Method for determining bond energy in nanostructured water

Vladimir Petrovich, Svetlana Volchek, Valentina Yakovtseva, Vitaly Bondarenko, Sergey Redko

Belarusian State University of Informatics and Radioelectronics, 6 P. Brovki str., Minsk, Belarus

ABSTRACT

Using water as an example, it is shown that monitoring the change in the loss tangent is a high sensitive method that allows determining the activation energy of relaxation processes in nanostructured water with high accuracy. The use of sensors, the electrodes of which are not in direct contact with the liquid under study is shown to be reasonable. The conditions for obtaining reliable information on the properties of water and its solutions are also justified, namely: measurements should be carried out using pulse methods for several seconds, and then measurements should be stopped to avoid contamination of the solutions studied by electrolysis products. The method of monitoring the magnitude of the loss tangent at fixed frequencies allows the acidity of solutions (pH value) to be controlled at the same time without using specialized instruments for acidity studying.

INTRODUCTION:

Water is one of the most important liquids used in modern micro and nanoelectronics technology. Authors [1, 2] have shown that both the electrophysical and physico-biological properties of the resulting aqueous solutions vary significantly depending on the initial water structuring, that is, the water interparticle bond energy. This paper discusses one possible method for monitoring the properties of water. Today, there are the following basic ideas about the structure of water as a partially self-organizing system with a dipole as an elementary structural element: (1) in addition to neutral dipole water molecules, water also contains the OH^- and H^+ ions that are products of the water dissociation; (2) water contains water molecules that are linearly associated with hydrogen bonds, and the closed (by the ring principle) structural organization of water is not excluded at that; (3) according to [3, 4], water forms three-dimensional nanoclusters. Each nanocluster can contain from 100 to 500, and even up to 910 water molecules. The nanocluster size is estimated to be equal to units of nanometers. The basis for the cluster construction is a tetragonal cell, at the vertices of which water

molecules linked by the hydrogen bonds are located. However, the question still remains to be clarified: which part of the total number of water molecules is included in these nanoclusters, and which part remains "free" in the form of H_2O dipoles.

Note that even in pure water, OH^- anions and H^+ cations are formed as a result of the dissociation process. The hydration of these ions (i.e. an attachment of water molecules to ions) by the ion – dipole interaction mechanism is inevitable. It is clear that the specific values of the determined bond energies should differ for all these varieties of nanostructured formations.

EXPERIMENT:

In this work, we recorded loss tangent (D) in the frequency range from 1 to 10^3 kHz. The loss tangent was registered at the water temperature of 20 and 50° C. The acidity value of deionized water was regulated by hydrochloric acid, and was recorded at 20° C with an accuracy of ±0.05 pH units. Fig. 1 shows a capacitor device used as a sensor to register frequency dependence of D.
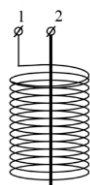

Figure 1. Sensor design for recording the loss tangent.

The outer spiral capacitor plate (1) was made of 15 turns of 1 mm platinum wire; the coil diameter was 10 mm. The second capacitor plate was made as a 1 mm platinum rod (2). The sensor length was 3 cm. This design provides a high degree of water availability in three coordinates both inwards and outwards of the sensor.

Electrodes of two types were used in these sensors. The first type electrode is the platinum electrode directly in contact with the water ("open" sensor, OS) and the second one is the platinum electrode electrically insulated from water by a dielectric layer with its own D of order 0.001 ("closed" sensor, CS).

The equivalent circuit of the "closed" type sensor is a capacitance formed by high-quality dielectric layers deposited on metal electrodes. These electrically isolated electrodes create the $\sim 10^{-6}$ V/cm electric field strength in the water under study. This weak alternating electric field probes the properties of the unperturbed layer of water.

The equivalent circuit of the "open" type sensor consists of two capacitances created by the Gouy-Helmholtz electric double layer (highly conductive layer) formed by structured water in the interelectrode space and the double electric layer capacitance at the contact of the second electrode of the small area. The distinctive feature of this two-electrode sensor of the "open" type is a sharp asymmetry in the electrode areas of approximately 1:100 [5, 6]. The smaller electrode allows data on the properties of nanostructured formations deformed by the double electric layer to be recorded. The electric field strength in the electric double layer reaches values of 10^5-10^6 V/cm. This field strength is often sufficient to break the bonds between the elements of

nanostructured formations. Therefore, the data obtained from sensors of the "open" and "closed" types are essentially complementary to each other.

RESULTS AND DISCUSSION:

Fig. 2 shows a loss tangent dispersion for water of different acidity when using the open type sensor. As can be seen from the figure, in the frequency range studied, the numerical values of the loss tangent are much greater than unity. This means that none of the options recommended by the standards [7] and related to the determination of the properties of liquids by resonance methods is applicable. In this case, measurement methods using bridges and RC dividers as well as immitance meters can be successfully used. The latter was just used in this work.

Referring to Fig. 2, the loss tangent dispersion has a pronounced extremum. At pH = 6.3, the loss tangent maximum equal to 35 is observed at the frequency of ~500 Hz. With the increase in acidity (pH = 4), the loss tangent equal to 55 is observed at the frequency of $\sim 5 \cdot 10^3$ Hz. A change in acidity by 2.3 units leads to the shift in the position of the loss tangent maximum along the frequency axis by an order of magnitude at that. The bandwidth defined at 0.707 of the maximum value is equal to $1.4 \cdot 10^3$ Hz for water with pH = 6.3 and $9 \cdot 10^3$ Hz for water with pH = 4.

Fig. 3 shows loss tangent dispersion for water of different acidity when using the closed type sensor. The numerical values of the loss tangent are two orders of magnitude smaller than in the case of using open type sensor as seen from the comparison of Figs. 2 and 3.
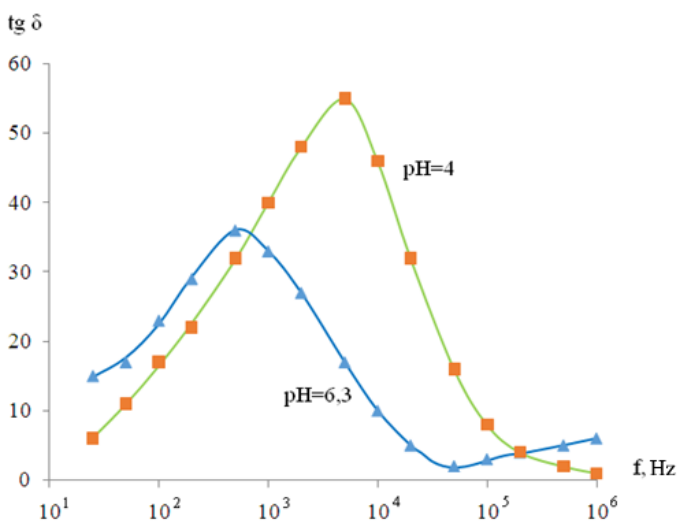

Figure 2. Loss tangent dispersion for water of different acidity when using an open type sensor.
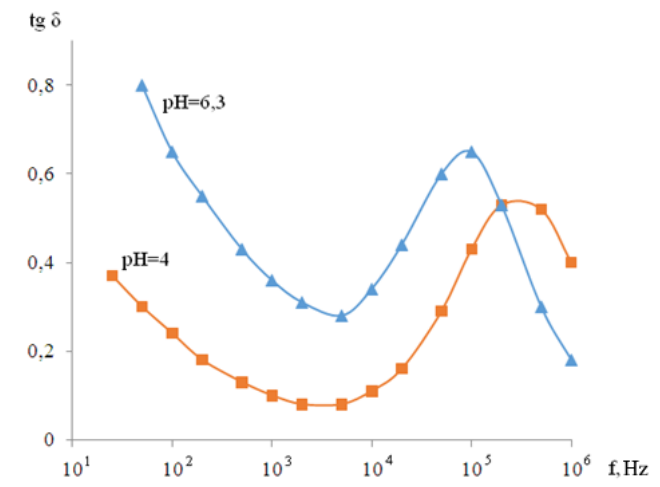
Figure 3. Loss tangent dispersion for water of different acidity when using an open type sensor.

The dispersion of the loss tangent is also extreme. With pH = 6.3, the loss tangent maximum equal to 0.65 is observed at the frequency of ~10^5 Hz. With the increase in acidity (pH = 4), the loss tangent equal to 0.55 is observed at the frequency of $3 \cdot 10^5$ Hz. Moreover, a change in acidity by 2 units leads to a 3-fold change in the frequency of the loss tangent maximum on the frequency axis. The bandwidth is $1.5 \cdot 10^5$ Hz for water with pH = 6.3 and $6 \cdot 10^5$ Hz for water with pH = 4.

In general, the behavior of the curve in Fig. 3 corresponds to the well-known dispersion of the loss tangent when registering the properties of polar dielectric liquids (oils). This behavior of the loss tangent for H_2O was unexpected: deionized water, and especially its solutions with hydrochloric acid, is not a dielectric.

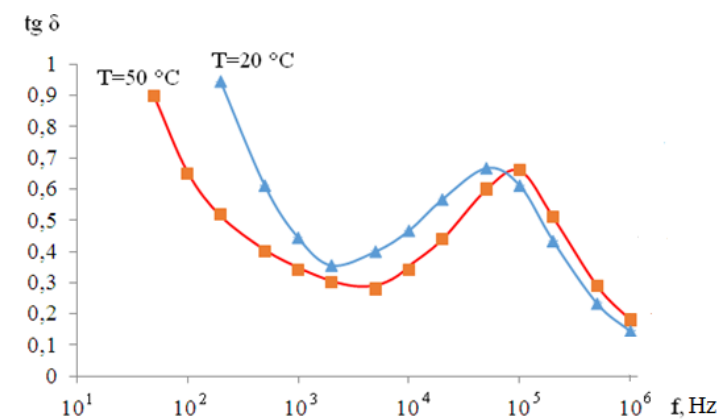Figure 4 shows the loss tangent dispersion for deionized water at pH = 6.3 obtained at 20 and 50 °C.

Figure 4. Loss tangent dispersion for deionized water at pH = 6.3 with the closed type sensor use.

As can be seen from Fig. 4, as the temperature rises, a shift in the maximum of the tangent of the loss angle is observed from about $7 \cdot 10^4$ Hz to 10^5 Hz. This shift is also accompanied by bandwidth broadening. In the frequency range up to 200 Hz the loss tangent decreases significantly with increasing temperature. At the frequency of 200 Hz this change is twofold and increases with decreasing frequency. The change in the loss tangent in the region of the maximum is insignificant with increasing temperature. When the temperature rises from 20 to 50 °C, it increases by about 10 - 20%. With further increase in the frequency, the loss tangent dispersions are almost parallel to each other.

The results of our experimental data can be analyzed as follows. Water is a polar liquid with a large dipole moment of the basic structural unit, that is, H_2O molecule. For polar liquids, one of the determining factors of their properties is the presence of a relaxation polarization effect. In accordance with the general thermodynamic concepts, the change in the free activation energy of the relaxation process ΔF (for example, for the polarization process of the particle ensemble) is associated with the relaxation time τ of this process by the following relation:[8]

$$\tau = \frac{hN}{RT} e^{\frac{\Delta F}{RT}}, \qquad (1)$$

where h is the Planck constant, T is the absolute temperature, R is the gas constant, N is the Avogadro number.

Since R is the product of the Boltzmann constant k on N, the Eq. (1) is converted into the following form:

$$\frac{1}{\tau} = f_{max} = \frac{kT}{h} e^{-\frac{E_a}{kT}}, \qquad (2)$$

where E_a is the free energy of the relaxation process in terms of a single particle, f_{max} is the frequency corresponding to the maximum values in the resonance D.

The maximum D in the dependences $D (f)$ corresponds to relaxation processes associated with intermolecular bonds. The energy of these bonds is reflected in the Eq. (2).

In accordance with formulas 2 and 3, we constructed the dependence of E_a on f_{max} at 300 K (Figure 5).
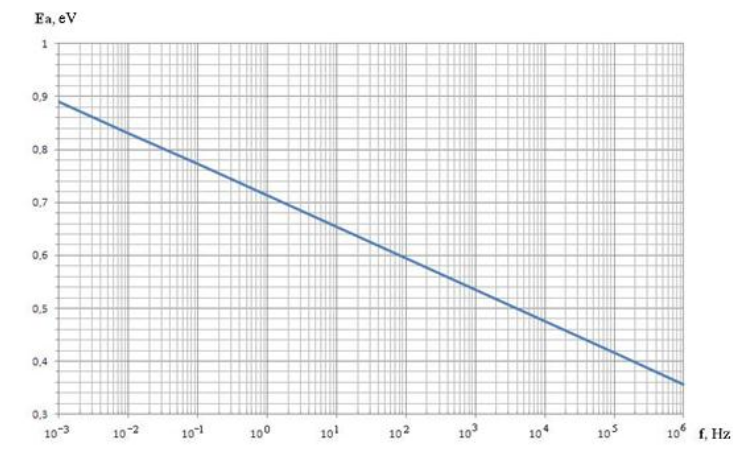

Figure 5. E_a versus f_{max} at 300 K

This dependence is very convenient for practical use in order to quickly estimate the activation energy if the f_{max} value is known (no routine calculations need to be repeated). Moreover, it is clearly seen that the frequency f_{max} shift by a factor of two (for example, from 100 kHz to 200 kHz) changes the value of E_a from 0.54 eV to 0.52 eV, i.e. about 4 %. This indicates the high resolution of the method for determining E_a by f_{max} value.

Inevitably there is a set of bond variations in water for the value of E_a. The more bond variations are present, the wider the bandwidth on curve the loss tangent dispersion in the region of the maximum.

In our opinion, the expansion of the bandwidth and the shift of the loss tangent maximum to the high frequency region with increasing acidity are due to two reasons: (1) a change in the binding energy of any type of interaction between the components of the aqueous solution, where each type of interaction has its own characteristic frequency, and, therefore, energy; (2) a decrease in total the binding energy between the pre-existing components of the solution.

It is impossible to identify whether the loss tangent maxima in Figs. 2–4 are responsible for the association of the OH^- anion or H^+ cation with the structural elements of water. However, it is obvious that the energies E_a and, consequently, the frequencies f_{max} for these two variants of associations should be different. The energy E_a for the association with the participation of the H^+ cation should be greater than the energy E_a for the association with the participation of the OH^- anion.

The following speaks in favor of associations with the participation of the H^+ cation. With an increase in the acidity of the solution by the introduction of hydrochloric acid, the concentration of associates with the participation of H^+ cations increases. In this case, associates with the participation of Cl^- anions should have appeared. However, in the frequency range used, additional maxima of the loss tangent did not appear.

When pH is changed to 4 (Fig. 2), the position of the loss tangent maximum at the frequency of 8 kHz indicates that the binding energy between the particles decreases from 0.6 to 0.55 eV compared to pure water. For this reason, it becomes possible to monitor the acidity of, for example, washing water in the process using only an immittance meter without specialized equipment for acidity recording.

An increase in the numerical value of the loss tangent to 5.5 with a change in the acidity of water from pH = 6.3 to pH = 4 is associated with an increase in the contribution of Faraday currents during the cathodic polarization of open type sensor electrodes. This means that the intensity of the process of cathodic reduction of hydrogen from H^+ ions increases, since with a decrease in the numerical value of pH per unit, the concentration of H^+ ions increases by a factor of 10, therefore the Faraday current, which causes this process, also increases.

When using a closed-type sensor (Fig. 3), Faraday currents are excluded, therefore in general the values of the loss tangent are recorded being tens of times smaller than for an open-type sensor. In addition, a closed-type sensor probes mainly the properties of the liquid volume.

The decrease in the numerical value of the loss tangent in the frequency range to 100 kHz with increasing acidity is due to the fact that the specific volume resistance of water decreases (in a water layer located in the interelectrode space of the sensor). In this case, the flow of alternating current through a lower resistance leads to less active power, and, consequently, to a smaller value of the loss tangent. The f_{max} value equal to 100 kHz at pH = 6.3 and f_{max} equal to $6 \cdot 10^5$ Hz at pH = 4 characterizes the decrease in the energy of interparticle bonds with the increase in acidity.

Thus, a closed-type sensor, recording mainly the volumetric properties of water, allows at any frequency not exceeding 10^5 Hz to uniquely determine the acidity of the

solution, i.e. solve the inverse problem. From formula 2 it also follows that when the position of the loss tangent maximum is shifted to the region of higher frequencies, we can speak of a decrease in the value of E_a at a fixed temperature.

These behavior patterns of the loss tangent are clearly visible in Figs. 3 and 4. It should be noted that the closed sensor electrodes in combination with a fluoroplastic coating essentially serve to create an electric polarizing field in the volume of the water studied. Electrode reactions associated with the passage of an electric current through the metal-dielectric-water interface (Faraday currents) during registration of the dispersion of the loss tangent and other immitance characteristics do not affect the results – they simply do not exist. At the same time, both polarization and ion transport processes occur in the volume of water and its solutions. It is advisable to present the equivalent electrical circuit for water in the form of R_e and C_e elements connected in parallel at that. At the same time, a thin fluoroplastic layer covering platinum in a closed-type sensor forms high-Q capacitors C_{01} and C_{02}, the capacitance numerical values of which differ in accordance with the difference between the areas of the electrodes 1 and 2 (Fig. 1).

As already noted, the dependences shown in Fig. 4 provide information on the bulk properties of water. They indicate the following (not taking into account electrode reactions). (1) The degree of water dissociation increases with increasing temperature, resulting in the increase in the conductivity of the solution and the decrease in active losses. To a certain extent, the behavior of the loss tangent observed with increasing temperature is similar to the behavior of the loss tangent with increasing acidity: the value of the loss tangent decreases in both cases. (2) The f_{max} shift to the region of higher frequencies (Fig. 5) can be explained by the weakening of the interparticle bond energy with the simultaneous expansion of the corresponding passband (similar to the known temperature smearing of absorption bands in optics).

Figure 6 shows as an example the loss tangent versus time during continuous monitoring of water with pH = 6.3 using an open type sensor. The use of the open type sensor, as noted above, inevitably leads to the implementation of redox processes and the accumulation of electrolysis products not only in the electrode layers, but also in the solution volume. Electrolysis products inevitably change the values of the recorded loss tangent, since the solution constantly changes its physical, electrochemical and other properties during the measurement process.
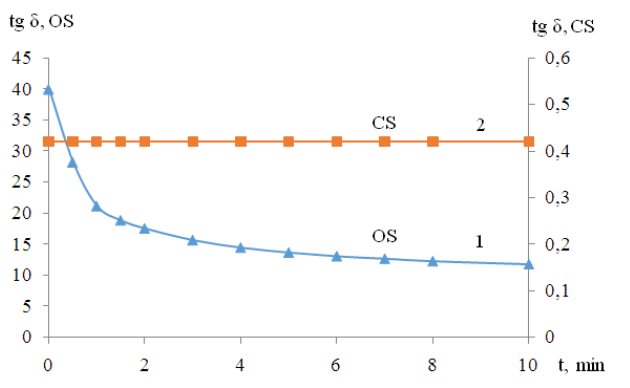

Figure 6. Time dependence of the loss tangent in the process of continuous monitoring of immitance characteristics.

Figure 6 allows us to draw the following practically important conclusions: in order to obtain reliable information on the properties of water and its solutions, it is necessary to measure water parameters (for example, resistivity) with pulses of a few seconds duration, after which the measurements should be stopped to avoid contamination of the studied solutions with electrolysis products.

CONCLUSIONS

1. Open type sensors are basically not suitable for monitoring the properties of liquids used in micro- and nanoelectronics. The open type sensor is suitable only for monitoring liquids and deionized water by sampling and their subsequent disposal. Such sensors should not be placed in highways supplying liquids to specific installations.

2. When using a closed-type sensor, there is no change in sensor readings over time. The closed-type sensor, the electrodes of which are isolated from direct contact with the solution (liquid) studied, is preferably used in technological processes of micro- and nanoelectronics, in the study of physical and biological processes, in pharmaceuticals.

3. The position of the loss tangent maximum on the frequency axis makes it possible to determine the value of the activation energy of the process under study with a high degree of certainty.

4. Monitoring the loss tangent at fixed frequencies allows the acidity of solutions (pH value) to be simultaneously controlled without the use of specialized instruments for acidity studying (pH meters, ionomers).

ACKNOWLEDGMENTS

REFERENCES

1. S.V. Zenin, PhD. Thesis, Moscow State University, 1999.
2. A.K. Lyaschenko, V.S. Dunyashev, *Water: Structure, State, Solvation. Achievements of Recent Years,* (Nauka Publishing House, Moscow, 2003), p. 107.
3. D. K. Lonsdale, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, **247** (1251), 424-434 (1958).
4. M. Kleman, O.D. Lavrentovich, *Fundamentals of Physics of Partially Ordered Media: Liquid Crystals, Colloids, Fractal Structures, Polymers and Biological Objects,* (Physmatlit Publisher, Moscow, Russia, 2007), p 680.
5. J.Yu. Ahadov, *Handbook of Dielectric Properties of Pure Liquids*, (Standards Publishing, Moscow, Russia, 1972), p 412.
6. A.R.von Hippel, *Dielectrics and Waves* (John Wiley & Sons, New York, 1954) p.438.
7. IEC 60247 Ed. 3.0 b:2004, Insulating liquids - Measurement of relative permittivity, dielectric dissipation factor (tan d) and d.c. resistivity. Available at: https://webstore.ansi.org/standards/iec/iec60247ed2004