ON THE CHANGES IN A STRUCTURE OF WATER DUE ITS CONTACT WITH A SOLID PHASE.

III. DETERMINATION OF RELATIONS $T_1/T_1^0 = f_1(m/M)$, $M_e = f_2(\alpha)$. ESTIMATION OF VARIATION EFFECT OF THE VALENCE ANGLE (α) IN A WATER MOLECULE ON WATER SOLUBILITY OF SUBSTANCES

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Calculated and experimental methods have been suggested to determine the valence angle in a water molecule in a volume with the solid phase mass variation in a system. The dependences of the dipole moment in H_2O and of static dielectric water permeability on the valence angle value have been established and the changes in water solubility of different substances in the presence of a solid phase have been substantiated.

In [1], it has been shown that the relative value of the longitudinal relaxation time in the NMR spectra in water is determined as follows:

$$\frac{T_1}{T_1^0} = \frac{a}{a_0} \exp\left(\frac{E_1 - E_0}{kT}\right) = \frac{\rho_0}{\rho} \exp\left(\frac{E_1 - E_0}{kT}\right). \tag{1}$$

In this equation E_1 is the kinetic energy of nuclear vibrations in a water molecule, calculated for the definite solid phase mass-to-total system mass ratio.

Take the relation $E_1 = f_3(m/M)$ for the systems under study.

Making use of the matrices of the kinematic coefficients of a H_2O molecule, we evaluate the values of E_1 for m/M established by experiment; in this case at m/M → 1, E_1 were determined from the matrix of the kinematic coefficients, corresponding to an adsorbed molecule (given by the authors in [2]), while at m/M → 0, $E_1 \to E_0$ (E_0 is the kinetic energy of nuclear vibrations in H_2O in a volume in the absence of a solid phase). Calculation results are presented in Table 1.

Let us approximate the function $E_1 = f_3(m/M)$ in the exponential form:

$$E_1 = \exp\left[b\left(\frac{m}{M}\right)^{n_1} + c_1\right].$$

$$\text{For } \frac{m}{M} = 0 \quad E_1 = \exp c_1, \text{ i.e., } c_1 = \ln E_0, \text{ for } \frac{m}{M} = 1, \tag{2}$$

$$E_1 = \exp\left(b - \ln E_0\right) = E_a, \text{ then } b = \ln\frac{E_a}{E_0} \text{ and}$$

$$E_1 = \exp\left[\ln\frac{E_a}{E_0}\left(\frac{m}{M}\right)^{n_1} + \ln E_0\right]. \tag{3}$$

Employing the data of Table 1, we estimate the values of n_1 for silica, γ-Al_2O_3, and montmorillonite correspondingly: 0.74, 0.46, 0.66. Determine the relation $\rho/\rho_0 = f_4(m/M)$.

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TABLE 1. Values of Kinetic Energies of Nuclear Vibrations E_1 in a H_2O Molecule and ρ/ρ_0 as a Function of m/M for Various Systems

Solid phase	$\frac{m}{M}$	$E_1\sqrt{\frac{m_0}{M_0}}$, a·u	$\frac{\rho}{\rho_0}$
Upper Creaceous silica	1,000	3,2061	1,100
	0,310	3,1856	1,056
	0,134	3,1843	1,042
	0,031	3,1831	1,031
	0,018	3,1822	1,022
γ-Al_2O_3	1,000	3,1864	1,100
	0,213	3,1833	1,032
	0,119	3,1815	1,015
	0,059	3,1808	1,012
	0,028	3,1793	1,002
Montmorillonite	1,000	3,1541	1,046
	0,135	3,1721	0,962
	0,105	3,1727	0,969
	0,088	3,1737	0,970
	0,068	3,1750	0,990
	0,033	3.1770	0,997

With account of the data of work [1], evaluate the values of ρ/ρ_0 for relations m/M established by the experiments; here, at m/M → 1, ρ will be equal to the adsorbed water density during formation of a double molecular layer d_w, and at m/M → 0, $\rho \to \rho_0 \to 1$. The calculation results are given in Table 1.

Approximate the function $\rho/\rho_0 = f_4(m/M)$ for the silica–water and γ-Al_2O_3–water systems in the exponential form:

$$\rho/\rho_0 = \exp{(m/M)^{n_2}c_2}. \tag{4}$$

At m/M → 1 $\rho/\rho_0 = \exp c_2 = d_w$, then

$$\rho/\rho_0 = \exp{(m/M)^{n_2} \ln d_B}. \tag{5}$$

Using the data of Table 1, we determine the values of n_2 for silica and γ-Al_2O_3 correspondingly: 0.41, 0.77. Then for minerals with a nonexpanding crystalline lattice we finally arrive at:

$$\frac{T_1}{T_1^0} = \exp\left[\frac{\exp\left[\ln\frac{E_a}{E_0}\left(\frac{m}{M}\right)^{n_1} + \ln E_0\right] - E_0}{KT}\sqrt{\frac{m_0}{M_0}} - \left(\frac{m}{M}\right)^{n_2}\ln d_B\right]. \tag{6}$$

According to our work [3], the density distribution of adsorbed water on montmorillonite within the limits of the double molecular layer is of a wave character with maxima in the vicinity of 5.18 and 27% moisture content. Therefore, we will approximate the function $\rho/\rho_0 = f_4(m/M)$ for the montmorillonite–water system in the form of other exponent:

$$\frac{\rho}{\rho_0} = \exp\left[\left(\frac{m}{M}\right)^{n_2} c_2 - \left(\frac{m}{M}\right)^{n_3} c_3\right]. \tag{7}$$

At m/M → 1 $\rho/\rho_0 = \exp{(c_2 - c_3)} = d_w$.

Taking $c_3 = d_w$, $c_2 = 2d_w$, and using the data of Table 1, we obtain $n_2 = 1.0$, $n_3 = 0.07$. Then for the minerals with an expanding crystalline lattice we finally derive:

$$\frac{T_1}{T_1^0} = \exp\left[\frac{\exp\left[\ln\frac{E_a}{E_0}\left(\frac{m}{M}\right)^{n_1} + \ln E_0\right] - E_0}{KT}\sqrt{\frac{m_0}{M_0}} - 2\left(\frac{m}{M}\right)^{n_2}\ln d_B + \left(\frac{m}{M}\right)^{n_3}\ln d_B\right]. \tag{8}$$

Figure 1 exhibits relations (6) and (8), which may be employed to calculate the valence angle in a water molecule, distances between molecules and hydrogen-bonded energies for any solid phase mass-to-total system mass ratio. The results of calculation of the valence angle value as a function of m/M for the silica–water, γ-Al_2O_3–water, montmorillonite–water systems are presented in Fig. 2.

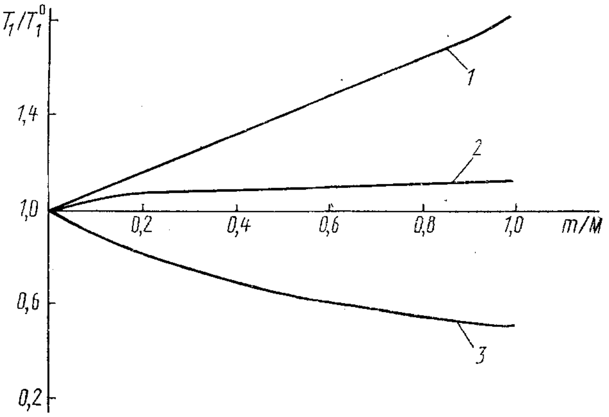

Fig. 1. Calculated relative values of longitudinal relaxation times of water molecules in NMR spectra (T_1/T_1^0) vs the solid phase mass-to-solid phase mass- and water ratio (m/M) for systems: 1) silica–water; 2) γ-Al_2O_3–water; 3) montmorillonite–water.

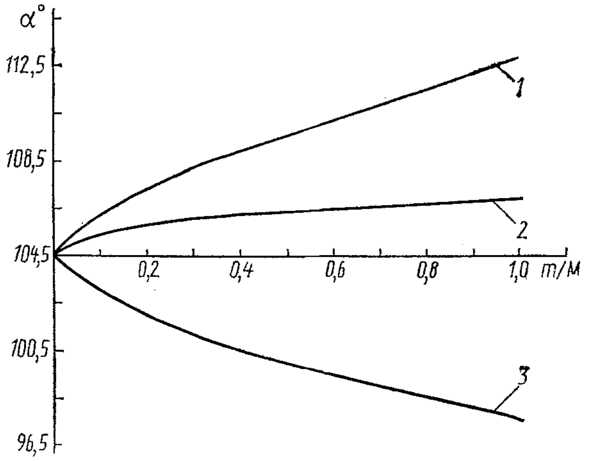

Fig. 2. Valance angle value (α) in a water molecule vs the solid phase mass-to-solid phase mass- and water ration (m/M) for systems: 1) silica-water; 2) γ-Al_2O_3–water; 3) montmorillonite–water.

Undoubtedly, the change in the already indicated parameters of a water structure causes the variation of a number of physicochemical and microbiological processes in water, but in many calculations we use one more characteristic for a water molecule, i.e. its dipole moment. It depends on the valence angle value, therefore, the following stage of the work is devoted to determination of this dependence.

The dipole moment of a water molecule is known to be defined by three components of the interaction between electrons in atoms, which form a molecule:

$$M_e = M_{e_1} + M_{e_2} + M_{e_3}, \tag{9}$$

where M_{e_1} is the component characterizing the ionic bond in a O–H group; M_{e_2} is the component evaluating the overlapping moment in this very O–H group; and M_{e_3} is the component, characterizing the moment of an unshared pair in an oxygen atom.

According to [4], we have:

$$M_{e_1} = eRf, \tag{10}$$

$$f = b_1^2 - a_1^2, \tag{11}$$

where b_1 and a_1 are the normalized coefficients in a molecular orbital of the O–H bond

$$\varphi = a\varphi_A + b\varphi_B\,. \tag{12}$$

In order to determine f, we make use of the coefficients before the atomic orbitals in the molecular orbitals of a H_2O molecule, obtained by Ellison and Shull during calculation by the self-consistent field method for the value of the valence angle H–O–H, equal to 105° and presented by Herzberg in [5].

For the binding molecular orbital $\bar{\varphi}_5(1b_2)$ $f_2 = 0.5428^2 - 0.7759^2 = -0.3074$. For the binding molecular orbital $\bar{\varphi}_3(3a_1)$ $f_1 = 0.8277^2 - 0.3341^2 = 0.5735$. The mean value $f = (f_1 + f_2)/2 = 0.133$. Then the value of M_{e1}, designed to the H_2O-molecule axis, passing along the valence angle bisectrix from two OH bonds, is taken to be equal to

$$M_{e_1} = 1{,}226\cos\frac{\alpha}{2}. \tag{13}$$

According to [4] and to other works, the overlapping moment in the bond between two atoms is equal to

$$M_{e_2} = (1+f)\frac{2\lambda}{1+\lambda^2}e\bar{\chi}_{sp}, \tag{14}$$

where λ is the hybridization parameter of the –s and –p orbitals of the oxygen atom for a H_2O molecule; κ_{sp} is the dimension of the overlapping region of atomic orbitals.

Following Coulson [6]:

$$\lambda^2 = -\frac{1}{\cos\alpha}. \tag{15}$$

The dimension of the overlapping region: $\bar{\kappa}_{sp} = a_{sp} - R/2 = 0.583$ Å $- 0.48$ Å $= 0.103$ Å. The quantity a_{sp} is determined by the coordinates of point charges in a H_2O molecule, given in [7]. Then M_{e2}, designed to the H_2O-molecule axis, passing along the valence angle bisectrix from two OH bonds, is found to be equal to

$$M_{e_2} = -\frac{2{,}24\sqrt{-\cos\alpha}}{1-\cos\alpha}\cos\frac{\alpha}{2}. \tag{16}$$

Substituting $\alpha = 104.5°$ into Eq. (16), we obtain quantity $M_{e2} = -0.548$D, which is close to the overlapping moment value H–O (sp^3), being equal to –0.61D, presented in [8]. Therefore, 1.64D is accounted for M_{e3} for $\alpha = 104.5°$ at the total dipole moment value of a H_2O 1.84D molecule, which also appears to be closed to the quantity 1.69D, given in [8].

In accordance with [4], the dipole moment from the unshared pair of electrons of the oxygen atom is defined as follows:

$$M_{e_3} = \frac{4e\lambda'}{1+\lambda'^2}\bar{\chi}'_{sp}, \tag{17}$$

where λ' is the hybridization parameter of the –s and –p orbitals of the oxygen atom placed in a plane, perpendicular to that of a H_2O molecule itself; $\bar{\kappa}_{sp}'$ is the dimension of the overlapping region of the atomic orbitals (this distance is already now counted off from the oxygen atom nucleus).

Obeying Herzberg [5], we have:

$$\lambda' = \frac{\cos\frac{\alpha}{2}}{\sqrt{-\cos\alpha}}, \tag{18}$$

then

$$M_{e_3} = \frac{3{,}34\sqrt{-\cos\alpha}}{\cos^2\frac{\alpha}{2} - \cos\alpha}, \tag{19}$$

$$M_e = M_{e_1} + M_{e_2} + M_{e_3} = 1{,}23\cos\frac{\alpha}{2} - \frac{2{,}24\sqrt{-\cos\alpha}}{1-\cos\alpha}\cos\frac{\alpha}{2} + \frac{3{,}34\sqrt{-\cos\alpha}}{\cos^2\frac{\alpha}{2} - \cos\alpha}\mathrm{ccs}\frac{\alpha}{2}. \tag{20}$$

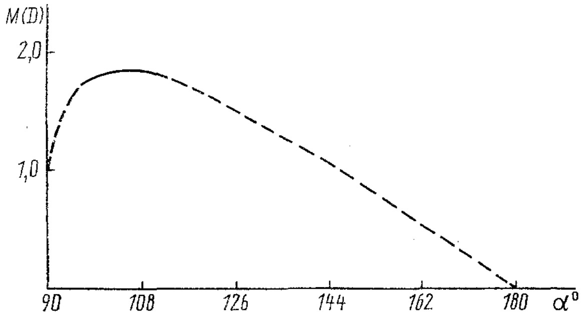

Fig. 3. Dependence of the dipole moment of a water molecule on the valance angle value α.

The hypothetical relation $M_e = f_2(\alpha)$ is shown in Fig. 3 and, as seen from this figure, the maximal value of the dipole moment 1.84D is within the range of the values of the angle $\alpha = 104\text{-}105°$. On using formula (16) in equations, presented in [2], we estimate the quantity $\alpha = 112.67°$ in H_2O adsorbed on silica powder.

According to the data of an analysis of the IR-spectra frequencies within the region of deformation vibrations (carried out also in work [2]), the valence angle value is taken to be equal to 113°. The obtained results, associated with estimation of the change of the valence angle in a water molecule, being in liquid water, contacting with a solid phase, allow one to determine the role of such changes (the role of solids) on the change in water solubility of various substances.

In order to solve this problem, we introduce here the already known formula for calculation of the ion activity coefficient in a solution [9]

$$\ln\gamma = -\frac{(ze)^3 L^2 \sqrt{2\rho m_1}\, T^{3/2}}{8\pi\,(\varepsilon_0 R_1)^{3/2}}. \tag{21}$$

Then we may write, that

$$\frac{\ln\gamma}{\ln\gamma_{[0]}} = \left(\frac{\rho}{\rho_{[0]}}\,\frac{m_1}{m_{1[0]}}\right)^{0,5}\left(\frac{\varepsilon_{0[0]}}{\varepsilon_0}\right)^{3/2}. \tag{22}$$

As follows from [10], it is possible to present the equation for defining the static dielectric permeability of water in such a way (the known Kirkwood equation):

$$\varepsilon_0 = 2\pi N^* \frac{Me^2 g}{kT}, \tag{23}$$

where N^* is the number of dipoles in a volume unit; g is the correlation Kirkwood parameter:

$$g = 1 + \sum_{i=1} N_i \langle \cos\gamma_i \rangle, \tag{24}$$

where N_i is the number of neighboring molecules in the i-th coordination envelope; $\langle \cos\gamma_i \rangle$ is the mean value of angle cosines, formed by the dipole moment of molecules in the i-th envelope with the central molecule dipole moment.

Pople [10] has used the Kirkwood equation in his model of the distorted hydrogen bonds and has found that the quantity g in this model is expressed as:

$$g = 1 + \sum_{i=1}^{\infty} N_i 3^{1-i} \cos^{2i}\frac{\alpha}{2}\left(1 - \frac{kT}{K_\varphi}\right)^{2i}, \tag{25}$$

where K_φ is the bending force constant of the hydrogen bond ($K_\varphi = 3.78 \cdot 10^{-13}$ erg/rad).

It has been shown in the earlier work performed by us, that under silica influence there occurs more intensive deposition of ions in the region of concentrations c = 0.001-0.0001. Within this concentration region $\ln\gamma \to \ln\gamma_{[0]} \to 0$. Then, substituting in (22), (23), and (25), we finally derive

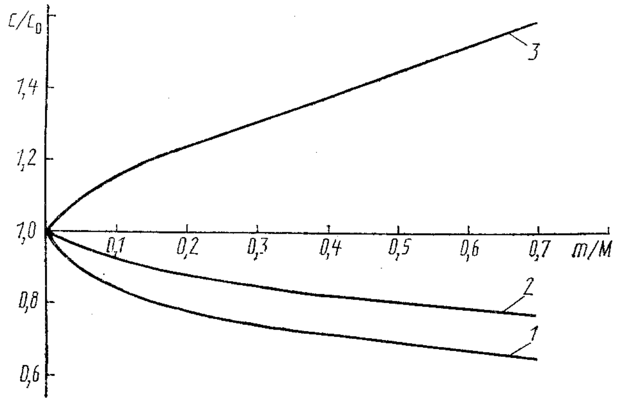

Fig. 4. Dependence of the change in water solubility of substances (c/c_0) under the influence of a solid phase on the solid phase mass-to-solid phase mass and water ratio (m/M) for systems: 1) silica–water; 2) γ-Al_2O_3–water; 3) montmorillonite–water.

$$\frac{c}{c_0}=\left[\exp\left(\left(\frac{m}{M}\right)^{n_2}\ln d_B\right)\right]^2\left[1+\sum_{i=1}^{\infty}N_i3^{1-i}\cos^{2i}\frac{\alpha_0}{2}\left(1-\frac{kT}{K_\varphi}\right)^{2i}\right]^{-3}\times$$
$$\times\left[1+\sum_{i=1}^{\infty}N_i3^{1-i}\cos^{2i}\frac{\alpha}{2}\left(1-\frac{kT}{K_\varphi}\right)^{2i}\right]^3\left[1{,}23\cos\frac{\alpha_0}{2}-\right.$$
$$\left.-\frac{2{,}24\sqrt{-\cos\alpha_0}}{1-\cos\alpha_0}\cos\frac{\alpha_0}{2}+\frac{3{,}34\sqrt{-\cos\alpha_0}}{\cos^2\frac{\alpha_0}{2}-\cos\alpha_0}\cos\frac{\alpha_0}{2}\right]^{-6}\times \tag{26}$$
$$\times\left[1{,}23\cos\frac{\alpha}{2}-\frac{2{,}24\sqrt{-\cos\alpha}}{1-\cos\alpha}\cos\frac{\alpha}{2}+\frac{3{,}34\sqrt{-\cos\alpha}}{\cos^2\frac{\alpha}{2}-\cos\alpha}\cos\frac{\alpha}{2}\right]^6.$$

Figure 4 exhibits the functions plotted according to Eq. (26), and, as follows from this figure, in the montmorillonite–water system, the water solubility of substances increases, while in the silica–water and γ-Al_2O_3–water systems, it decreases, and in the region m/M = 0.5-0.7 under the silica effect (at relatively low concentrations of substances in water) the solubility diminishes by 1.5 times. In order to confirm this statement concerning the solubility, we have carried out the experimental investigations, associated with estimation of the silica effect on the deposition processes of salts of some metals dissolved in running water. So, at the initial zinc concentration of 30 mg/liter ($ZnSO_4$ was dissolved) the zinc deposition process under the silica effect is intensified by 1.3 times on the second day, on the third day by 1.6, and on the seventh day by 1.3 times.

During dissolving of the $FeSO_4\cdot 7H_2O$, $NiSO_4$, $MgSO_4$ mixture in water under the silica effect, on the second day after the formation of a solution one observes the intensification of the iron deposition process by 1.6 times, on the fourth day by 1.8, and on seventh day by 2 times. Such effect occurs at definite concentrations of iron in water.

Thus, the results obtained in [1, 2] and in this work indicate that under the action of adsorption processes of water molecules on the active centers of the solids surface adsorbed molecules are deformed with the change in the valence angle. During transition of the molecules into a volume the traces of this deformation are conserved; this fact causes the change of the longitudinal relaxation times of water molecules in the NMR spectra, the hydrogen-bonded energy, the dipole molecule moment, the density, and of the water static dielectric permeability. The relations, established in the works, may be used for explaining a number of physicochemical and microbiological processes, which occur in water solutions.

At the same time from the obtained results it may not be yet drawn the conclusion that there is a mechanism, which explains the reasons of the formation of different valence angles in a water molecule adsorbed on the surface of various solids. It is obvious, that this mechanism is connected with the charge transfer onto an adsorbed molecule. But for the time being, it is a rather complex problem for us to appreciate the character of this transfer. We try to solve it by means of investigations of deformation of crystalline lattices of solids during adsorption. These results will be reported in the next communication.

NOTATION

T_1, T_1^0, longitudinal relaxation time of water protons in NMR spectra, correspondingly contacting with the solid phase surface and in the absence of a solid phase; m, M, mass of a solid phase and a liquid; M_e, $M_{e[0]}$, molecular dipole moment of water, correspondingly contacting with a solid phase and in the absence of a solid phase; α, α_0, values of valence angles in a water molecule; a, a_0, distances between oxygen atoms in two neighboring water molecules; ρ, ρ_0, water densities; E_1, E_0, kinetic energies of nuclear vibrations in a water molecule in a volume; E_a, kinetic energy of nuclear vibrations in a water molecule adsorbed on a solid surface; m_0, mass of electron rest; M_0, mass of proton rest; e, electron charge; R, length of the O–H bond in a water molecule; f, bond charge; γ, coefficient of ion activity in a solution; z, ion valence; m_1, $m_{1[0]}$, ion molarity; L, Avogadro number; ε_0, $\varepsilon_{0[0]}$, static dielectric permeability of a solvent; k, Boltzmann constant; T, temperature; c, c_0, concentrations of ions in a solution.

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