;

b) NaCl or other minerals are added to the water solution.

2. What parameters of the activated water play a major role for the explanation of its unusual properties?

3. What the mechanism of the action of the activated water on the living things is?

In this paper attention is paid to the question 1a) i.e. the activation of water without additional mineralization, free of ions of other elements. A model of the corresponding physicochemical processes is proposed.

Every model has to describe satisfactory the observed effects of the modeled process. In our case the known effects of the activated water (catholyte and anolyte) reported by different investigators concern especially its influence on the living things. An explanation for the described effects could be the increased presence of both molecular hydrogen ( $H_2$ ) in the catholyte solution and molecular oxygen ( $O_2$ ) in the anolyte solution. But such an increase can be achieved through saturation of the water solution with these gases as well. It is true that in this case the water properties will be changed but without same effects. It is reasonable to assume that the increased concentration of OH–ions in the catholyte as well as H<sup>+</sup> ions in the anolyte cause such an action. Therefore, one may conclude that the action of the direct current on distilled or de-ionized water leads to changes in its chemical composition and structure different for the catholyte and anolyte.

#### Electrolysis of pure water.

According to the modern notion the following reaction takes place at the cathode :

0	â	1	
2	$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \mathrm{I}$		(1)
The analogous re	eaction at the anode is as follows:		
2	$2O^{2-} - 2e^- \rightarrow O_2 \hat{1}$		(2)
Actually, the abo	ve reactions run in two stages.		
At the cat	hode:		
First stage	$H^+ + e^- \rightarrow H^*$		(3)
Second stage	$H^* + H^* \rightarrow H_2$		(4)
At the anode:			
First stage	$OH \rightarrow O^* + 2e^- + H^+$		(5)
Second stage	$O^* + O^* \rightarrow O_2$		(6)

Therefore, according to formula (3)  $\mathbf{H}^*$  – atomic hydrogen is produced at the cathode during the first stage. It is called also nascent hydrogen and possesses high reactivity. Atomic oxygen  $\mathbf{O}^*$ called also nascent oxygen is produced at the anode, and it is highly reactive as well. These atoms can react between them according to formulae (4) and (6), and the obtained hydrogen and oxygen molecules can be either separated from the solution and go to the air or remain dissolved in the water. If there are molecules of hydrogen and oxygen at the cathode and the anode obtained according to formulate

(4) and (6) they can react with the nascent hydrogen and oxygen respectively as follows:

$4\mathbf{H}^*$	+	$0_2$	$\rightarrow$	$2H_2O$	(7)
<b>O</b> *	+	$H_2$	$\rightarrow$	$H_2O$	(8)

and water molecules will be produced.

## 2. Materials and Methods

## 2.1. Electrolysis apparatus for catholyte and anolyte

The experiments were conducted with the diaphragm electrolysis apparatus "Wasserionisierer Hybrid PWI 2100", equipped with four titanium electrodes coated with platinum. The voltage of the electric power supply – 220 V, the frequency of the electric current – 50 Hz, the power of the electric current 0.2–0.7 A; the time of electro processing – 30–40 min; the volume of the electroactivated water: anolyte – 0.3 l; catholyte – 0.9 l; power consumption – 70 Watts.

The electrolysis cell was formed by two electrodes – a positively charged anode and a negatively charged cathode connected to different poles to a DC source. Interelectrode space was filled with water, which is an electrolyte capable of conducting the electrical current.

The analyte had pH = 3.2 and ORP = +1070 mV;

The catholyte had pH = 9.0 and ORP = -300...-500 mV);

#### 2.2. NES and DNES Spectral Analysis

The device for DNES spectral analysis was made by A. Antonov on an optical principle. For this was used a hermetic camera for evaporation of water drops under stable temperature (+22–24 °C) conditions. The water drops were placed on a water-proof transparent pad, which consists of thin maylar folio and a glass plate. The light was monochromatic with filter for yellow color with wavelength at  $\lambda = 580\pm7$  nm. The device measures the angle of evaporation of water drops from 72.3° to 0°. The DNES-spectrum was measured in the range of -0.08– -0.1387 eV or  $\lambda = 8.9-13.8 \,\mu\text{m}$  using a specially designed computer program. The main estimation criterion in these studies was the average energy ( $\Delta E_{\text{H...O}}$ ) of hydrogen O...H-bonds among H<sub>2</sub>O molecules in water samples and human blood serum.

#### 3. Results and Discussion

#### 3.1. Nascent hydrogen in catholyte and nascent oxygen in anolyte

It is supposed in the proposed model that nascent hydrogen and nascent oxygen are produced in the catholyte and anolyte respectively. Their presence is substantial for the processes that may occur in the above solutions. The most probable assumption is that they will take part in reactions (4) and (6) or for example (7) and (8). Another possibility for them is to be stabilized in small quantity. It has to be underlined that the stabilization possibility depends on the probability to encounter corresponding re-agents from the above mentioned reactions. If this probability is small there is a possibility other molecules that can not react with them to play the role of stabilizers. For example, the water molecules due to their dipole character allowing for the formation of dimmers, thrimmers and larger structures could play such a role. In that case stabilized atoms of nascent hydrogen will remain in the catholyte, and stabilized atoms of nascent oxygen will remain in the anolyte. Since the nascent hydrogen is an active reducer it will attack admixtures that could be reduced when the catholyte is blended with another medium. This could explain the catholyte action as a strong antioxidant (Hanaoka, 2001; Kokichi et al., 2004). Probably, this could explain its healthy influence in case of different stress-related or due to the action of free radicals deceases. Such influence has been observed by many researchers (Hayashi, Kawamura, 2002; Komatsu, 2001; Lee et al., 2006; Sanetaka Shirahata et al., 2012; Yahagi et al., 2000; Ye, et al., 2008; Ye et al., 2004).

In a similar way the anolyte put in another medium will demonstrate its strong oxidative property and will oxidize all present organic admixtures and will destroy microorganisms, bacteria and viruses (Gluhchev et al., 2015; Karadzov et al., 2014; Kirkpatrick, 2009; Kumar et al., 1999; Miroshnikov, 2002; Suzuki et al., 2002; Tanaka et al., 1996; Zinkevich et al., 2000), which makes it an excellent biocidal, disinfection and harmless for the people and the environment mean.

#### 3.2. Differential Non-equilibrium spectrum NES and DNES

A convenient method for studying of liquids is non-equilibrium differential spectrum. It was established experimentally that the process of evaporation of water drops, the wetting angle  $\theta$  decreases discreetly to zero, and the diameter of the water drop basis is only slightly altered, that is a new physical effect (Antonov, 1995; Antonov, Yuskesselieva, 1983). Based on this effect, by means of the measurement of the wetting angle within equal intervals of time is determined the function of distribution of H<sub>2</sub>O molecules according to the value of f( $\theta$ ). The distribution function is denoted as the energy spectrum of the water state. The theoretical research established the dependence between the surface tension of water and the energy of hydrogen bonds among individual H<sub>2</sub>O-molecules (Antonov, 1995).

For calculation of the function f(E) represented the energy spectrum of water, the experimental dependence between the wetting angle ( $\theta$ ) and the energy of hydrogen bonds (E) is established:

$$f(E) = \frac{14,33f(\theta)}{[1-(1+bE)^2]^2}$$
(9)

where  $b = 14.33 \text{ eV}^{-1}$ 

The relation between the wetting angle ( $\theta$ ) and the energy (E) of the hydrogen bonds between H<sub>2</sub>O molecules is calculated by the formula:

$$\theta = \arccos\left(-1 - 14.33E\right) \tag{10}$$

The energy spectrum of water is characterized by a non-equilibrium process of water droplets evaporation, therefore, the term non-equilibrium spectrum (NES) of water is used.

The difference  $\Delta f(E) = f$  (*Esamples of water*) – f (*Econtrol sample of water*) – is called the "differential non-equilibrium energy spectrum of water" (DNES).

Thus, the DNES spectrum is an indicator of structural changes in water, because the energy of hydrogen bonds in water samples differ due to the different number of hydrogen bonds in water samples, which may result from the fact that different waters have different structures and composition and various intermolecular interactions – various associative elements etc (Ignatov et al., 2014; Ignatov et al., 2015). The redistribution of  $H_2O$  molecules in water samples according to the energy is a statistical process of dynamics.

Figure 1 shows the average NES-spectrum of deionised water. On the X-axis are depicted three scales. The energies of hydrogen bonds among  $H_2O$  molecules are calculated in eV. On the Y-axis is depicted the function of distribution of  $H_2O$  molecules according to energies f(E), measured in reciprocal unit eV<sup>-1</sup>. Arrow A designates the energy of hydrogen bonds among  $H_2O$  molecules, which is accepted as most reliable in spectroscopy. Arrow B designates the energy of hydrogen bonds among  $H_2O$  molecules the value of which is calculated as:

$$\bar{E} = -0.1067 \pm 0.0011 \,\mathrm{eV}$$
 (11)

Arrow C designates the energy at which the thermal radiation of the human body, considered like an absolute black body (ABB) with a temperature +36.6 °C, is at its maximum.

A horizontal arrow designates the window of transparency of the Earth atmosphere for the electromagnetic radiation in the middle infrared range of the Sun toward the Earth and from the Earth toward the surrounding space. It can be seen that the atmosphere window of transparency almost covers the NES-spectrum of water.



**Fig. 1.** The NES-spectrum of deionized water (chemical purity – 99.99 %; pH – 6,5–7,5; total mineralization – 200 mg/l; electric conductivity – 10  $\mu$ S/cm): the horizontal axis shows the energy of the H...O hydrogen bonds in the associates – E (eV); the vertical axis – the energy distribution function – f (eV<sup>-1</sup>); *k* – the vibration frequency of the H–O–H atoms (cm<sup>-1</sup>);  $\lambda$  – wavelength ( $\mu$ m)

The presence of nascent hydrogen and nascent oxygen in the hydrolyzed water could produce changes in its state. Indeed, using the method NES (Antonov, 1995; Ignatov, Mosin, 2014) as a measure of the energy spectrum of the water stage a useful information could be obtained about the structural changes in water and the average energy of hydrogen bonds among individual H<sub>2</sub>O molecules in samples. It was experimentally established (Ignatov, Mosin, 2014) that the surface pressure was increased in the catholyte and more molecules were included in a unit volume. The average energy E of the hydrogen bonds H...O between water molecules H<sub>2</sub>O, measured for the catholyte and anolyte, accordingly when a de-ionized water is used is E = -0.1293 eV for the catholyte and E = -1221 eV for the anolyte. The difference  $\Delta E_{H...O}$  between the average energy of the control sample of water E = -0.1251 eV, evaluated by the method DNES (Ignatov, Mosin, 2014) and the average energy of the catholyte and anolyte is respectively  $\Delta E$ = -0.0042 ± 0.0011 eV and  $\Delta E$ = 0.003 ± 0.0011 eV.

## 4. Discussion and Conclusions

A two-stage model describing physicochemical processes stemming from the electrolysis of pure water is suggested in the paper. The production of nascent hydrogen and nascent oxygen during the first stage is used as a basic assumption. The enriched concentration of these components in the solutions explains the antioxidant action of the catholyte the strong biocidal effect of the anolyte. The observed difference in the average energy and hydrogen bonds between catholyte and anolyte is an indication of structural changes that have taken place in the activated water. The development of more general model describing the physicochemical processes and analysis of the content and structure of activated water in case of electrolysis of weak water mineralization is a subject of future work.

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