

ON CHANGES IN THE STRUCTURE OF WATER DUE TO ITS CONTACT WITH A SOLID PHASE. I. NMR-SPECTROSCOPY STUDIES

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It is found that the longitudinal relaxation time in the NMR spectra of water molecules in contact with a surface of a solid phase differs from the same parameter for water in the absence of a solid phase.

This work opens a new, in principle, series of research studies of the changes in the structure of liquids due to their contact with a solid phase.

Numerous publications are known in which structural changes in adsorbed substances, as compared to their structure in the bulk, are noted to a certain extent. Amongst these publications are also our works that are concerned with the determination of changes in the density of different dispersion media [1-3] used as a tool to evaluate the density of adsorbed water [4-7].

A great number of investigations have been devoted to the study of the properties of wetting films, including the changes in viscosity, specific heat, and freezing point in thin films under the influence of solid substrates [8]. The thicknesses of these thin films reach hundreds of angströms. However, in the present work a change in the liquid structure has been revealed in layers which are at a distance of 10,000 to 15,000 μm from a surface of a solid phase, i.e., in this case the changes observed are far beyond the limits of surface films. Experimentally, the mentioned changes were established by measuring the longitudinal relaxation times in liquids in contact with a surface of a solid phase in the high-resolution NMR spectra obtained in a pulse mode.

As objects of investigation we used upper Cretaceous silica, $\gamma\text{-Al}_2\text{O}_3$, montmorillonite, hydromica, and kaolinite. Doubly distilled water and tap water were used as liquids. The investigations have revealed the maximum effect of changes in the longitudinal relaxation times measured at the same ratios of the mass of a solid phase to that of a liquid in the system "silica-water" and the opposite, with respect to direction, effect in the system "montmorillonite-water."

These effects are explained in terms of the mechanism of adsorption of water molecules with active centers of crystal lattices of minerals under investigation.

It should be noted that it is the changes in the longitudinal relaxation times in NMR spectra in water that allow an evaluation of the changes of: distances between protons in a water molecule, i.e., the change of a valence angle; intermolecular distances; and energies of hydrogen bonds in water. Certainly, the occurrence of deformed water molecules in a volume is attributed to their interaction with a surface of a solid phase, followed by their diffusion into the volume. That is why we have employed such methods in our investigations which permit a study of the spectra of a liquid, adsorbed, and solid states of a substance, i.e., NMR spectroscopy, infra-red spectroscopy, and x-ray analysis.

The present communication offers the results obtained mainly by the NMR spectroscopy technique.

Experimental studies were made on a pulse spectrometer NMR VS-597 adjusted for operation in the Fourier-transform mode. In the same device, a pulse generator operating in conjunction with a computer ADT-4500 provided the pulse control of the signal processing circuitry.

In this work, we measured the longitudinal relaxation times (T_1) of protons of water in contact with a surface of a solid phase and of water in the absence of a solid phase.

A measurement procedure involved the application of a train of 180° pulses followed after time τ by 90° pulses. For the train of pulses at which the signal amplitude was zero, the longitudinal relaxation time was determined by the formula

$$T_1 = \frac{\tau}{\lg 2}. \quad (1)$$

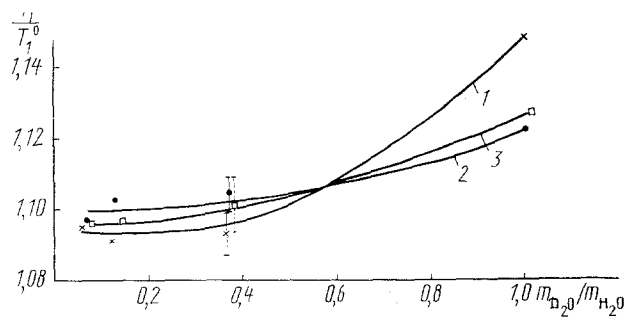


Fig. 1. Relative values of longitudinal relaxation times in NMR spectra in different systems (1, silica-doubly distilled water; 2, silica-tap water (sealed cuvettes); 3, silica-tap water (unsealed cuvettes)) versus deuterated water content in doubly distilled water.

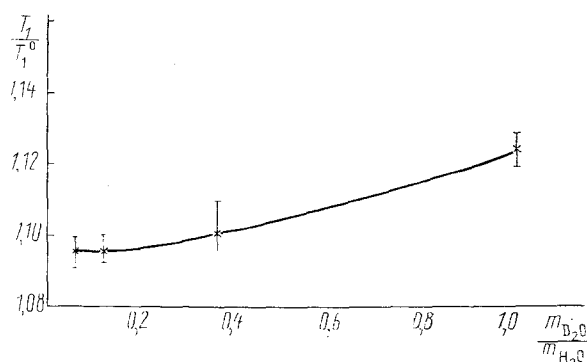


Fig. 2. Relative values of longitudinal relaxation times in NMR spectra in the system $\gamma\text{-Al}_2\text{O}_3$ -doubly distilled water versus deuterated water content in doubly distilled water.

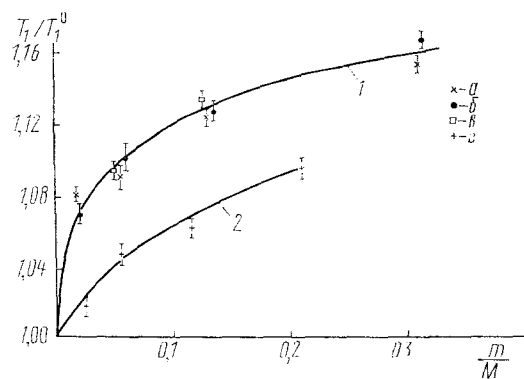


Fig. 3. Relative values of longitudinal relaxation times in NMR spectra versus the solid phase-to-entire system mass ratio: 1, silicon-doubly distilled water (a), silica-tap water (b) (sealed cuvettes), silica-tap water (c) (unsealed cuvettes); 2, $\gamma\text{-Al}_2\text{O}_3$ -doubly distilled water (d) (sealed cuvettes).

In our investigations, the NMR signal of deuterium nuclei in a solution of a test substance was applied to provide the internal nuclear stabilization of a magnetic field. Measurements were made at the following proportions of deuterated and ordinary water: 50% D_2O and 50% H_2O ; 25% D_2O and 75% H_2O ; 10% D_2O and 90% H_2O ; 5% D_2O and 95% H_2O . The

TABLE 1. Calculation of b , a , ΔU , α , and $(E_1 - E_0)/kT$ in Water in Contact with Silicon, $\gamma\text{-Al}_2\text{O}_3$, and Montmorillonite

Solid phase	$\frac{m}{M}$ g/g	$\frac{T_1}{T_1^0}$ (exp.)	α , deg	b , Å	$K_\alpha \cdot 10^6$, cm ²	ΔU , kcal/mole	a , Å	$\frac{E_1 - E_0}{kT}$	$\frac{T_1}{T_1^0}$ (calc.)
Upper Cretaceous silica	0,310	1,155	106,76	1,541	0,859	0,056	1,768	0,201	1,159
	0,134	1,121	106,36	1,537	0,868	0,037	1,776	0,156	1,123
	0,031	1,093	106,00	1,533	0,876	0,026	1,782	0,128	1,101
$\gamma\text{-Al}_2\text{O}_3$	0,213	1,096	105,07	1,534	0,876	0,028	1,781	0,130	1,103
	0,119	1,060	105,55	1,529	0,886	0,013	1,791	0,090	1,078
	0,059	1,046	105,31	1,526	0,892	0,006	1,793	0,070	1,060
Montmorillonite	0,135	0,895	102,75	1,500	0,9545	0,037	1,823	-0,161	0,884
	0,105	0,905	102,94	1,502	0,9496	0,024	1,819	-0,146	0,891
	0,088	0,917	103,03	1,503	0,9473	0,026	1,818	-0,138	0,897

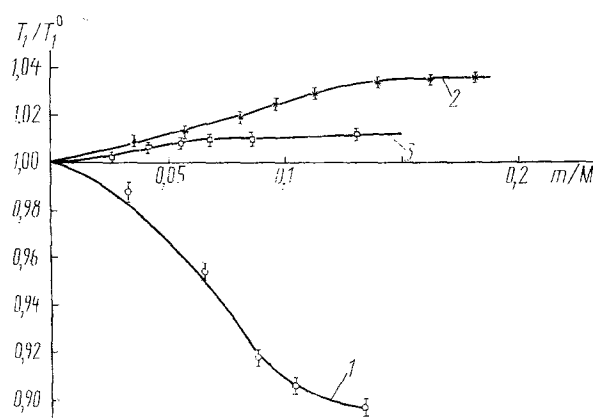


Fig. 4. Relative values of longitudinal relaxation times in NMR spectra versus the solid phase-to-entire system mass ratio: 1, montmorillonite-doubly distilled water; 2, hydromica-doubly distilled water; 3, kaolinite-doubly distilled water.

working samples were prepared as follows: a different amount of a mineral powder or, in the case of silica, of lumps of rock of different sizes were placed into cuvettes in the form of glass ampoules with a diameter of 5 mm. The cuvettes were filled with a certain amount of a test liquid mixed with the deuterated water in such a manner that there was only liquid in the operating region of the spectrometer probe, while a solid phase was below this region, i.e., at the bottom of the cuvette. To determine the relative values of longitudinal relaxation times, replicate experiments were performed with samples with and without a solid phase. All the measurements were made at room temperature. In T_1 calculations, temperature corrections were made for each sample. When preparing the samples, oxygen was removed from the liquid by injecting argon through it for a few minutes. The results of experimental studies are shown in Figs. 1-4. Figures 1 and 2 exhibit the ratios of relaxation times T_1/T_1^0 obtained by varying the D_2O content in the samples.

As seen from Figs. 1 and 2, the ratios of longitudinal relaxation times T_1/T_1^0 increase with content of heavy water in the mixture. At the same time, there is a limit below which T_1/T_1^0 does not depend any more on the heavy water content. This limit corresponds to $m_{\text{D}_2\text{O}}/m_{\text{H}_2\text{O}} = 0.1$. In further experiments on the determination of T_1/T_1^0 versus the ratio of the mass of a solid phase to that of the entire system, D_2O was introduced into the system in such an amount that the condition $m_{\text{D}_2\text{O}}/m_{\text{H}_2\text{O}} = 0.1$ might be obeyed. These experimental dependences (Figs. 3 and 4) served as a basis in the calculations of the changes in the structure parameters of water in contact with a solid.

According to A. Abragam [9], the spin-lattice relaxation time due to rotary and translational motion is written as

$$\frac{1}{T_1} = \frac{2\pi\gamma^4\hbar^2 a^3 \eta}{b^6 kT} + \frac{6\pi^2}{5} \frac{\gamma^4 \hbar^2 N \eta}{kT} \quad (2)$$

Then

$$\frac{T_1}{T_1^0} = \frac{b^6}{b_0^6} \left[\frac{5a_0^3 + 3\pi b_0^6 N_0}{5a^3 + 3\pi b^6 N} \right], \quad (3)$$

where the parameters with index '0' stand for the liquid not in contact with a solid phase.

Performing a successive division of one polynomial by the other and neglecting the terms in the quotient which make small corrections as well as those cancelling each other, we finally arrive at

$$\frac{T_1}{T_1^0} = \frac{b^6 a_0^3}{b_0^6 a^3} \quad (4)$$

As Figs. 3 and 4 show, T_1/T_1^0 increases in the case of silica, γ - Al_2O_3 , hydromica, and kaolinite and decreases in the case of montmorillonite, thus implying that the parameters b , a , and the valence angle α in a H_2O molecule must change.

According to [10], a change in the potential energy of a H_2O molecule in water at mean angular distortion of the angle H-O-H with respect to its equilibrium value α_0 is given by the equation

$$\Delta U = \frac{1}{2} K_\alpha r^2 (\Delta\alpha)^2, \quad (5)$$

where ΔU is expressed in ergs per molecule; r is the length of the bond O-H in cm; α is in radians; and K_α is the force constant of the valence angle in dyne/cm.

Also, a change in the potential energy of a water molecule due to the distortion Δa of a hydrogen bond is determined by the expression [10]

$$\Delta U = 3 \left(\frac{\Delta a}{2.76} \right) + 162 \left(\frac{\Delta a}{2.76} \right)^2 - 195 \left(\frac{\Delta a}{2.76} \right)^3, \quad (6)$$

in which ΔU is in kcal/mole and Δa is in Å.

Equations (4) through (6) have been employed to calculate b , a , α , and ΔU at different solid phase-to-entire system mass ratios. In all these calculations $\alpha_0 = 104.5^\circ$, $b_0 = 1.518$ Å, and $a_0 = 1.8$ Å have been assumed.

In Table 1, calculation results are presented for silica-water, γ - Al_2O_3 -water, and montmorillonite-water systems.

An inspection of the table reveals that at the same ratios the values of the valence angle in a water molecule and the change in hydrogen binding energies between neighboring water molecules in the system silica-water are much in excess of the same quantities obtained for the system γ - Al_2O_3 -water and especially for the hydromica-water and kaolinite-water systems (see Fig. 4). At the same time, the montmorillonite-water system exhibits changes in structure parameters of water which are close to those in the silica-water system but opposite in nature. A theoretical interpretation of this experimental finding will be offered in the next communication.

The results listed in Table 1 demonstrate the character of the changes in structure parameters of water in contact with a surface of a solid phase but do not allow quantitative relations to be obtained to calculate these parameters at any ratios m/M for different solids. In order to derive such relations, further research studies are needed.

Following [11], molecular relaxation (T_1) in different processes may be represented as

$$\frac{1}{T_1} = \eta_0 \exp \left(- \frac{\Delta E}{kT} \right), \quad (7)$$

in which ΔE is the change in energy required to induce relaxation (the activation energy) and η_0 is the frequency of processes, which is approximately equal to the frequency of molecule collisions.

The number of collisions, in accordance with [11], is determined by the formula

$$\eta_0 = 1,41\pi\rho d^2\bar{v}. \quad (8)$$

Thus we may write

$$\frac{T_1}{T_1^0} = \frac{\rho_0}{\rho} \exp\left(\frac{E_1 - E_0}{kT}\right) = \left(\frac{a}{a_0}\right)^3 \exp\left(\frac{E_1 - E_0}{kT}\right). \quad (9)$$

In connection with the fact that the spin-lattice relaxation time characterizes the rate at which a system of nuclear spins attains thermal equilibrium with other degrees of freedom of a given sample, E_1 and E_0 are assumed to be the kinetic energies of the nuclear vibrations in a H_2O molecule.

In order to prove this assumption, we carried out concrete calculations.

According to [12], an expression for the kinetic energy of nuclear vibrations in a water molecule may be written in the following form:

$$T' = \begin{bmatrix} \varepsilon_H + \varepsilon_O & \varepsilon_O \cos \alpha & -\varepsilon_O \sigma_{OH} \sin \alpha \\ \varepsilon_O \cos \alpha & \varepsilon_H + \varepsilon_O & -\varepsilon_O \sigma_{OH} \sin \alpha \\ -\varepsilon_O \sigma_{OH} \sin \alpha & -\varepsilon_O \sigma_{OH} \sin \alpha & \varepsilon_O (2\sigma_{OH}^2 - 2\sigma_{OH}^2 \cos \alpha + 2\varepsilon_H \sigma_{OH}^2) \end{bmatrix}, \quad (10)$$

where $\varepsilon_H = m'/m_H$; $\varepsilon_O = m'/m_O$; $\sigma_{OH} = s_0/s_{OH}$; $m' = 1.088$ a.u.; $s_0 = 1.09$ Å; $s = 0.96$ Å; $m_H = 1.088$ a.u.; and $m_O = 16$ a.u.

The results of the calculations for some values by formulas (9) and (10) are also included in Table 1. To determine $(E_1 - E_0)/(kT)$, the ratio of electronic and vibrational energies of particles was taken into account according to [13].

As seen from the table, the predicted and experimental values of the relative longitudinal relaxation times are close. Hence, the assumption that the spin-lattice relaxation process, during which a system of nuclear spins attains thermal equilibrium with other degrees of freedom of a given sample, is determined by the kinetic energy of nuclear vibrations is proved to be valid.

It is obvious that the parameters a and E_1 are functions of m/M . For $m/M \rightarrow 0$, $a \rightarrow a_0$, $E_1 \rightarrow E_0$. It is necessary to find the second boundary conditions for $(M - m) \rightarrow p_0$, where p_0 is the mass of a double molecular layer consisting of adsorbed water molecules. Such investigations have been conducted by using IR-spectroscopic methods, the results of which will be given in the next communication.

NOTATION

T_1 , longitudinal relaxation time of water protons in NMR spectra; b , distance between two spins in a molecule (for a water molecule, this distance is between two atoms of hydrogen); a , distance between two atoms of oxygen in two neighboring water molecules; j , gyromagnetic ratio of a nucleus; \hbar , Planck constant; k , Boltzmann constant; T , temperature; η , dynamic viscosity; N , number of spins in 1 cm^3 ; ΔU , change in a potential energy of a molecule; r , length of the OH-bond in a H_2O molecule; K_α , force constant of a valence angle; η_0 , frequency of molecular collisions; ρ , water density; d , effective diameter of a molecule; \bar{v} , average thermal velocity; E_1 , E_0 , kinetic energies of nuclear vibrations in a H_2O molecule; m , mass of a solid phase in a system under investigation; M , total mass of a solid phase and a liquid; p_0 , mass of a double molecular layer consisting of adsorbed water molecules.

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ON CHANGES IN THE STRUCTURE OF WATER DUE TO ITS CONTACT WITH A SOLID PHASE. II. IR-SPECTROSCOPY STUDIES

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The experimental data on vibrational spectra and the theory of polyatomic molecular vibrations have been used to determine the valence angle in water molecules adsorbed at active centers on a surface of the solids under study.

In [1], it has been shown that the longitudinal relaxation time in the NMR spectra of water molecules interacting with a surface of a solid phase differs from the same parameter for water in the absence of a solid phase. The experimental data obtained and the available analytical dependences have allowed the determination of the changes in distances between two spins in a H₂O molecule, those between oxygen atoms in two neighboring water molecules, the valence angle, and hydrogen bond energies in liquid water in contact with a solid.

Also, it has been established in [1] that the process of spin-lattice relaxation, in which a system of nuclear spins attains thermal equilibrium with other degrees of freedom of a test sample, is determined by the kinetic energy of nuclear vibrations. But in liquid water, the kinetic energy of nuclear vibrations will change with the valence angle in a H₂O molecule. It is quite obvious that the change in the valence angle of a molecule in a volume is caused by its adsorption on active sites of a solid surface, i.e., during adsorption the H₂O molecule deforms and, passing into a volume, retains the traces of this deformation.

The present communication reports the results of valence angle determination in a H₂O molecule adsorbed on a surface of upper Cretaceous silica, γ -Al₂O₃, and montmorillonite. The results are obtained from the data on experimental vibrational spectra and from calculations using the theory of polyatomic molecular vibrations.

The experimental technique and measurement procedure were the same as in [2]. Figure 1 exhibits the spectrum of H₂O adsorbed on silica powder prepared without vacuum at a temperature of heating determined by a global lamp. Under vacuum conditions, the spectrum disappears at the same temperature. Whence it is obvious that the bonding energy (the bonding diagram is given in Fig. 3) of H₂O molecules with active centers of silica surface is insignificant. As seen from Fig. 1, the frequencies from 1300 to 1500 cm⁻¹ within the region of deformation vibrations and their overtones in a range of 2700 to 3000 cm⁻¹ have been found. The maximum of the band in the region of deformation vibrations is at 1458 cm⁻¹.

To analyze this frequency, we use the formula

$$v_{\alpha\alpha}^2 = D_{\alpha\alpha} + \sum \frac{D_{\alpha\mu} D_{\mu\alpha}}{D_{\alpha\alpha} - D_{\mu\mu}} \quad (1)$$