DECELERAREA RELAXĂRII LONGITUDINALE A SPINILOR PROTONILOR ÎN REZONANȚA MAGNETICĂ NUCLEARĂ A APEI SUB ACȚIUNEA ULTRASUNETULUI

DECELERATION OF LONGITUDINAL SPIN RELAXATION OF PROTONS IN NUCLEAR MAGNETIC RESONANCE OF WATER UNDER THE INFLUENCE OF ULTRASOUND

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It is shown that the ultrasound acting on water under ambient conditions causes an increase in the longitudinal spin relaxation time T_1 of the ^1H nuclei measured by means of nuclear spin echo method at low levels of ultrasound irradiation when the cavitation effects can be neglected. This effect is due to ultrasonic heating of the water and, as a consequence, to the increase in the relaxation time T_1 with increasing temperature. In the absence of cavitation effects, at low doses of ultrasonic irradiation, the relaxation time T_1 in the distillated water increases linearly with increasing ultrasound power. In the case of tap water there is a supplementary increase in T_1 with an increasing in ultrasound power P from P = 0 to P = 3.5 W caused by the removal of adsorbed paramagnetic oxygen molecules from water due to ultrasonic heating. It is given a theoretical interpretation of the observed linear increase in T_1 under increasing in P.

***Keywords**: minispec, random motion, spin relaxation, ultrasonic radiation.*

INTRODUCTION

One of the main mechanisms of longitudinal nuclear spin relaxation in liquids is due to random rotational and translational motions of molecules containing nuclear spins with dipole-dipole interactions between them [1]. In the case of proton longitudinal spin relaxation in water, these mechanisms prevail, because there are no effects of interaction between the electric field gradient and the quadrupole moments of the ^1H nuclei that are zero. It is also less significant the mechanism of the longitudinal proton spin relaxation in water due to the small correction term $-\gamma\hbar\boldsymbol{H}\cdot\mathbf{A}\cdot\boldsymbol{I}$ in the Hamiltonian of the interaction of the nuclear spin with the magnetic field [1]. Here A is the tensor of chemical shift; γ, $\hbar$, $\boldsymbol{H}$, and $\boldsymbol{I}$ are the nuclear gyromagnetic ratio, Planck constant, the magnetic field strength, and the spin operator of the ^1H nucleus. Recent advances in nuclear spin relaxation in liquids are given in [2]. In the case of liquids, the interactions of nuclear spins with fluctuating rotations and translations of molecules, these movements are internal, that is, they are not caused by an external action, for example, by an ultrasonic field. In the nuclear magnetic resonance (NMR) and nuclear acoustic resonance (NAR) phenomena, the magnetic component of the electromagnetic field and the acoustic field cause transitions

between nuclear spin levels. In the case of NAR, if the frequency of the acoustic wave is not strictly resonant, then part of its energy will be spent on heating the test sample in the resonant cavity of the NAR spectrometer. As a result, the nuclear spin-lattice relaxation time T_1 increases. This will occur at a large number of non-resonant phonons in an acoustic wave that excite the quantum transitions between nuclear spin levels (in the case of NAR spectrometers of a relatively low-quality factor of the acoustic resonator). Therefore, the experimental data for T_1 obtained in NAR experiments can be somewhat overestimated as compared with the data obtained in NMR experiments. In this regard, it needs to be considered separately a comparative analysis of the experimental data on nuclear spin-lattice relaxation as a whole, obtained by the NMR and NAR methods.

In this paper, here are given the results of an experimentally found increasing in the proton longitudinal spin relaxation time T_1 in tap and distillated water under a $\nu = 22$ kHz non-resonant ultrasound irradiation (the energy of a quantum, $h\nu$, is not equal to the Zeeman splitting of ^1H nuclei spin levels of water molecules) using the Hahn spin echo method. The first experimental data on the effect of ultrasonic radiation on the longitudinal spin relaxation time of ^1H nuclei of water molecules were reported in [3].

THE STUDY OBJECTS AND METHODS

The study objects are the tap and distillated water. The proton longitudinal spin relaxation time of ^1H in the tap and distillated water was measured on the Bruker Analyzer “Minispec” both in the absence and the presence of a 22 KHz ultrasound irradiation. An ultrasonic generator UZG13-01/22 was used as an irradiation source. All measurements were carried out on the Bruker Analyzer “Minispec” at an ambient temperature in the range of ($18\ ^0C < t < 22\ ^0C$). Before measurements, the Analyzer “Minispec” was calibrated using the Solid 0% 82731109 standard. It was used the Application for determining the proton spin-lattice relaxation time T_1 based on the inversion recovery pulse sequences and the subsequent mono- or bi-exponential fitting. Each T_1 measurement lasted 3.84 minutes at a fixed ultrasound power P with an interval of 0.5 hours between measurements. The average values of T_1, both without exposure to ultrasound and at different powers of ultrasonic irradiation, have been found in five (sometimes ten) consecutive measurements of T_1 for each P.

RESULTS AND DISCUTIONS

In the absence of the ultrasonic irradiation at temperature $t = 20\ ^0C$, the value of T_1 in tap water is 3.29 s (Fig. 1), which is 0.16 s less than in distilled water (Fig. 2). This can be due to adsorbed oxygen molecules, leading to a decrease in T_1. The O_2 paramagnetic molecules change the tap water NMR spectrum leading to the enhancement of the proton longitudinal spin relaxation time T_1. Therefore, the linear increase in T_1 with increasing P becomes the same as in the case of distilled water (Fig. 2) only at the ultrasound power $P = 3.5\ W$ and higher (Fig. 1), after the thermal removing of O_2 molecules from tap water. An ultrasonic generator UZG13-01/22 was used as an irradiation source. Figures 1

and 2 show the proton longitudinal spin relaxation time T_1 in tap and distillated water on power of irradiating ultrasound at room temperature.

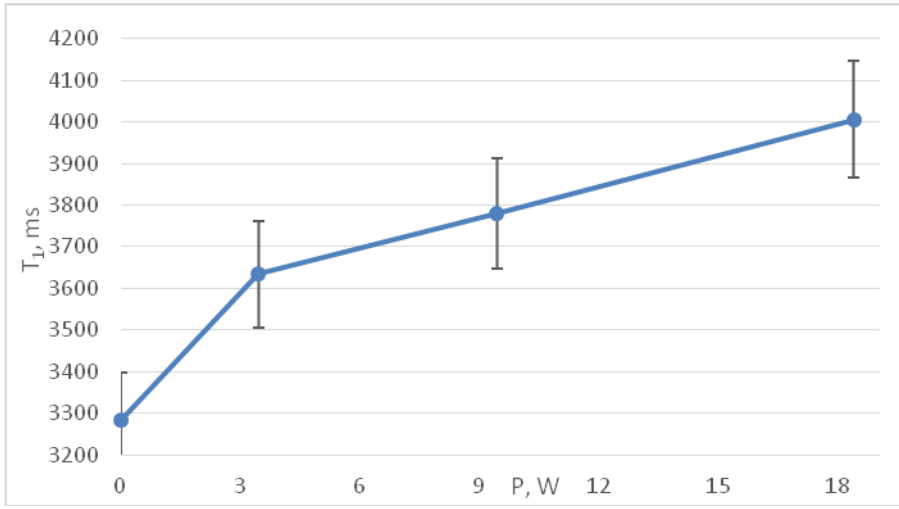


Fig. 1. The proton longitudinal spin relaxation time in tap water vs. the power of irradiating ultrasound.

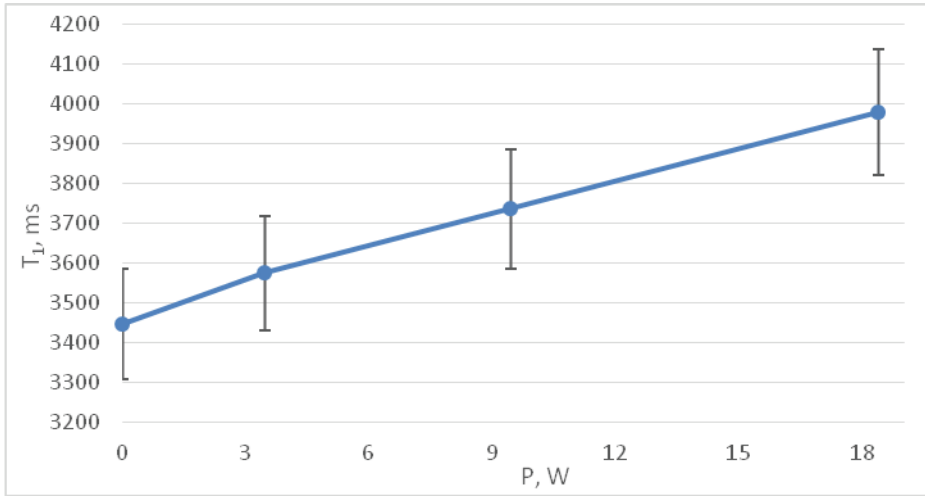


Fig. 2. The proton longitudinal spin relaxation time in distillated water vs. the power of irradiating ultrasound.

According to figures 1 and 2, at low levels of ultrasonic irradiation of both types of water, a linear increase in the proton longitudinal spin relaxation time occurs with increasing the power of ultrasound P from 3.5 W to 18 W for tap water (Fig. 1) and from

0 to 18 *W* for distillated water (Fig. 2). The indicated line segments in figures 1 and 2 are strictly parallel. The increase in T_1 with increasing *P* from 0 to 3.5 *W* for tap water (Fig. 1) is caused by two effects: the release of adsorbed O_2 molecules from the tap water surface under influence of ultrasound and the ultrasound heating of water as a whole.

The change of longitudinal spin relaxation time T_1 of the protons in water molecules upon ultrasonic irradiation is an expected effect, since the water heats up under the action of ultrasound, and the value of T_1 depends on temperature. A more detailed discussion of this effect together with a theoretical interpretation of the linear dependence of the relaxation time T_1 on the ultrasound power at low doses of radiation is given below.

If the correlation time is much shorter than the Larmor period, then the proton spin-lattice relaxation time caused by rotational and, respectively, translational random motions of water molecules is determined by the formulas [1]:

$$(1/T_1)_{\text{rot}} = 2\pi\cdot(\gamma^4\hbar^2a^3/kb^6)\cdot\eta(T)/T, \quad (1)$$

$(1/T_1)_{\text{trans}} = (3\pi/5)\cdot(Nb^6/a^3)\cdot(1/T_1)_{\text{rot}}$, (2) where *N*, $\eta(T)$, *k*, *T*, *a*, and *b* are, respectively, the number of ^1H nuclei in the unit volume, the temperature dependent water dynamic viscosity, the Boltzmann constant, the absolute temperature, the water molecule radius, and the distance between two hydrogen atoms in the water molecule.

The proton longitudinal spin relaxation time, T_1, caused both by rotational and translational motions of water molecules, is determined by the expression

$$1/T_1 = (1/T_1)_{\text{rot}} + (1/T_1)_{\text{trans}}. \quad (3)$$

Substituting (1) and (2) in (3), we find

$$T_1(T) = cf(T), \quad (4)$$

where the function $f(T)$ is

$$f(T) = T/\eta(T) \quad (5)$$

and the constant *c* is given by the formula

$$c = 5kb^6/[2\pi\gamma^4\hbar^2(5a^3+3\pi Nb^6)]. \quad (6)$$

According to (4), the temperature dependence of the proton longitudinal spin relaxation time is determined by the function $f(T)$ from (5). On the other hand, under the action of ultrasound, water is heated. It is easy to understand that at low doses of ultrasonic irradiation, the water temperature will linearly increase with increasing radiation dose, that is, with increasing power of ultrasound. In order to explain the observed at low radiation doses (Figs. 1 and 2) a linear increase in the longitudinal spin relaxation time T_1 with increasing ultrasound power, it is enough to show that $f(T)=T/\eta(T)$ is a linear function of *T*. In this case, a linear increase in water temperature with increasing radiation dose will manifest itself as a linear dependence of T_1 on *P*, when the function $f(T) = T/\eta(T)$ will depend linearly on temperature.

Figure 3 shows the function $f(T)=T/\eta(T)$ built on the basis of experimental data from [4] on a temperature dependence of the dynamic viscosity of water. In [4] there is a table containing the experimental values of the viscosity of water $\eta(T)$ in units of mPa•s determined with high accuracy (up to $10^{-5}10^{-5}$ mPa·s) in a wide temperature range (from 0.01 ^{0}C to 360 ^{0}C). The experimental data given in [4] show how water viscosity changes with temperature at water saturation pressure (which for particle use, gives the same result as atmospheric pressure at temperatures < 100 °C). This circumstance makes it possible to use data on the temperature dependence of the viscosity of water to interpret the slowing down of the proton longitudinal spin relaxation in water under the influence of ultrasonic radiation at atmospheric pressure. As the water temperature T rises above room temperature, which corresponds to the heating of water under the action of ultrasound, the product of the values T and $1/\eta(T)$ increases linearly with increasing temperature (Fig. 3). This corresponds to figures 1 and 2, with the exception of the part of figure 1 associated with a supplementary increase in T_1 with an increase in P from 0 to P = 3.5 W caused by the removal of adsorbed paramagnetic oxygen molecules from tap water due to ultrasonic heating. Thus, the function $f(T)=T/\eta(T)$ repeats the dependence of the proton longitudinal spin relaxation time T_1 on the power of ultrasonic irradiation. In the region of low ultrasonic heating temperatures, when cavitation effects do not appear, the linear increase in T_1 at increasing P (Fig.1 at P ≥≥ 3.5 W and Fig. 2 at P ≥≥ 0) is due to the linear growth of $T/\eta(T)$ with fairly high accuracy at increasing temperature T above room temperature.

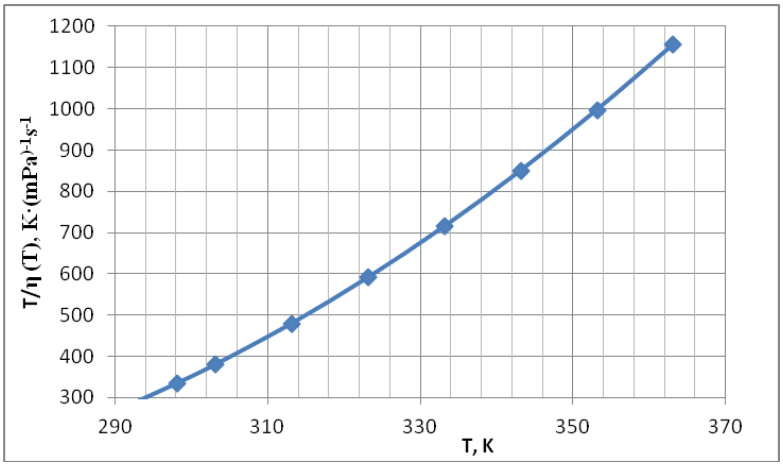


Fig. 3. Temperature dependence of the function $f(T)=T/\eta(T)$ in the temperature range corresponding to a weak heating of water by ultrasound.

Despite the good correlation between theoretical and experimental results, the following two circumstances should be noted. First, in our experiments, the gaseous oxygen dissolved in water was not removed before applying ultrasound to water (this

only applies to tap water, since freshly prepared distilled water did not contain adsorbed oxygen molecules). Since oxygen molecules are paramagnetic, the presence of the oxygen dissolved in water in the resonance cavity led to a decrease in the initial proton longitudinal spin relaxation time equal to 3.4 s (before the action of ultrasound on water). When removing oxygen molecules dissolved in water, which are rapidly relaxing centers, the T_1 value should increase slightly.

The second circumstance is connected with the cluster structure of water. The water molecules have a polar structure and form long-range hydrogen bonds. These bonds are relatively weak. They are constantly breaking and changing on a picosecond (10^{-12} s) time scale. Each water molecule has two hydrogen atoms and, correspondingly, two possible hydrogen bonds. Therefore, the water can form a network of bonds known as a cluster. There is a wide variety of water clusters in their size and structure [5-11]. The tunneling lifetime of water clusters depends on their size and structure.

CONCLUSIONS

The main conclusion that follows from our results is the deceleration of longitudinal spin relaxation of protons in nuclear magnetic resonance of water under influence of a non-resonant ultrasonic radiation. This effect is caused by the ultrasonic heating of the water and leads to a linear increase in the proton longitudinal spin relaxation time T_1 with increasing ultrasound power at low doses of ultrasonic irradiation. For freshly prepared distillated water, which does not contain adsorbed oxygen molecules, the longitudinal proton spin relaxation time T_1 increases linearly with increasing ultrasound power P from 0 to 18 W. For tap water, such a linear dependence occurs with an increase in P from 3.5 W to 18 W. At $P << 3.5$ W there is an additional increase in T_1 due to the removal of adsorbed oxygen molecules from the water surface under the influence of ultrasound.

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