
**BIOPHYSICS
AND MEDICAL PHYSICS**

Slow Variations of the Electroconductivity of Distilled Water

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Abstract—The conductivity of distilled water with a slow change in temperature has been measured experimentally and studied. Periodic variations in the electrical conductivity of water have been found, which are observed at the rate of temperature change $dT/dt < 0.1$ K/h. The periods were longer than 24 h; the amplitudes of the variation ranged from +2.7% to –2.3%. The possible causes of the observed phenomena are discussed.

Keywords: specific conductivity of water, rate of temperature change, temperate factor of conductivity, long-term fluctuations of water electroconductivity.

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INTRODUCTION

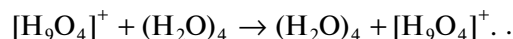
The effects of different external physical factors on the properties of water, including its conductivity, are well known [1, 2]. It is believed that this effect is caused by structural changes of water and the formation or destruction of chains of hydrogen bonds, clusters, etc. However, many of the observed phenomena, in particular the effect of weak electric and magnetic fields on water and the correlation of its properties with solar activity, have not been explained to date [3, 4].

The state-of-the-art ideas on the structure of water were reported in the review [5]; it follows from the review that in spite of considerable efforts by theorists and experimentalists this question remains unsolved. The situation is complicated by the fact that water is practically never free from impurities; their impact on the structure of water is explained by different and often opposing opinions [6, 7]. Consequently, the mechanisms of the transport properties of water are unclear, in particular the mechanism of its electroconductivity.

It is known that the mobility of the main carriers of electricity in water, viz., hydroxyl and proton (hydroxonium) ions, is high compared with the mobility of ions of other substances. In 1806, von Grotthuss assumed that a pair of particles with opposite charges in a molecule that is part of a chain that stretches from one electrode to another could be rotated to connect with the next pair, thus transmitting one charge in one direction and the opposite charge in the other direction.

N. Agmon [8, 9] hypothesized that the anomalously high mobility of protons is caused by a sequence

of the isomerization of H_9O_4^+ and H_5O_2^+ cations. Subsequent development of this idea leads to the following simplified scheme of charge movement [10, 11]. A water molecule is connected to a cluster of the $\text{H}^+(\text{H}_2\text{O})_n$ type and the resulting less-stable cluster is destroyed, with the water molecule being released from the opposite side. Therefore, the charge is shifted relative to its initial position. Mechanisms for moving the charge without the destruction of the structures are also discussed, such as the process studied in [12], which is described by the reaction



All the proposed models are based on the existence of a continuous network of molecular bonds or related cluster formations, assuming different mechanisms of charge movement [10–13].

Such mechanisms may occur in the case of water with dissolved impurities when foreign ions take part in the formation of clusters. In real conditions water always has impurity conductivity; therefore, in contact with air containing 0.033% carbon dioxide the conductivity of ultrapure water increases from 0.055 to 1 $\mu\text{S}/\text{cm}$ due to the effective dissolution of CO_2 . The dissolution of metal electrodes, air components, and the material of the container with water also increases the concentration of hydrated ions in water. The structure of the water shell of an ion can vary with changes in the parameters of the external medium and under the actions of different factors on water. The knowledge of the dynamics of formation and destruction of structural formations in water is far from the required understanding. Some researchers even believe that we can speak about the structure of water only condition-

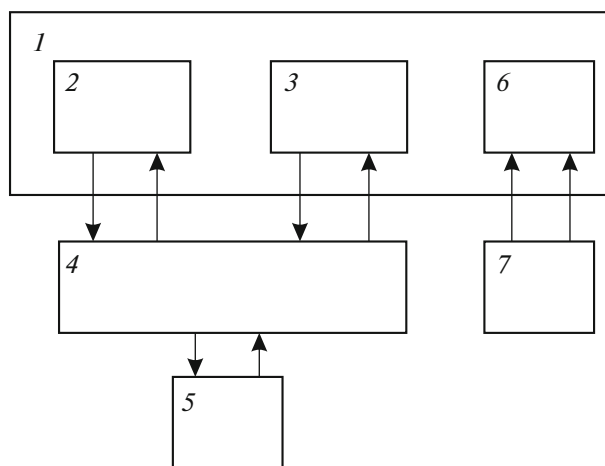


Fig. 1. The scheme of the experimental complex.

ally because the lifetime of hydrogen bonds is of the order of picoseconds. On the other hand, it is known that although the exchange of a single molecule with bulk water near a calcium ion actually proceeds during less than a nanosecond, the relative arrangement of the molecules around this ion remains virtually unchanged. There are theoretical studies in which time changes in the structure of water are estimated in seconds [1, 14] or even a few days [15].

The solution of these problems requires further experimental study of the properties of water. Here, the electroconductivity of water was measured in a very slow temperature change; the results do not have a convincing explanation.

MATERIALS AND METHODS

The experimental studies were performed using water conductivity cells (sensors) consisting of a hardware/software system, whose scheme is shown in Fig. 1.

A passive thermostat (thermal insulator) *I* was used to reduce the rate of the change of the water temperature dT/dt in sensors with respect to the rate of the change of the ambient temperature. The thermostat, *I*, was equipped with electric heating element *6* which, when required, allowed increasing the water temperature in the sensors at a higher rate. A heater, *6*, was connected to an external source, *7*, with a constant voltage of 3.8 V and a current consumption of approximately 0.5 A. During the experiments, the thermostat with sensors were placed in an isolated dark room. The interior working volume of the thermostat had a cylindrical shape with a height of 28 cm and a diameter of 8 cm. Two identical sensors were placed at a distance from each other of not more than 4 cm. The difference between the values of the conductivity and the temperature of water measured by two sensors was small and was caused only by the quality of calibration. The

thermostat provided the stabilized rate of the change in water temperature in the sensors dT/dt of approximately 0.03 K/h.

Two identical sealed sensors *2* and *3* were placed into the thermostat. The sealing extent that was achieved excluded the possibility of contact between the air inside the sensor with the ambient air, i.e. the possibility of the evaporation of water from the sensor during prolonged experiments.

Polyethylene was used as the material of the sensor bodies; the thickness of the walls of the sensor was 0.5 mm. The sensors had a shape close to cylindrical with a diameter of approximately 11 mm and a height of approximately 40 mm. Two electrodes in each sensor were fabricated from stainless steel wire with a diameter of 0.65 mm and were vertically placed near the cylinder walls. Each electrode was immersed into water to ~10 mm; the distance between the electrodes was approximately 10 mm. A thermistor in a glass body was embedded in each sensor to measure the water temperature. It was located on the axis of the cylindrical sensor body vertically (between the electrodes) and was immersed in water along with the electrodes for approximately 10 mm. The synchronicity in the water-conductivity measurements by both sensors allows one to exclude random changes that are not associated with the test process. Distilled water with a specific conductivity of approximately 2 $\mu\text{S}/\text{cm}$ was used in the experiments. The volume of the water that was poured into each sensor was approximately 1 mL; the volume of the air above the water surface was approximately 2 mL. Sinusoid voltages (reference signals) were applied from the outputs of the matching device, *4*, on electrodes with an amplitude of 0.5 V and a frequency of approximately 200 Hz to measure the electroconductivity of water and a frequency of approximately 300 Hz was applied to thermistors to measure its temperature. Reference signals were formed by a software generator using a PC, *5*, and fed to the matching device, *4*, from the output of the sound card. These voltages were maintained on the sensors during the entire time of the experiment. The amplitude of the alternating current that flowed through the water during the measurement of its conductivity was approximately 0.25 μA , which corresponded to a release with a power of 0.09 μW . The alternating current through the thermistor was approximately 5 μA , which led to the release of power on it of approximately 1.8 μW . The total electrical power released due to the flow of these currents led to an increase of the water temperature in the sensor by no more than 0.001°C in 1 h, excluding heat transfer between the sensor and the environment. In view of the heat energy, the contribution of these signals to the measurement results can be considered negligible.

The signals received from the sensors were applied to the inputs of a two-channel matching device, *4*; a summed signal from a mixture of the two frequencies

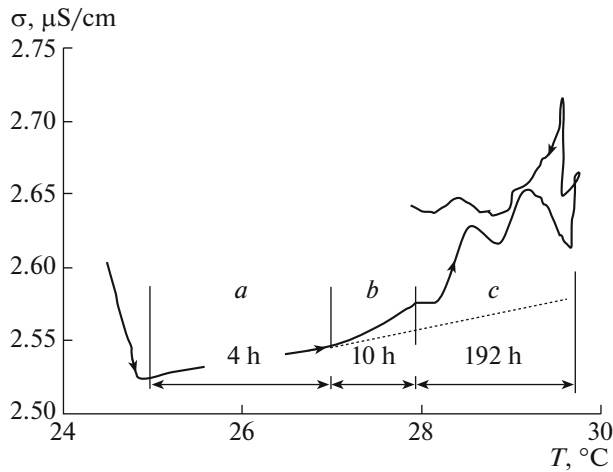


Fig. 2. The conductivity of water as a function of the water temperature during heating at different rates of temperature change. The arrows indicate the direction of time.

was formed in each channel of the device, which carries information about the values of the conductivity of water and the conductivity of the channel thermistor. The PC sound card was used as the receiver, which received signals from the outputs of the matching device, 4. Recording and digital-signal processing were carried out by a special program. The program provided digital frequency filtration of the signal, demodulation, the calculation of the conductivity and current temperature of water, and graphical representation of the processed results in the form of time dependencies [16, 17].

The measurements and registration of the results were carried out continuously in the automatic mode by writing software that is a part of the program. Preliminary experiments showed that the test parameters vary relatively slowly over time; therefore, the conductivity and temperature of the water in the sensors were measured and recorded once per hour for a 1-minute period.

The hardware/software measuring complex provided a relative accuracy of the water conductivity measurements in the sensors at least $\pm 0.001 \mu\text{S}/\text{cm}$ and the relative accuracy of water-temperature measurements at least $\pm 0.001^\circ\text{C}$.

RESULTS AND DISCUSSION

Using this hardware/software system we carried out 18 measurement cycles during the period from May 2013 to March 2015 with a duration from 1 to 32 days at the water temperature falling in the range from 8 to 32°C . The total duration of the records of the conductivity and temperature of the water was 3000 h.

In almost all of the experiments we observed the dependence of the conductivity of water on the rate of the temperature change. To illustrate this dependence,

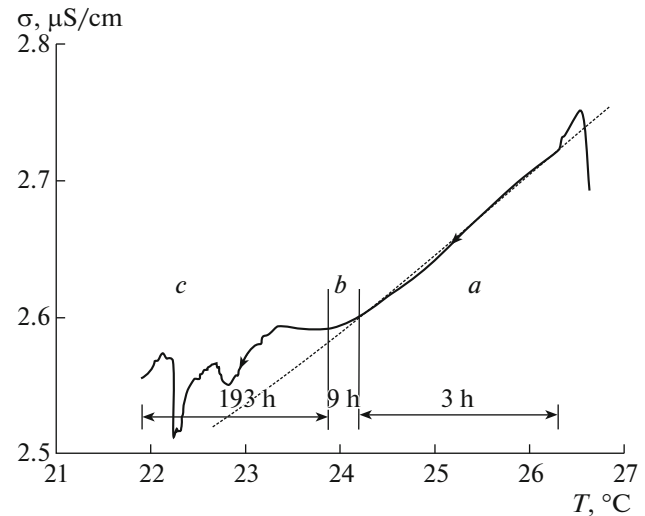


Fig. 3. The conductivity of water as a function of the water temperature during cooling at different rates of temperature change. The arrows indicate the direction of time.

curves based on the results of two 10-day experiments that were carried out from June 4, 2014 to June 26, 2014 are shown in Figs. 2 and 3.

Figure 2 shows the dependence of the specific conductivity of water in one of the sensors on the water temperature, where the *a*, *b*, and *c* sections correspond to different values of the temperature change rate dT/dt when heating water.

Prior to the *a* region, water was in the condition of slowly changing temperature ($dT/dt \sim 0.02 \text{ K}/\text{h}$) for 140 h. At the same time, a decrease in the conductivity was observed with a small increase in temperature. At the beginning of the *a* region the electric heater, 6, was switched on, which from that time remained in the switched on state (it was turned off during the next experiment, Fig. 3). As the heater, 6, was switched on, the water temperature in the sensor increased from 25 to 27°C within ~ 4 h, the rate of its growth then decreased and the temperature was stabilized at $\sim 28^\circ\text{C}$. The rate of the temperature change on the *a* region was approximately $0.5 \text{ K}/\text{h}$. It can be seen that in this region the dependence of the conductivity on temperature is almost linear. The dotted line indicates the slope of the linear site. When the water temperature approaches the $27\text{--}28^\circ\text{C}$ range the rate of the temperature change gradually decreased to approximately $0.1 \text{ K}/\text{h}$ (part of the curve *b*, the measurement time of approximately 10 h), the slope of the curve of the temperature dependence of conductivity is significantly different from the slope of the linear section *a*. Finally, in section *b* of the curve the water temperature initially increased from 28 to 29.5°C for 48 h and then decreased to 28°C at a rate of not more than $0.03 \text{ K}/\text{h}$. These increases and decreases of temperature are associated with its changes in the room, which were made smooth by the thermostat. It is clear that in the

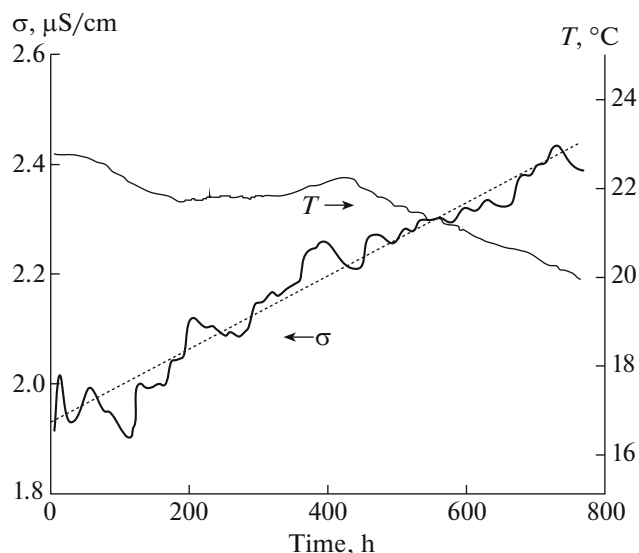


Fig. 4. Changes in the conductivity of water and its temperature over time during 32 days.

c section of the curve, slow periodic variations of the conductivity are observed against the temperature changes of conductivity.

The curve of the temperature dependence of the conductivity of water in the same sensor during monotonic cooling at different values of the temperature change rate dT/dt is shown in Fig. 3.

The experiment shown in Fig. 3 was a continuation of the experiment from Fig. 2. Before the *a* section begins, the water experienced a slowly varying temperature ($dT/dt \sim 0.02$ K/h) for 140 h and the heater, δ , was switched on. It is clear that when the water temperature decreased from 26.6 to 26.4°C, the conductivity of water first increased and then decreased, i.e., the temperature dependence is irregular. As the heater was switched off, at the beginning of the *a* section the water temperature in the sensor decreased from 26 to 24.5°C for 3.3 h with a rate of approximately 0.46 K/h. It is obvious that, as occurred on heating, in the section with a relatively high rate of temperature decrease the temperature dependence of conductivity is generally linear. The slope of the linear section is also indicated by the dotted line. When the system approached the temperature range of 24.5–23.8°C, the water cooling rate was reduced to a value of approximately 0.1 K/h (section *b* of the curve), while the slope of the curve of the temperature dependence of the conductivity also began to differ from the slope of the linear section *a*. Finally, on the *c* section of the curve the water temperature decreased from 23.8 to 22°C during 8 days with an average rate not exceeded 0.03 K/h. It can be seen that in this part of the curve, as well as when heating the water (Fig. 2), no slow periodic variations are observed of the change in the conductivity of the water.

The above data concerns only one of the sensors. Data from the other (parallel) sensor had some differences in the absolute value of the conductivity and temperature, but all the function dependences of the measured values in both sensors were identical.

It is clear from the curves presented in Figs. 2 and 3 that the nonlinear and even non-monotonic temperature dependence of the conductivity of water was observed at a low rate of its heating (cooling) in the 28–29°C and 22–24°C temperature ranges, respectively. Similar effects were observed in a 2-day experiment on June 17, 2013 at a water temperature of approximately 8°C (using an additional cooler) and a 2-day experiment on April 17, 2014 with the water temperature equal to $\sim 32^\circ\text{C}$. In all of the described experiments the specific conductivity of water in the sensors varied from 1.4 to 2.9 $\mu\text{S}/\text{cm}$.

Dependencies similar to those shown in Figs. 2 and 3 were observed in most of the other experiments. The curves of the changes of temperature and conductivity that were obtained in a long-term experiment in September 2014 are shown in Fig. 4.

The thin line in the figure shows the temperature change, the thick line corresponds to the change in conductivity, and the dashed line shows the linear drift of conductivity. The drift is caused by the dissolution of the elements of the sensor structure (primarily, the glass body of the thermistor), which averaged 0.96% per day. At the same time, for 200–400 h at a relatively constant temperature of the water the drift was approximately 1.2% per day. During the 400–768 h period while cooling the water by 2°C the drift was approximately 0.88% per day, i.e., here, the water conductivity increase due to the dissolution process dominated the decrease in conductivity that resulted from the cooling of water. It is clear that relatively small fluctuations in temperature (approximately 3°C for 768 h) can be taken into account and the appropriate adjustments in the conductivity values can be made assuming the dependence to be linear and the known temperature coefficient of conductivity equal to 2–3% per 1°C. After this point, excluding the trend of the curve, we obtain the curve shown in Fig. 5. Here, conductivity deviations from a straight drift line are shown (dashed line in Fig. 4), which show the nature and magnitude of non-temperature long-term variations of conductivity of water in the experiment for 32 days of the measurements.

The total duration of the obtained conductivity and temperature records exceeds 3000 h; this indicates the existence of variations of the conductivity of water that are observed at low temperature-change rates and are periodic in nature.

These experimental results show that the conductivity of water was followed by slow temperature changes, but its linear dependence (noted as a dashed line in Figs. 2 and 3) is due to a strong quasi-periodic

perturbation caused by some external factor, whose nature is not clear.

As the temperature changes rapidly, the slow change in conductivity caused by external influences does not distort the linear nature of the dependence; however, it changes the temperature coefficient of the conductivity. In particular, the measurement corresponding to the *a* section (Fig. 2) corresponds to the phase of the reduced conductivity of water under the influence of external factors. Thus, the temperature conductivity coefficient upon heating turned to be much less than the known value (2–3% when heated by 1°C). When cooling the water (section *a*, Fig. 3) the decrease in the conductivity due to cooling is summed with its decrease due to external influence, and the thermal conductivity coefficient is greater than the table value.

It is easy to estimate the minimum rate of the temperature change, in which the effect of an unknown factor will be sufficiently pronounced. The changes in conductivity caused by the action of this factor while heating or cooling should be comparable with conductivity changes due to temperature changes. Since the characteristic value of the conductivity factor changes, as follows from Fig. 5, is approximately 0.05 $\mu\text{S}/\text{cm}$ and the period of the observed variations is more than 1 day, the irregular temperature dependence of the conductivity should be clearly observed at a heating or cooling rate of no more than 0.04 K/h.

The conductivity of water is determined by the concentration of ions and their mobility. Since the conductivity of extremely pure water is two orders of magnitude lower than the conductivity of the water used in our experiments, the presence of impurity ions in water is of critical importance. It seems that the most significant impact in our conditions is due to the CO_3^{2-} and HCO_3^- ions and the metal ions from the electrodes. In contrast to OH^- and H^+ ions that have a mobility of 20.5×10^{-8} and $36.3 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, the mobility of other ions in water is typically in the range of 4×10^{-8} – $8 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Considering these ideas, we can conclude that the dissolution of impurities in water has two important consequences. First, the dissolution of carbon dioxide in water finally results in an increase in the concentration of the most mobile ions, viz., hydrogen ions [18] according to the reaction:



The dissociation of the HCO_3^- ion is insignificant and did not result in an increase in the concentration of hydrogen ions (the reaction constants are 4.32×10^{-7} and 4.69×10^{-11} , respectively). Secondly, the dissolution of impurities leads to significant changes in the internal structure of the liquid resulting from the formation of inside (near) and outer (distal) hydration shells around the ions; the proportion and properties

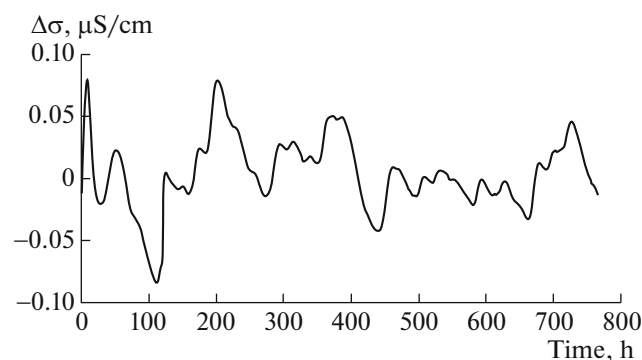


Fig. 5. Fluctuations of the conductivity of water after adjustment of temperature changes and the constant trend.

of these shells, which are considered as separate phases, are determined by the structure of the hydrated solution and the solvent structure [19].

There is also a high probability of the existence of flat closed structures with the number of oxygen atoms that do not exceed a few units or dozens, but many researchers do not exclude the possibility of the existence of clusters that consist of hundreds or thousands of molecules, and even the existence of complexes with dimensions larger than $10 \mu\text{m}$ [20]. It is assumed that in this case the proton transfer to the molecules that form the cluster surface is possible, while the proton migrates over the surface of the cluster and stabilizes it. We also note that the stability of clusters formed near multiply charged ions, such as CO_3^{2-} , is much higher than the resistance of pure water clusters.

If this situation actually occurs, then with an increase in (decrease in) temperature simultaneously with an increase (decrease) of the ion concentration the destruction (formation) of hydration shells or molecule chains occurs, which cause a decrease (increase) in the mobility of protons. These processes operate in the opposite direction in relation to the change in the conductivity of water. Therefore, assuming that the time to transform the hydration shell during temperature changes is different from the dissociation time, it can be expected that the temperature coefficient of conductivity will be dependent on the rate of temperature change.

Despite the high degree of the sensor sealing, its thin walls do not prevent a change in pressure inside it when the external pressure changes. Because the amount of dissolved gas is dependent on the pressure of air above the water surface, it can be assumed that the observed conductivity variations are associated with periodic changes in atmospheric pressure. In order to evaluate this relationship, we calculated the coefficients of the correlation between variations in the conductivity of water measured in two 30-day experiments in January 2015 and March of 2015 and variations of atmospheric pressure from the corre-

sponding database of meteorological observations. In the experiment carried out in January the correlation was observed with a 0.4 correlation coefficient, while in the experiment carried out in March there is practically no correlation (the coefficient is less than 0.01). Therefore, not completely excluding the influence of the external pressure on the conductivity of water, we have to acknowledge the existence of another external factor that has an effect on water. In this case, we can assume that this unknown factor effects the structure of water of hydration shells, because the latter is a formation which can be easily destroyed. As a result, the conductivity is changed by changing the mobility of hydrogen and hydroxyl ions. The above considerations on the physical mechanisms of the observed phenomenon are assumptions that require further studies.

CONCLUSIONS

An irregular dependence of the electroconductivity of distilled water at slow changes of its temperature has been observed. At the same time, variations of conductivity over time have a pronounced periodic character.

It has been shown that at the rates of temperature change that fall in the 0.1–0.5 K/h range, the temperature dependence of the conductivity of water is practically linear, but the values of the thermal conductivity coefficient in this case substantially differ from the known table values. If the temperature change rate is less than 0.1 K/h, the temperature dependence of conductivity has an irregular (nonlinear) character.

We believe that these slow variations of the conductivity of distilled water are caused by variations of the mobility of the main charge carriers in water, viz., hydrogen ions.

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