REVIEW ARTICLE

Structure and Physicochemical Properties of Water Treated with Low-Temperature Low-Frequency Glow Plasma

Tomasz Bialopiotrowicz¹, Wojciech Ciesielski², Jerzy Domanski³, Marek Doskocz⁵, Karen Khachatryan⁶, Maciej Fiedorowicz⁶, Katarzyna Graz¹, Henryk Koloczek⁷, Adam Kozak³, Zdzislaw Oszczeda⁸ and Piotr Tomasik³,*

¹Institute of Environmental Engineering, Department of Physical Chemistry and Physicochemical Fundamentals of Environmental Engineering, John Paul II Catholic University of Lublin, Off-Campus Faculty of Law and Social Sciences, Kwiatkowskiego Stalowa Wola, Poland; ²Institute of Chemistry, Environmental Protection and Biotechnology, Jan Długosz Academy, Częstochowa, Poland; ³Krakow College of Health Promotion, Poland. ⁴University of Physical Education, Cracow, Poland; ⁵R&D Department, Stomatent, Bolesławiec, Poland; ⁶Institute of Chemistry and Physics, University of Agriculture, Krakow, Poland; ⁷Institute of Chemistry and Inorganic Technology, Krakow University of Technology, Krakow, Poland and ⁸Nantes Nanotechnological Systems, Bolesławiec, Poland

Abstract: Physical and selected physicochemical properties of distilled water treated with low-temperature low-frequency glow plasma (LPGP) for 5, 15, 30, 45, 60 and 90 min are given. Particular properties of PTW non-linearly vary with the time of exposure to plasma. PTW is characterized as declusterized solution of normal water consisting of clathrates of excited, probably singlet oxygen molecules, inside the clathrates. PWT is free of hydrogen peroxide and ozone. Raman spectroscopy is the best tool for diagnostic assessment of PTW.

Keywords: Clathrate hydrates, singlet oxygen, water stretching modes.

INTRODUCTION

Structure and physicochemical properties of single water molecules such as size, O-H bond lengths, charge distribution, molecular and bond vibrations, are well recognized and relevant data can be found elsewhere [1-3]. Recently, the results of simulation of effect of external electric field of varying strength upon water molecules was published [4]. However, several properties of water considered as macrostructure composed of abundant number of molecules still remains unclear [1-3]. Such properties as water memory [5], the Mpemba effect [6] and several other effects have to be reasonably interpreted. It should be stressed that absolutely pure water is practically unavailable as even redistilled water in contact with the atmosphere absorbs (dissolves) its components. Likely, the diverse composition of the atmosphere, temperature and pressure as well as the time of setting corresponding equilibrium can be responsible for limited reproducibility of certain measurements. Aqueous solubility of the material of the containers in which water is stored should also be taken into consideration when precise results of the measurements are required.

Recently, considerable attention has been paid to properties of magnetically treated liquid water. Toledo et al., [7] assumed that static magnetic field disrupted hydrogen bonds forming clusters promoting formation of smaller size structural units. It has been observed [8] that certain physicochemical properties of liquid water, that is its vibrations and electrolytic properties, changed on treatment with static magnetic field provided the water was exposed to contact with air. This fact was interpreted in terms of a better solubility of oxygen in magnetically treated water (MTW). Indeed, in ice, air clathrates were identified [9, 10].
Interactions with oxygen molecules and possibly also with nitrogen molecules seemed to be a driving force for the formation of such clathrates. Involving numerical method (Gaussian 09 and the 6-311+G** basis set) structure of oxygen clathrate hydrates was simulated [11].

In 2009, Oszczeda et al., [12] patented a reactor for treating water with low-pressure glow plasma (LPGP). LPGP enjoys several physical applications such as surface abrasion [12] and was also used in chemical synthesis [13-15]. There is also a report [16] on application of cold plasma for disinfection of water. According to the authors the bacteria were killed with hydrogen peroxide formed on the plasma treatment jointly with generated electric fields.

Preliminary studies [17] on the effect of LPGP on deionized water and saline revealed changes of their pH, electric conductivity and surface tension but the explanation of the origin of observed effects was not approached and the structure of PTW remained unknown.

In contrast to the former, preliminary studies [17], this paper presents a complex examination of the structure of redistilled water subjected to LPGP and the link between the structure and properties of PTW and the time of the water exposure to plasma. This paper also reveals that changes in the water macrostructure on treating with LPGP resemble these induced by the magnetic field.

METHODS

Preparation of PTW

Distilled water (200 mL) in 250 mL polyethylene bottles was placed in the chamber of the reactor [15] and exposed to plasma for 5, 15, 30, 45, 60 and 90 min. Plasma of 38°C was generated at 5x10⁻³ mbar, 600 V, 50 mA and 280 GHz frequency. The produced water was stored at ambient temperature in 100 mL closed Teflon containers.

Physicochemical Properties of PTW

Boiling Points

PTW samples (20 mL) were distilled under identical atmospheric pressure and their boiling point was determined with the 0.2°C precision. Estimations for each sample were triplicated.

Osmotic Pressure

Osmotic pressure was determined with a Marcel OS3000 osmometer (Marcel S.A., Zielonka, Poland) equipped with 100 mL tubes.

pH and Oxygen Content

They were measured using a laboratory multifunction meter Cx-505 (Elmetron, Zabrze, Poland) equipped with glass electrode.

Conductivity

Estimations were performed at 25°C with an ELMETRON CPC-505 instrument (Zabrze, Poland) equipped in an ELMETRON EC-60 sensor.

Active Oxygen Content

Active oxygen was determined by a method similar to that for the iodometric determination of the peroxide value of animal and vegetable fats and oils with a visual endpoint detection. Namely, to 100 ml sample of water 2 ml of the saturated KI solution was added. After 30 min small amount of soluble starch was added. The color of the solution changed to pink. Next the sample was titrated with 0.01 M Na₂S₂O₃ solution up to obtain colorless solution. Miliequivalents of active oxygen [meqO₂] were calculated from the formula:

\[ LO = V \times 0.01 \times 1000/100 = 0.1 \times V \text{ [meqO₂/kg]} \]

where V is a volume of 0.01 M Na₂S₂O₃ solution used.

Surface Tension

Surface tension measurements were made at 25°C with the Platinum Du Noüy ring technique using the KSV Sigma 702 (Helsinki, Finland) tensiometer.

Refractive Index

Lab refractometer RL from PZO Warsaw, Poland was used.

Density

Each water sample was tested in 3 different pycnometers. Prior to experiments the pycnometers were washed subsequently with detergent for washing dishes, distilled water and ethanol and left for drying at 22°C for 48 h. The dry pycnometers were weighed with the precision of 0.0001 g then calibrated with distilled water and repeatedly conditioned for 24
h. The determined weights were divided by the value of density of distilled water at 22°C (d = 0.9982 g/cm³). The determinations were run in triplicates.

**Vapor Pressure**

Samples of PTW and control water (2.7 ± 0.0001 g) were stored in weighed dishes closed in desiccator for 87 days. Every third day, the desiccator was open, evaporated water condensed on the inner surface of the desiccator cover was removed with a filter paper and the weight of the water remained inside particular weighing dishes was estimated with the same precision as above. The experiments were duplicated.

**FTIR Spectra**

The FTIR-ATR spectra of the film were recorded in the range of 4000 – 700 cm⁻¹ at resolution of 4 cm⁻¹ using a Mattson 3000 FT-IR (Madison, Wisconsin, USA) spectrophotometer. That instrument was equipped with a 30SPEC 30° reflectance adapter fitted with the MiRacle ATR accessory from PIKE Technologies Inc., Madison, Wisconsin, USA.

**EPR Spectra**

The spectra were recorded at room temperature employing an instrument constructed at Wroclaw Technical University. The range of the X-band (ν=9.5 GHz, λ = 3.2 cm) was employed at the 20–25 dB attenuation and 2048 s swiping time. An EPR controller software designed for taking the EPR spectra was applied.

**UVVIS Spectra**

The spectra were recorded with a Thermo Scientific Evolution 220 (USA) spectrophotometer in the wavelength range of 190–1100 nm in a quartz cell of 10 mm path length.

**Raman Spectra**

The spectra were taken with a Perkin-Elmer MPF44A Fluorescence Spectrophotometer equipped with a xenon lamp and 4 mL quartz cell. The spectra were recorded for:

- control distilled water,
- PTW from the treated control water exposed to LPGP for 5, 15, 30, 45, 60 and 90 min. The spectra were taken for freshly prepared samples and the samples stored at room temperature in closed containers for 1 week, 1 and 3 months, and for samples boiled for 1 min in the open in a microwave oven,
- distilled water (3 mL) to which 30% aq. solution of hydrogen peroxide (1 mL) was admixed,
- distilled water collected from slowly melting ice. Relevant spectra were taken immediately and after 10, 20, and 30 min,
- PTW treated with LPGP for 15 min to which either SDS detergent (sodium dodecylsulfate) (4.3 mg/3 mL water sample), NaOH (1 mL of 0.25 M aq. solution in 3 mL water sample), or conc. hydrochloric acid (1mL in 3, 6 and 12 mL water sample) were added.
- MTW maintained in quartz cell for at least 6 days between two round neodymium magnets (ϕ = 6 cm) of 0.5 T induction.

**¹HNMR Spectral**

The spectra were taken at 26°C with a Mercury-VX 300MHz Varian instrument. Glass capsules with DMSO-d₆ immersed in the measurement tubes served as the standard.

**Results and Discussion**

The Table 1 collects fundamental physical and physicochemical properties of the plasma treated water (PTW).

It can be seen that independently of the time of exposure to plasma the estimated properties only subtly differ from these taken for control water. Thus, the longest, 90 min. exposure water to LPGP declined the boiling point of PTW hardly by 0.2–0.25°C. It was accompanied by a gradual rise in density from original 0.9980 to 0.9984 g/cm³ and decrease in the vapor pressure by almost 10% of original value estimated for control water. Measured osmotic pressure (osmolality), refractive index and surface tension remained practically unchanged whereas pH subtly varied in non-linear manner against the increase in time of exposure to plasma. Initial pH 5.56 absolutely stable in 10 repetitions increased after the 5 min exposure, then decreased after the 15 and 30 min exposure. It again increased after the subsequently prolonged exposure even to 6.41 in order to
stabilize at 5.83 in water treated with plasma for 90 min. It might suggest a solubility of CO₂ varying with the time of exposure of water to plasma as a result of accompanying structural transformations in PTW.

Table 1. Physical properties of PTW.

<table>
<thead>
<tr>
<th>Property</th>
<th>Time of exposure to plasma [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 (Control)</td>
</tr>
<tr>
<td>Boiling point [°C]</td>
<td>100.00</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>0.9980</td>
</tr>
<tr>
<td>Vapor pressurea</td>
<td>11.64</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.3330</td>
</tr>
<tr>
<td>Osmotic pressure [mOsm/kg H₂O]</td>
<td>16</td>
</tr>
<tr>
<td>pH</td>
<td>5.56±0.00</td>
</tr>
<tr>
<td>Conductivity [microS]</td>
<td>2.32±0.00</td>
</tr>
<tr>
<td>Oxygen content [%]b</td>
<td>61.93±1.10</td>
</tr>
<tr>
<td>Surface tension [mN/m]</td>
<td>72.20±0.21</td>
</tr>
<tr>
<td>Active oxygen [meqO₂/kg]</td>
<td>0.0±0.001</td>
</tr>
</tbody>
</table>

*a*Given as a weight loss of samples [%].

*b*Expressed as a percent of saturation.

Fig. (1). The EPR spectra of original water (1) and water exposed to plasma for 60 min (2) and 5 min (3). For the clarity, the spectra for PTW after exposure to LPGP for 15, 30, 45 and 90 min are not presented. They are identical with the spectra (2) and (3).
The conductivity for control water was higher than that for PTW. The conductivity of control water could originate from the dissolved carbonic acid. Its concentration in PTW decreased as a result of declining number of water molecules for the reaction with CO₂ as they were engaged in building clathrates.

The total solubility of oxygen in PTW varied non-linearly against its exposure time to LPGP suggesting that not only concentration but also structure of clathrates in PTW varied with the exposure time. Simultaneously, the content of active oxygen, likely that arrested inside clathrates in PTW slightly but monotonously rose with the time exposure of water to LPGP.

The EPR spectra shed a light upon the status of the active oxygen. The spectrum of controlled water showed a week signal of free radical triplet oxygen. That signal ceased in the spectra of PTW (Fig. 1).

Fig. 2 presents the Raman spectrum of control, untreated water. That spectrum contains peak at 400 nm (peak I) followed by a weak shoulder (S) and another peak at 700 nm (peak II). The peak I: S: peak II intensity ratio was approximately 3.33: 1: 1.67.

On treating water with plasma, an additional peak appeared with its maximum around 440 nm (Fig. 3), that is, in the region of the week and broad shoulder observed in the spectrum of original water. Its intensity depended on the time of exposition. Also the ratio of the intensity of the former peaks depended on the latter parameter.

Fig. (2). Raman spectrum of control water.

Fig. (3). Raman spectrum of water treated with plasma for 15 min.
Fig. 4 presents FTIR spectra of control and PTW. In the range of 4000 – 1250 cm\(^{-1}\) the spectrum invariantly consisted of three bands.

According to Chaplin [1], the bands reflect \(v_{OH}\), combination band and \(\delta_{OH}\) bands, respectively. One might see that positions of all three bands are insensitive to the treatment with plasma and the intensity of these bands are subtly dependent on it. The intensities of the 3500-3000 cm\(^{-1}\) bands in the 5 min treated water slightly increased in respect to control, then they declined fairly regularly against the exposure time (Table 2).

The band situated at 3243 cm\(^{-1}\) is, in fact, composed of two bands [1] reflecting asymmetric (longer wavelength) and symmetric (shorter wavelength) vibrations in the water molecule. The Gaussian distribution of that band showed that water treated with plasma for 5 min contained more asymmetrically vibrating molecules whereas prolonged treatment of water favored formation of symmetrically vibrating molecules (Table 3).

That result suggests that PTW after the 5 min treatment could be more hydrophobic than original water and water exposed to the prolonged treatment. In these spectra no peaks were observed at 1050 cm\(^{-1}\) and 2400 cm\(^{-1}\) which might be attributed to ozone. In the spectrum of ozone [18] a strong double peak resides at 1050 cm\(^{-1}\) accompanied by medium intensity peak at 2400 cm\(^{-1}\). Therefore, lack of ozone in PTW is postulated.

In the \(^1\)H NMR spectra of every PTW invariantly one signal could be observed. In the

![Fig. (4). FTIR spectrum of water (0 – control water, 1-6 – water treated with plasma for 5, 15, 30, 45, 60 and 90 min, respectively).](image)

**Table 2. Intensity changes of the bands in the FTIR spectrum of PTW.**

<table>
<thead>
<tr>
<th>Sample after treatment with plasma for min.</th>
<th>Intensity of bands (positions in cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3243.5</td>
</tr>
<tr>
<td>0</td>
<td>0.3345</td>
</tr>
<tr>
<td>5</td>
<td>0.3365</td>
</tr>
<tr>
<td>15</td>
<td>0.3185</td>
</tr>
<tr>
<td>30</td>
<td>0.3189</td>
</tr>
<tr>
<td>45</td>
<td>0.3151</td>
</tr>
<tr>
<td>60</td>
<td>0.3097</td>
</tr>
<tr>
<td>90</td>
<td>0.2763</td>
</tr>
</tbody>
</table>
spectra of controlled water and PTW from the 60 min exposure to LPGP it was located at 4.42 ppm and in the spectra of PTW after 1, 5 and 30 min exposure moved to 4.44 ppm. The UV absorption spectra invariably demonstrated two bands at 195 and 230 nm (Table 4) which result from Rayleigh scattering and $^{1}A_1 \rightarrow ^1B_1$ transition, respectively [1]

However, Table 4 reveals that both processes are obscured by the plasma treatment and these changes in the Rayleigh band at 195 nm were most remarkable in PTW after the 15 min exposure to LPGP. The Rayleigh band in the spectrum of that PTW is unusually intensive. That observation is in concert with other physicochemical properties of that PTW demonstrated in Table 1. It confirms the specific character of that PTW. One can speculate that it might result from a exposure time dependent conversions of the PTW macrostructure. The postulated variety of the aqueous oxygen clathrates [11] which could be formed would rationalize the non-linearity against the exposition time of changes in some parameters quoted in Tables 1-4. Particularly convincing is the increase in the concentration of active oxygen under absence of hydrogen peroxide. This behavior together with simultaneously

Table 3. Ratio of the intensity of the bands resulting from the Gaussian distribution of the band at 3243.5.

<table>
<thead>
<tr>
<th>Sample after treatment with plasma for min</th>
<th>Band 3240 cm$^{-1}$</th>
<th>Band 3379 cm$^{-1}$</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2545</td>
<td>0.2159</td>
<td>1.1788</td>
</tr>
<tr>
<td>5</td>
<td>0.2314</td>
<td>0.2347</td>
<td>0.9859</td>
</tr>
<tr>
<td>15</td>
<td>0.2924</td>
<td>0.1968</td>
<td>1.4858</td>
</tr>
<tr>
<td>30</td>
<td>0.2875</td>
<td>0.2071</td>
<td>1.3882</td>
</tr>
<tr>
<td>45</td>
<td>0.283</td>
<td>0.2085</td>
<td>1.3573</td>
</tr>
<tr>
<td>60</td>
<td>0.2845</td>
<td>0.2031</td>
<td>1.4008</td>
</tr>
<tr>
<td>90</td>
<td>0.2531</td>
<td>0.1902</td>
<td>1.3307</td>
</tr>
</tbody>
</table>

Table 4. Changes of the intensity of the bands in the UV spectrum of PTW.

<table>
<thead>
<tr>
<th>Time of exposure [min]</th>
<th>$\lambda$ [nm]</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>195</td>
<td>-0.0002</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0.0004</td>
</tr>
<tr>
<td>5</td>
<td>195</td>
<td>-0.041</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.047</td>
</tr>
<tr>
<td>15</td>
<td>195</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.041</td>
</tr>
<tr>
<td>30</td>
<td>195</td>
<td>-0.024</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.046</td>
</tr>
<tr>
<td>45</td>
<td>195</td>
<td>-0.032</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.047</td>
</tr>
<tr>
<td>60</td>
<td>195</td>
<td>-0.028</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.047</td>
</tr>
<tr>
<td>90</td>
<td>195</td>
<td>-0.027</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>-0.046</td>
</tr>
</tbody>
</table>
decreasing osmolality would suggest that PWT could be a vector delivering oxygen, likely the singlet oxygen molecules, to living cells.

The status of oxygen in the clathrates needs to be commented. The presence of the atmospheric, triplet oxygen in water prior to the treatment was well documented with the EPR spectroscopy. The absence of the relevant signals in the EPR spectra of plasma treated water could be interpreted as the result of either shielding triplet oxygen molecules within clathrates making them non-accessible for the outer field or a conversion of triplet oxygen molecules into excited singlet state that is into singlet oxygen [19,20]. The comparison of the Raman spectra of water collected from melting ice and plasma treated water spoke in favor of the presence of singlet oxygen molecules arrested in the clathrates. The Raman spectrum of ice cold water exhibited considerably intensified shoulder around 440 nm, however, it ceased within 30 minutes as that water approached ambient temperature. The initial 400 nm: shoulder: 700 nm intensity ratio (1.35: 1: 1.48) changed into 1.36: 1: 2.06, 1.39: 1: 2.03 and 1.29: 1: 2.17 after 10, 20 and 30 minutes, respectively. The Raman spectra of PTW stored for 4 months did not change. Therefore, it is likely, that the high stability of oxygen clathrates from the plasma treatment could result from clathrate stabilizing interactions of the cage with singlet oxygen. This property implies that the clathrate can play a stabilizing role for singlet oxygen which is known as a very short time living species.

PTW stored in closed Teflon containers for up to 4 months and PTW taken to their boiling point in a microwave oven were fully stable as demonstrated by the Raman spectra. The same spectra confirmed that PTW was stable in alkaline solution and SDS but strong acid decomposed PTW rapidly.

MTW was examined solely by the Raman spectroscopy. Its spectrum was identical as the spectrum of PTW compared to the spectra of PTW. Based on the Raman spectra of MTW Ramya and Venkatnathan [11] postulated formation of several clathrates with oxygen molecules arrested inside. In our study on the treatment of water with magnets as well as with LPGP without any contact with atmosphere, no changes in the Raman spectrum of control water could be observed.

CONCLUSIONS

1. Treatment of water with low-temperature low-frequency glow plasma deteriorates macrostructure of water to the extent dependent on the time of exposition of water to the plasma.

2. The resulting water is an aqueous solution of clathrates of water with included molecules of singlet oxygen.

3. The structure of the clathrates depends on the duration of the exposure of water to the plasma.

4. PTW can be efficient vector for oxygen.

5. PTW is stable on long storage, survives boiling and contact with alkali but it is unstable in acidic solutions.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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REFERENCES


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