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Manifestation of the Widom line in microwave measurements of sorbents moistened with hydrogen peroxide

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For deeply supercooled bulk water, known are anomalies of thermodynamic quantities near the Widom line, the locus of increased fluctuations of entropy and density. In this work, we measured the reflected power of microwave radiation at the frequency of 18 GHz from a silicate sorbent sample moistened with a hydrogen peroxide solution. In the experiment, we observed variations in the recorded reflected radiation power in the range of -46 to -47°C determined by structural changes in the liquid. Thus, it is shown that fluctuations of water parameters near the Widom line manifest themselves in changes not only in thermodynamic, but also in electrophysical quantities.

Keywords: Widom line, second critical point, nanoporous materials, hydrogen peroxide, microwaves.

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At present, 75 anomalies of bulk water are known; among them, the most pronounced ones are associated with supercooled water. As an example we can consider a recent discovery of the second critical point (the liquid–liquid phase transition) taking place at the temperature of -60°C and pressure of ~ 100 MPa [1–3]. The Widom line, the locus of increased fluctuations of entropy and density, emanates from this point towards the single–phase region. At the pressure of 0.1 MPa, the Widom line temperature (T) is -45°C. Multiple experiments have demonstrated that in approaching the Widom line there occurred an anomalous increase in constant–pressure heat capacity C_p), isothermal compressibility, volume expansion coefficient, and in some other physical quantities. The Widom line existence was confirmed experimentally via scattering of a femtosecond X-ray laser radiation from micrometer–sized water droplets evaporating in vacuum [4]. All the anomalies may be explained in the framework of the distructural model of water consisting of LDL (low density water) clusters and HDL (high density water) clusters [1,3]. Contrary to previous models, this model implies continuous modification of cluster structures in the picosecond mode. The cluster concentrations and sizes depend on temperature. All the specific features of physical properties of liquid bulk water in the entire range of its existence are defined by the interaction between clusters of the two types. The cluster concentrations and sizes depend on temperature. All the specific features of physical properties of liquid bulk water in the entire range of its existence are defined by the interaction between clusters of the two types. HDL clusters dominate at temperatures higher than that at the Widom line; vice versa, the LDL cluster concentration increases with decreasing fluid temperature. However, there is yet a lack of relevant experimental data for negative temperatures because of the difficulty of obtaining deeply supercooled bulk metastable water. Moreover, we have to notice that there are no investigations of anomalies in electromagnetic characteristics of supercooled water near the Widom line. Obtaining this data could allow using well developed techniques for measuring electrophysical parameters of fluids.

To get deep supercooling of bulk water, many researchers used moistened nanoporous silicate sorbents. As shown in [5,6], characteristics of the major part of water in these sorbents are close to those of bulk water at temperatures reaching approximately -70°C. In addition, it is possible to retard water crystallization by adding to it salts or other water–soluble substances, which enables reaching even lower temperatures. In some cases, cold water of the solutions retains properties of the bulk supercooled water and its characteristic anomalies. For instance, recently there were discovered aqueous solutions of hydrazinium trifluoroacetate (N_2H_5TFA) that do not crystallize before reaching their glass transition point. On the droplets of this solution, an anomalous increase in C_p was observed which is characteristic of the behavior at the Widom line in the narrow temperature range near -87°C (under the atmospheric pressure) [7].

The goal of this work was to investigate variations in dielectric characteristics of cold solutions in passing the Widom line. Power (P) of the microwave radiation reflected from silicate sorbents moistened with solutions was measured. As the moistening solution, hydrogen peroxide (H_2O_2) was used. The H_2O_2–H_2O system possesses two eutectic points near $-(52-54)^{\circ}$C at the peroxide weight concentrations of 45 and 61% [8].

This is why it is easier in this case to cool a considerable amount of fluid to temperatures below -45°C.

The layout of the setup for measuring reflected power of microwave radiation is presented in Fig. 1. In the experiment, the chamber *1* temperature was linearly decreased from room temperature to -68°C. The measured

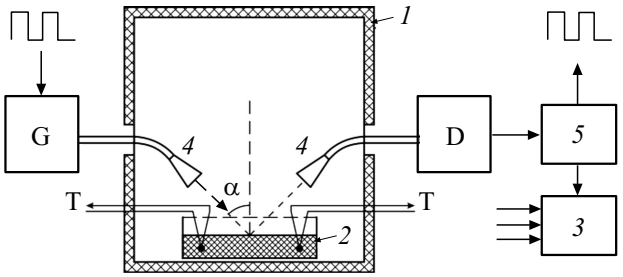

Figure 1. Layout of the setup for measuring the temperature dependence of the factor of reflection from the silica gel moistened with the solutions. *1* is the climate chamber ESPEC-SU, *2* is a metal cuvette with the sample, *3* is the data acquisition system, *4* are the horn antennas, *5* is the processing unit. G is the microwave radiation source, D is the detector.

sample in the form of moistened powder was placed in a flat–bottom metal cuvette *2*. The sample temperature was measured with three thermocouples (T) having the time constant of 0.5–1 s. The cuvette was sealed with a cover made from radiation–transparent film. The generator (G) radiation was directed to the sample with an 18 GHz pyramidal horn antenna *4* at angle α to the surface normal line at the horizontal polarization. Angle α was set to 45°. The distance between the antenna plane and sample surface was 10 cm. The antenna aperture size was 5×3 cm. The cuvette size (16×12 cm) was chosen so as to be larger than the antenna pattern spot on the sample surface. In the detection circuit comprising a crystalline detector (D), a synchronous demodulator *5* was used. For this purpose, the generator radiation was modulated by using a reference signal. The measured signals were recorded by an Agilent data acquisition system. Temperature was measured accurately to 1°C.

The presented technique implies determination of variations in radiation power reflected from a flat layer of moistened sorbent powder several millimeters thick. When the sample temperature changes in case phase transitions or variations in the dielectric permittivity occur, variations in the reflection factor are observed near the Widom line. To detect the anomalies, the $\partial P/\partial T$ derivative was found. The measurement rate was 2 counts per second, the sample temperature variation rate was 0.2–0.1°C/min. The ratio between the P and T increments was calculated for the time of 0.5 s.

In the experiments, a concentrated hydrogen peroxide (40%) was used; hydroperit was also dissolved which, being solved, decomposes into hydrogen peroxide and carbamide (with the peroxide content of 35% of the initial mass). As it turned out, the obtained results are easier interpretable if hydroperit is used. A special experiment on the solution thermometry showed that in the case of pure hydrogen peroxide two eutectic points were observed (below −52°C), as well as jumps at −29°C in the $\partial P/\partial T$ derivative curves in the range of sample heating. These peculiar features were not observed in the case of moistening the sorbent with the hydroperit solution.

The measurement results are shown in Figs. 2 and 3. In the samples, silica gel KCKG with the mean pore size of 8 nm was used; the sample was moistened with the hydroperit aqueous solution with the weight concentration in water of 32%. The expected weight concentration of H_2O_2 in the solution was ∼ 11.2%, that in the sample was ∼ 1.8%. Thickness of the layer of silica gel powder with particle size of ∼ 100 μm was 4–5 mm. The moistened silica gel skin–layer thickness calculated for the temperatures of −20 to −40°C based on the data on dielectric permittivity of deeply supercooled water [9] was 2–3 mm.

In calculating the derivative, its values were averaged in order to reduce the fluctuations and reveal the temperature ranges where fast variations in electrophysical characteristics

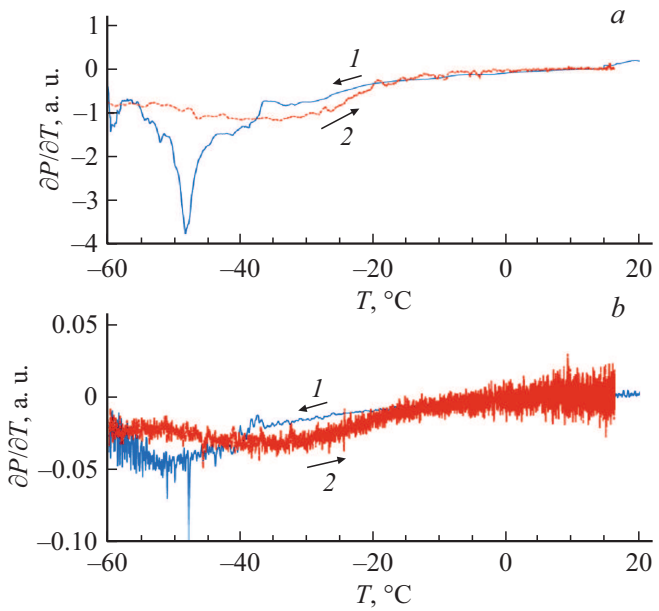

Figure 2. *a* presents the derivative of the reflected microwave radiation power versus temperature of the sample moistened with the hydroperit solution; the results were averaged over 1000 points. *b* presents a similar dependence for another sample after averaging over 500 points. Curve *1* corresponds to the cooling section, curve *2* is for the heating section. Arrows indicate the temperature change direction.

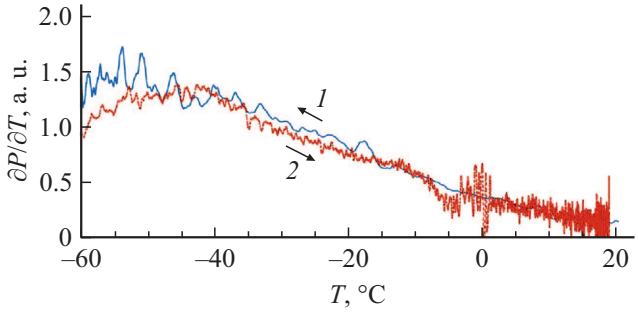

Figure 3. derivative $\partial P/\partial T$ of the reflected microwave radiation power versus temperature of the sample moistened with the hydrogen peroxide solution; the results were averaged over 100 points. The curve designations are the same as in Fig. 2

occurred. Fig. 2, *a* shows that the curve representing the process of sample cooling exhibited a $\partial P/\partial T$ extremum at -47°C. Negative derivatives at all the temperatures corresponded to the increase in the detected power with decreasing temperature, which was caused by the sample geometry and values of the real and imaginary parts of the complex relative dielectric permittivity.

The measurements obtained by using the hydrogen peroxide solution filling the silica gel pores are given in Fig. 3. The hydrogen peroxide weight concentration in the sample was $\sim 6\%$. The data were averaged over 100 points. The dependence extremums are smeared; the most pronounced extremum takes place in the case of the fluid heating and is located at approximately -47°C. The cooling curve exhibits additional extremums possibly associated with the existence of two known eutectics [8]. In this case, the extremums are expanded by temperature as compared with the measurements for the case of moistening with hydroperit (Fig. 2, *a*, *b*).

The difference in data obtained in measuring silica gels whose pores are filled with hydroperit and with aqueous solution of pure hydrogen peroxide may be explained as follows. While the sample is being cooled (Fig. 2, *a*, *b*), supercooling of the metastable liquid takes place. When the Widom line temperature is reached, entropy and density fluctuations cause destruction of the metastable state and sharp change in the dielectric permittivity. In the reverse process there takes place slow thawing of the hydrogen peroxide crystalline hydrates formed in the fluid. In the case of pure hydrogen peroxide, crystalline hydrates arise below -50°C at the eutectic points; there formation manifests itself in the derivative oscillations. During the sample heating, crystalline hydrates still stay in the solutions for some time. Their destruction occurs in a wide temperature range.

A certain shift of temperature positions of the $\partial P/\partial T$ extremums (by $\sim 1^\circ$C) relative to the known value -45°C at the pressure of 0.1 MPa for pure water is connected with the use of the solutions which is equivalent to the pressure increase in water [10,11]. In some cases, at high concentrations of the dissolved substance, this temperature shift reaches a few tens of degrees [7] with retention of water anomalies.

The obtained results exhibit such an interesting feature as the effect of a sharp variation in electromagnetic characteristics in a narrow temperature range. In a number of cases, initial plots exhibit signal jumps in time intervals of about a minute. This resembles the case of reaching the reaction activation threshold. Possibly, this feature may be explained by explosive instability of ice crystals [12] which takes place in reaching the pressure at the Widom line for the relevant temperature. Another assumption on extraordinary water characteristics was proposed in [13]; according to it, acceleration of chemical transformations is possible upon reaching the conditions for increased fluctuations in water structure energies near the Widom line.

Thus, the paper shows that the Widom line effect may be studied not only based on variations in thermodynamic quantities but also by microwave measurements of characteristics defined by the fluid dielectric permittivity in metastable aqueous systems.

Conflict of interests

The authors declare that they have no conflict of interests.

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