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Structural-Energy States of Water and Aqueous Solutions under External Influences

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Abstract. Methods are proposed for evaluating changes in the structure of water or aqueous electrolyte solutions under the influence of temperature, magnetic field and surface material by means of determining the electrical capacity of the liquid and the quality factor of the anti-resonant circuit in the frequency range from 1 kHz to 3000 kHz. The condenser plates in different types of electrochemical cells are placed one in front of the other, each at a distance of more than 5 cm, or relative to each other in parallel planes, or in one plane in which case the liquid is located on the condenser plates. The current density on the plates in various cells ranged from 10 to 100 nA/cm^2. When measuring the electrical capacity, the voltage applied to the plates was reduced in proportion to the increase in the frequency of oscillator. The apparatus allows us to increase the dynamic range of the signal change from an electrochemical cell, reduce the impact of measurements on the structure of liquids, and also evaluate the direction and extent of changes in the structure of water and aqueous solutions under various external influences. Criteria are proposed for evaluating the structure of fluids.

INTRODUCTION

It is well-known that water molecules are in continuous thermal movement and it is possible to speak about a particular position of certain dipoles of water relative to each other in a time interval of less than 10^{-13}seconds. Using currently available methods this is impossible. On the other hand, the concept of structure of water and aqueous systems generally includes not only the determination of the coordinates of all its molecules, but also knowledge of the laws and principles of their interaction [1].

The presence of hydrogen bonds in water and hydrated ions in aqueous solutions is already a manifestation of the structure of water and aqueous solutions [2]. The modern view of the structure of water is that there is a more complex structural organization in water, a three-dimensional network formed by molecules, connected by hydrogen bonds. It has been shown that individual water molecules are combined in associates (clusters) distributed in the "continuum" liquid phase [3-5]. The size of clusters in water and aqueous solutions depends on the concentration and composition of the solutions and the temperature in liquids [6,7]. Since the mobility of water dipoles is determined by the nature of their relations with each other, according to changes in the mobility of water dipoles under various influences it is possible to make conclusions about the changes in the relations between them and, consequently, about changes in the structures of water and aqueous solutions.

It is well-known that water and aqueous systems have a high sensitivity to external influences [8]. Therefore, to study them adequately we need non-destructive methods of research in a wide range of frequencies – from 1 to 10^{14} Hz. Thus, assessment of the structure of water and aqueous systems in volves the determination of permittivity at different frequencies (the method of dielectrics) [9,10]. This approach allows us to obtain data on molecular dynamics and structural transformations of liquid systems during changes in their composition and temperature. Therefore, the processes occurring in water and aqueous systems in the range from $10^4$to 10^6Hz are poorly studied [10].

There is a well-known method for determining the dielectric parameters of water and its solutions during which the tested liquids in an electrochemical cell are sequentially presented into the various solenoid coils, and measurements are taken in the frequency range above 10 kHz [10]. The value of the intensity of the vortex

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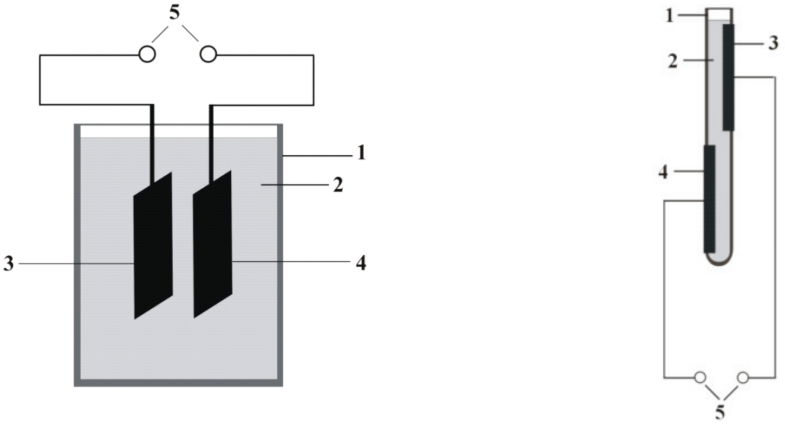
electric field inside the cell varies from 5 to300 mcV/cm. This changes by 60-fold the magnitude of reactive current in one liquid during the process of measurement, which can lead to various uncontrollable changes in the structure of the liquid, thereby generating some inconvenience during the research.

The aim of the study is to develop methods to evaluate the structure of water and aqueous solutions in an electrochemical cell under various influences, including the effects of temperature, magnetic field, surface material in the near-wall layer, and other factors.

MATERIALS AND METHODS OF STUDY

Distilled water and also aqueous solutions of chlorides of sodium, potassium, calcium and magnesium in concentrations ranging from $1\cdot10^{-6}$ M to 1.0 M were used in the experiments. The fluid was placed in the measuring cell of one of the species comprising a container of dielectric material and condenser plates of non-magnetic material without direct contact with the liquid.

We used the measuring cells shown in Fig. 1 for the evaluation of structural changes in aqueous solutions in the near-wall layer.



(a)

(b)

FUGURE 1. Measuring cells with a different placement of electrodes.(a) - two flat electrodes of nonmagnetic stainless steel placed in a glass container;(b)– condenser plates on the measuring cell are placed relative to each other in parallel planes and do not have surfaces situated opposite one another. 1 –the container for liquid, 2 –the tested liquid, 3 and 4 –condenser plates, 5 – terminals for connecting the signal from a generator of sinusoidal oscillations

The voltage to the measuring cells is supplied by a generator of sinusoidal oscillations AFG 2025, the signal from the cells is amplified by an instrumentation amplifier on the basis of an AD8067 microchip and measured on an oscilloscope PDS5022S. The magnitude of inductance is measured with an instrument LCR-9063.

The voltage generator of sinusoidal vibrations applied to the measuring cell is reduced inversely proportional to its frequency. Firstly, it provides a constant (reference) amount of current through the measuring cell at different frequencies of the generator in case of connection of the reference condenser cell between the condenser plates. Secondly, the dependence of the current density through the measuring cell decreases because of its frequency, which reduces the effect of the magnitude of the reactive current on the structure of liquids.

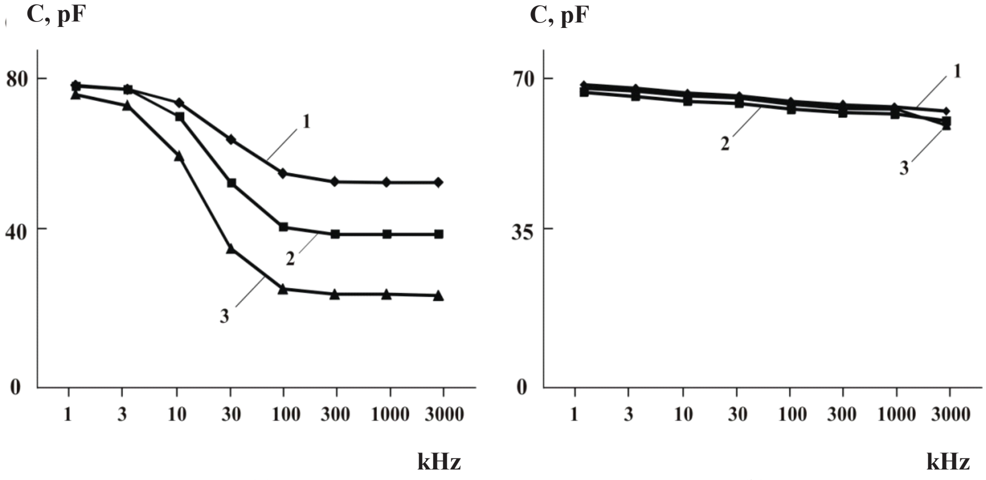
The installation allows us to determine the electrical capacity of fluids in the measuring cell of one of the species (by the change in the reactive current magnitude through them and after calculating the electrical capacity of the measuring cell without liquid from the total size of the condenser), and the quality of the anti-resonant circuit formed by variable inductance and the condenser in liquids located between its insulated plates. When measuring the electrical capacity of fluids, the current frequency linked up with the condenser plates varies from 1 to 3000 kHz. When measuring the quality factor of the anti-resonant circuit, the inductance values are set at a level which allows us to obtain the resonant frequency of 10 kHz, 30 kHz, 100 kHz, 300 kHz or 1000 kHz.

The minimum values of the electric field voltage inside the measurement cell (from 15 to 75 mcV/cm depending on the distance between the condenser plates in various types of measuring cells) and current density on the plates of the condenser (from 10 to 100 nA/cm^2 depending on the area of the condenser plates in various types of measuring cells) are used for the evaluation ofchanges inthe structure of water and aqueous solutions under various influences.

EXPERIMENTAL RESULTS AND DISCUSSION

In earlier studies we evaluated the influence of the distance between the electrodes and, respectively, the electric field on the dynamic of the electrical capacity and quality factor of the anti-resonant circuit with theaid of a measuring cell (Fig. 1a). It was discovered that the electrical capacity of distilled water at a distance between the condenser plates of 2 cm with an increase in the frequency of the reactive current of 1 to 3000 kHz decreased by 66% (Fig. 2a) from the initial level. With an increasing frequency from 300 kHz to 3000 kHz, this rate remained practically unchanged. With an increase in the distance between the condenser plates to 5 and 10 cm, the electrical capacity in the case of an increase in frequency from 1 kHz to 3000 kHz reduced to 48% and 27% respectively.

The quantity of the quality factor of the oscillation circuit with an increase in the distance between the condenser plates from 2 to 10 cm at frequencies of 30 kHz, 100 kHz and 300 kHz reduced to 39%, 64% and 78% respectively. The most significant reduction in the quality factor was observed at a lesser resonant frequency.



(a) (b)

FIGURE 2. The dependence of the electrical capacity (C pF) of distilled water (a) and $1 \cdot 10^{-2}$ M sodium chloride solution (b) on the frequency of the reactive current at different distances between the condenser plates: 1– 2 cm, 2– 5 cm, 3– 10 cm

The electrical capacity of $1 \cdot 10^{-2}$M sodium chloride at a distance between the condenser plates of 2 cm with an increase in the frequency of the reactive current from 1 to 3000 kHz decreases less significantly in comparison with that for distilled water (up to 91% of the initial level). When increasing the distance between the condenser plates to 5 and 10 cm, the electrical capacity decreases to 89% and 87% respectively as the frequency increases. When the distance between the condenser plates is 2 cm, the quality factor of the anti-resonant circuit, in comparison with the distilled water, repeatedly increases, and with an increase in the distance between the condenser plates from 2 to 10 cm at frequencies of 30 kHz, 100 kHz and 300 kHz, the quality factor reduces to 97%, 78% and 50% respectively. The decrease in the quality factor is more significant at a higher resonant frequency.

An analysis of the experimental data shows that for the detection of structural changes in water and aqueous solutions, firstly, it is advisable to use a measuring cell in which the condenser plates are parallel to each other and at a distance of more than 5 cm from each other (Fig. 1a), or placed relative to each other in parallel planes (Fig. 1b).

Below we see the data obtained with the help of variant (b) (Fig. 1) of the measuring cell [11]. In this case, at a temperature of 20 °C with an increase in the reactive current frequency from 1 to 100 kHz, the electrical capacity of distilled water reduces (Fig. 3a) by several times (up to 7% of the initial level).

With further increase in the frequency to 3000 kHz, there is virtually no reduction in electrical capacity. It should be noted that even at a frequency of 3 kHz, the electrical capacity decreased to 42% in comparison with a frequency of 1 kHz.

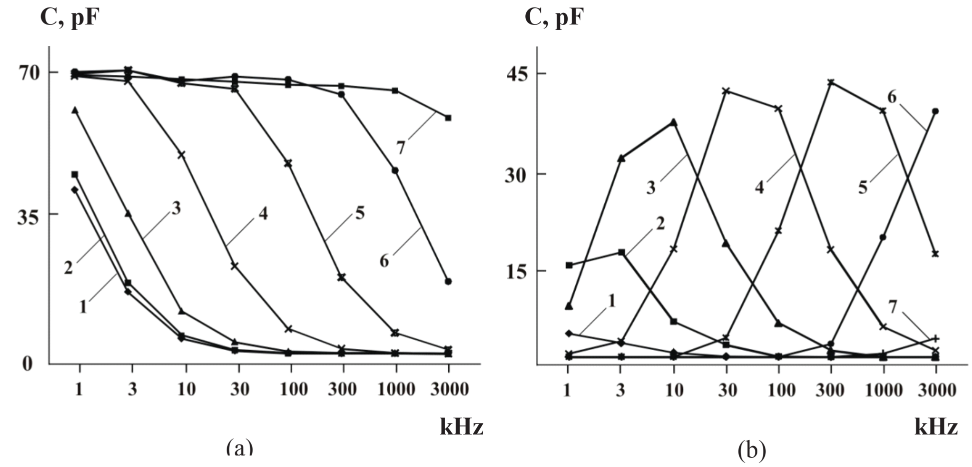


FIGURE 3. (a) – dependency of the electrical capacity of distilled water and aqueous solutions on the frequency of the reactive current:
1–distilled water, 2,3,4,5,6 and 7– sodium chloride salt solutions at concentrations of $1 \cdot 10^{-6}$M, $1 \cdot 10^{-5}$M, $1 \cdot 10^{-4}$M, $1 \cdot 10^{-3}$M, $1 \cdot 10^{-2}$M and $1 \cdot 10^{-1}$M respectively. (b) – the relative change in electrical capacity at different frequencies of reactive current and concentrations of solution NaCl: 1 – $1 \cdot 10^{-6}$ M solution in comparison with distilled water; 2 – $1 \cdot 10^{-5}$M solution in comparison with $1 \cdot 10^{-6}$ M solution; 3 – $1 \cdot 10^{-4}$ M solution in comparison with$1 \cdot 10^{-5}$ M solution; 4 – $1 \cdot 10^{-3}$ M solution in comparison with $1 \cdot 10^{-4}$M solution; 5 – $1 \cdot 10^{-2}$ M solution in comparison with$1 \cdot 10^{3}$M solution, 6 – $1 \cdot 10^{-1}$ M solution in comparison with$1 \cdot 10^{-2}$M solution, 7 – $1.5 \cdot 10^{-1}$ M solution in comparison with$1 \cdot 10^{-1}$M solution

Taking into account the data from the literature, our calculations and the results obtained earlier [3,4, 6,11,12-14], one can assume that molecules of distilled water are firmly linked between each other in the associates. This considerably reduces the mobility of the dipoles of water already at a low frequency of the reactive current (1-10) kHz.

When using an aqueous solution of NaCl with a concentration of $1 \cdot 10^{-6}$M, an increase in its electrical capacity (as compared to the electrical capacity of distilled water) is observed at frequencies of 1, 3, 10 and 30 kHz with its maximum at 1 kHz (Fig. 3b). With a concentration of $1 \cdot 10^{-5}$ M the electrical capacity of the solution (as compared to $1 \cdot 10^{-6}$ M of NaCl solution) maximally increases at a frequency of 3 kHz, and with a concentration of 10^{-4}M (as compared to 10^{-5} M solution), the maximum increase in this parameter is observed at a frequency of 10 kHz ($P < 0.001$). With a further increase in the concentration of the solution to $1 \cdot 10^{-3}$M, $1 \cdot 10^{-2}$M and up to$1 \cdot 10^{-1}$M, the maximum relative increase in electrical capacity occurs at a frequency of 30 kHz, 300 kHz and 3000 kHz respectively. With the maximum concentration of NaCl solution (0.15M), the decrease in the distilled water electrical capacity in the case of an increase in frequency from 1 to 3000 kHz is considered to be only 10%. Thus, when the concentration of salt solutions increases there isa sequential increase intheir electrical capacity as well, first at low and then at higher frequencies.

The increase in NaCl solution electrical capacity starts at small concentrations in comparison with that in distilled water. This indicates that, in addition to quantitative changes, a change occurs in the structure of the solution, which leads to an increase in the number of dipoles oscillating at frequencies of (1-3000) kHz. Further, it can be assumed that the dynamics of the electrical capacity in the case of increasing concentrations of NaCl solutions reflects: 1) water molecule changes in the structure of associates, in particular in the ratios of dimensions and the number of clusters; 2) peculiarities of the processes of ion hydration; 3) the dynamics of the interaction between the associates of water molecules and hydrate formations.

These assumptions are corroborated by our earlier research and studies by other authors [4,12,13-16], which show that the clusters can be characterized by oscillations in a frequency range from 1 to 10^3 kHz. Moreover, compared with distilled water, in NaCl solution at a concentration of $1 \cdot 10^{-3}$ M, the content of larger clusters increases and the content of smaller clusters decreases. An increase in the concentration of the solution to 0.1 M and more leads to an increase in the content of smaller clusters. It should be noted that similar results of electrical capacity dynamics have been observed in our earlier studies carried out with solutions of NaCl, KCl, $MgCl_2$ and $CaCl_2$ [12,13], in which it has also been shown that salt solutions differ significantly from each otherin terms of the amount of electrical capacity.

Furthermore, there are the results of studies on the heating and cooling of water and aqueous solutions, the influence of the magnetic field, and assessing the effects of surface material in the near-wall layer [13,11-14].

Based on the results obtained by measuring the electrical capacity and quality factor of the anti-resonant circuit, it was established that the mobility of the water dipoles in water and aqueous solutions varies in multidirectional ways at different frequencies under various influences. These changes are likely to depend on, for example, the ratio of free and associated (in clusters) water molecules, hydrate formations and interaction between them, and also on the concentration of dissolved gases and temperature.

Thus, at a temperature of 20°C the electrical capacity of distilled water in the case of an increase in the frequency of the reactive current from 1 to 3000 kHz repeatedly reduces. The electrical capacity of aqueous solutions of NaCl, KCl, $CaCl_2$and $MgCl_2$ multiplies firstly at low (1-30 kHz) and then at higher frequencies (100-3000 kHz)with an increase in their concentrations up to $1^{.}10^{-1}$M and increase in the frequency of the reactive current. The solutions differ from each other according to the severity of the changes of this parameter

When increasing the concentration of NaCl aqueous solution from $1^{.}10^{-6}$ M to $1^{.}10^{-2}$M, the quality factor of the anti-resonant circuit at a resonant frequency of 10 kHz increases many times over the entire range of increasing concentrations of NaCl solution. Thus for frequencies of 30 and 100 kHz, the quality factor reduces at first, but then repeatedly increases in the case of an increase in NaCl concentration of more than$1^{.}10^{-4}$ M at a frequency of 30 kHz and over$1^{.}10^{-3}$M at a frequency of 100 kHz.

When heating fluids at temperatures up to 40°C, the electrical capacity of distilled water increases in the case of frequencies of 10 kHz and 30 kHz, and the electrical capacity of $1^{.}10^{-4}$ M solutions of NaCl, KCl, $MgCl_2$ and $CaCl_2$ increases at a higher frequency – 300kHz. Thus, the quality factor of the anti-resonant circuit in experiments with distilled water decreases in the case of resonant frequencies of 30 kHz and 100 kHz, but increases in experiments with $1^{.}10^{-4}$M solutions of NaCl, KCl, $MgCl_2$ and $CaCl_2$.

The reduction in electrical capacity at low frequencies (1-10) kHz and the increase of the quality factor at higher frequencies occur upon activation of distilled water by heating it from 20°C to 60°C, followed by cooling to 20°C without access to air, upon its magnetic treatment and temperature decreasing to 10°C.Inverse dynamics of these parameters are observed while heating distilled water.

When increasing the length (L) to the glass surface from 5000 microns to 16 micron sand with a concentration of aqueous solutions of NaCl, KCl from 0.01 M to 1.0 M in the near-wall thin layer of liquid, the electrical capacity at frequencies of 1000 and 3000 kHz and the quality factor of the anti-resonant circuit at frequency of 30 kHz repeatedly reduce. These changes depend on the concentrations of the solutions, the natureof the substance and the material of the surface.

Taking into account the data obtained, a coefficient *Kg* [15] was developed which characterizes the gradient of change in the quality factor of the anti-resonant circuit according to the formula:

$$K_g = 100\left(\frac{Q_i - Q_{i+1}}{H_i - H_{i+1}}\right),$$

where *Kg* is the coefficient, defined as the ratio of change in the quality factor of the anti-resonant circuit when changing the depth of the liquid layer to the amount of change in the depth of the liquid layer (rel. unit). H_i, H_{i+1}–the distance between the two depths of the liquid layer (microns), and $Q_i u$ Q_{i+1} –quality factors of the anti-resonant circuit at these depths of the liquid layer.

It was found that while using 0.15 M sodium chloride and potassium chloride solutions the value of this coefficient was maximal in the range of 50-200 microns (Fig. 4).

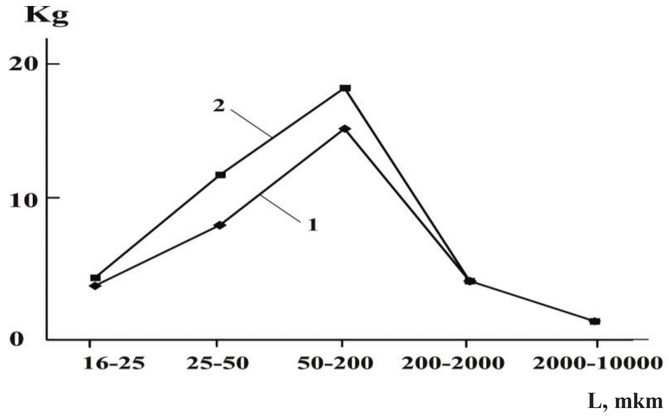


FIGURE 4. Evaluation of the structure of solutions in the boundary (near-wall) layer using the coefficient *Kg*. 1– 0.15 M NaCl solution; 2– 0.15M KCl solution

This allows us to propose that in the case of a decrease in the depth of the liquid layer from 200 to 50 microns in the structure of the solutions, the most significant changes occur, accompanied by a decrease in the mobility of water dipoles in a resonant mode. To a lesser extent, these changes are preserved in the case of a decrease in the depth of the liquid layer up to 16 microns and increase up to 2000 microns.

The results obtained in the experimental studies can be and already are used partially in medical practice, construction and industrial materials science, and in other areas [7,13,15,17].

CONCLUSIONS

1. The approach developed to the indirect evaluation ofthe structure of waterand aqueous solutions, measuring cells and a method for measuring electrical parameters make it possible to record changes in the structural and energy state of water and aqueous solutions under various influences, including changes in temperature, magnetic field, the influence of surface material in the near-wall layer and other factors.
2. An increase (decrease) in electrical capacity and the quality factor of the anti-resonant circuit under various influences reflect an increase (decrease) in the mobility of water dipoles in an alternating electric field and, obviously, can be considered as the evidence of decrease (increase) in the degree of structuring of water and aqueous solutions.

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