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CHANGES IN THE MOLECULAR STRUCTURE OF WATER FILTERED THROUGH COARSELY DISPERSED NATURAL MINERAL FLINT

P. P. Olodovskii and O. V. Karpel’

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Based on nuclear-magnetic resonance spectroscopic and diffractometric studies, the authors obtained new data on the changes in all parameters of the molecular structure of water after its filtration through columns filled with natural mineral flint.

In [1–5], it is shown that in interaction of any solid phase with water the following parameters of the water structure undergo changes: the valence angle, the distance between the oxygen atoms of two neighboring molecules, the energies of hydrogen bonds, the length of valence and hydrogen bonds, the angle of bending of hydrogen bonds, and the dipole moment of a water molecule. The largest changes were observed in the system *water–flint*, and for all the studied systems they were obtained from the data of measurement of the longitudinal relaxation times of nuclear spins in a water molecule in nuclear-magnetic resonance (NMR) spectra of high resolution. Table 1 presents information on the parameters of the structure of distilled water at the moment of its contact with flint powder.

In [2], it is asserted that the valence angle in a water molecule adsorbed on an oxygen atom of the surface layer of flint attains 113^{o}, in γ-oxide of aluminum in adsorption of a water molecule simultaneously on two oxygen atoms this angle is equal to 107^{o}, and in the adsorption scheme where one of the oxygen atoms of a water molecule interacts simultaneously with a coordination-unsaturated aluminum atom (a Lewis center) and an OH-group (a Brönsted center) and the oxygen atom of the molecule interacts with the oxygen atom of the crystal lattice, the value of the valence angle is 104.3^{o}; in montmorillonite in adsorption of a water molecule simultaneously on two oxygen atoms the value of the valence angle attains 97.5^{o}. In the adsorption scheme where one of the oxygen atoms of a water molecule interacts with an exchange cation or a hydroxyl group while the oxygen atom interacts with the oxygen atom of the crystal lattice, the valence angle turns out to be 104.5^{o}.

Consequently, a substantial change in the valence angle of a water molecule occurs only in the case of its adsorption on oxygen atoms. Moreover, the dipole moment of the water molecule and, consequently, its electron charge undergoes a change.

In [5], the authors gave an answer to the question: "why do the oxygen atoms located in the surface layers of different minerals determine different transfer of an electron charge to adsorbed water molecules?" For this purpose, evaluations were made of the deformation of crystal lattices of different metals in the course of water sorption based on x-ray diffractometry. From a series of investigated minerals, the maximum relative value of the deformation of the volume of the elementary lattice in natural "black" flint turned out to be 0.00445. The experimental value of the deformation of the crystal lattice was used to calculate a cross charge that occurs due to the displacement of the atoms inside the lattice and characterizes the charge redistribution between the atoms of oxygen and silicon. We carried out this calculation on the basis of [6].

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TABLE 1. Parameters of the Structure of Water in the System Distilled Water–Flint Powder in Relation to the Mass Ratio of the Solid Phase and of the Solid Phase and Water

m_0/M	T_1/T_1^0	α^o	r, Å	b, Å	$2a$, Å	ΔU, kcal/mole	R, Å	θ	M_0, D
0.30	1.1931	110.70	0.962	1.5828	2.4630	0.374	1.750	51.880	1.8185
0.20	1.1771	110.15	0.962	1.5775	2.4814	0.319	1.753	50.201	1.8245
0.15	1.1533	109.50	0.961	1.5696	2.5080	0.245	1.750	46.764	1.8835
0.10	1.0919	107.40	0.961	1.5490	2.5620	0.090	1.743	45.267	1.8385
0.05	1.0595	106.40	0.961	1.5390	2.5950	0.040	1.802	42.260	1.8428

In [6], wide use is made of the concept of a cross charge determining the relation between the transverse lattice vibrations and the light waves and characterizing the local polarization of atoms in their relative displacement in the lattice. According to our calculations, the value of the charge transferred from the flint surface to one adsorbed water molecule was 0.0246 *e*.

In [5], it is noted that the reasons for the formation of different valence angles in the water molecule adsorbed on the surface of different minerals are attributable to the changes in the binding energy of atoms in a crystal, i.e., to the different degree of deformability of the crystal under the influence of water molecules. It is the deformation of the crystal that determines the change in the molecular structure of water in the volume.

It is pertinent to note that in [1–5] an analysis is made of the data found in the systems solid–water. However, in our subsequent works we found new effects that were related to a change in the molecular structure of liquids after their filtration through coarsely dispersed natural "black" flint. These investigations were carried out in connection with the creation of technologies of production of a wide assortment of vodka, cognacs, and bottled water. The methods of nuclear magnetic resonance spectroscopy, and diffractometry underlie these technologies.

In NMR spectroscopic investigations, the longitudinal relaxation times of protons belonging to water molecules, to water molecules interacting with ethyl-alcohol molecules, and to the CH_2 and CH_3 groups of an ethyl-alcohol molecule were evaluated. A study was made of water, ethyl alcohol, blends (a water–ethyl alcohol mixture), cognac spirits, and cognacs.

Experimental determinations were carried out on an NMR VS-597 pulsed spectrometer adjusted for operation in the Fourier-transformation regime. In this device, a pulse generator integrated with an ADT-4500 computer provided pulsed control of the circuits processing a signal.

The measurement procedure consisted of using a train of a 180-degree pulse followed by a 90-degree pulse switched in the time interval τ. For the pulse train at which the signal amplitude became equal to zero, the longitudinal relaxation time was determined from the formula

$$T_1 = \tau/\ln 2 \, . \tag{1}$$

In our investigations, for the internal nuclear stabilization of a magnetic field we applied an NMR signal of deuterium nuclei that are in the solution of the investigated substance.

To determine the relative values of the longitudinal relaxation times, we studied in parallel two specimens of liquids, one of which was filtered through coarsely dispersed "black" flint.

Table 2 gives the mean values of T_1/T_1^0 of the relative longitudinal relaxation times of protons belonging to water individually and to water in the blend, cognac spirit, and cognac. The number of concurrent measurements of T_1/T_1^0 in the experiments varied from 6 to 15; moreover, the variation coefficient did not exceed 1–2.5%.

TABLE 2. Parameters of the H_2O Molecules in Water, in the Blend, in Cognac Spirit, and in Cognac Filtered through Coarsely Dispersed "Black" Flint and Their Change as a Result of the Filtration Process

$\frac{T_1/T_1^0}{\Delta T_1/T_1^0}$	$\frac{r}{\Delta r}$, Å	$\frac{\alpha^o}{\Delta\alpha^o}$	$\frac{a}{\Delta a}$, Å	$\frac{b}{\Delta b}$, Å	$\frac{K_\alpha}{\Delta K_\alpha}\cdot 10^6$, cm^{-1}	$\frac{K_n}{\Delta K_n}\cdot 10^6$, cm^{-1}	ΔU_α, kcal/mole	ΔU_r, kcal/mole	$\Sigma\Delta U$, kcal/mole	$\frac{R}{\Delta R}$, Å	$\frac{\theta^o}{\Delta\theta^o}$	$\frac{N_{O_2^-}}{\Delta N_{O_2^-}}$, mg/liter	$\frac{T_{H(H_2O)}}{\Delta T_{H(H_2O)}}$ eV	$\frac{T_{O(H_2O)}}{\Delta T_{O(H_2O)}}$ eV	$\frac{E_{(H_2O)}}{\Delta E_{(H_2O)}}$ kcal/mole
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Softened Water Filtered Once through Flint (Flint Water)															
1.1236 +0.1236	0.9650 +0.0050	107.6 +3.100	1.2715 –0.0430	1.5574 +0.0390	0.8443 –0.0670	12.6795 –0.1492	0.1046 –	0.0290 –	0.1336 –	1.7930 –0.0320	47.882 +7.3620	1.83 +1.830	8.6526 –0.5479	11.7336 –0.2394	4.6511 –0.8849
Blend Prepared with the "Flint Water" and Ethyl Alcohol "Super Lux"															
1.1268 +0.1268	0.9650 +0.005	107.75 +3.350	1.2720 –0.0430	1.5589 +0.040	0.8377 –0.0736	12.6795 –0.1922	0.1121 –	0.0290 –	0.1410 –	1.7700 –0.0550	44.578 +4.362	1.94 +1.94	8.6364 –0.5641	11.7266 –0.2464	5.1111 –0.4248
Cognac Spirit Filtered Once through Flint															
0.8527 –0.1473	0.9700 +0.010	99.400 –5.100	1.3955 +0.0805	1.4796 –0.0384	1.0476 +0.1363	12.484 –0.3942	0.3487 –	0.1142 –	0.4629 –	1.8936 +0.0680	27.233 –13.287	8.62 +8.62	10.144 +0.9438	12.386 +0.4131	7.8003 +2.2643
Cognac Prepared with the Initial Cognac Spirit and Filtered Once through Flint															
0.9454 –0.0546	0.9700 +0.010	102.20 –2.300	1.3665 +0.0515	1.5098 –0.0082	0.9643 +0.530	12.484 –0.3942	0.0656 –	0.1142 –	0.1798 –	1.8850 +0.060	35.553 –4.967	2.57 +2.57	9.8917 +0.6912	12.2758 +0.3027	6.7267 +1.1907
Cognac Prepared with the "Flint" Cognac Spirit and Filtered Once through Flint															
0.9344 –0.0651	0.9700 +0.001	101.80 –2.700	1.3666 +0.0516	1.5055 –0.0125	0.9800 +0.0687	12.4845 –0.0394	0.0914 –	0.1142 –	0.2056 –	1.8980 +0.0730	37.350 –3.1700	3.006 +3.01	9.9381 +0.7376	12.296 +0.3229	6.5814 +1.0454

Table 2 also presents the calculated parameters of the molecular structure of water filtered through the coarsely dispersed "black" flint both individually and in the composition of the blend, cognac spirit, and cognacs and also the variation in these parameters as a result of the filtration process.

In [4], we have published the method of calculation of the parameters α, a, b, K_α, K_r, ΔU_α, ΔU_r, $\sum \Delta U$, R, and θ.

Numerous estimates of the chemical composition of water taken in different sources and passed through columns filled with flint are indicative of one important circumstance. The water filtered through the natural "black" flint differs from the initial water only by the increased content of molecular oxygen, the increase in whose concentration can vary from 10 to 100%.

From [7] (in which the molecular structure of oxygen is described in detail), it follows that an O_2 molecule is lacking four electrons, namely, two electrons on the molecular orbital $1\pi_g$ and two on the orbital $3G_u$ that were supposed to be present in two filled shells. It is also noted that the bonds in the O_2 molecule become less stable if these orbitals are filled with electrons, and therefore they can be considered to be antibonding. It is natural to suggest that the water molecules adsorbed on the flint surface will be a source of transfer of an electron charge to the O_2 molecule. As a result of such transfer, the hydrated cluster $O_2^- \cdot (H_2O)_n$ will be formed.

We determine the ionic concentration of molecular oxygen in water in interaction of water molecules with the surface of a solid phase. This problem will be solved based on the propositions of statistical mechanics.

Using simultaneously the Boltzmann and Bose distribution laws (the interpretation of which is taken, respectively, from [8, 9]), we write

$$N_j = \frac{N_i \left[\exp \dfrac{(\varepsilon_i - \mu_i)}{KT} - 1 \right]}{\exp \dfrac{(\varepsilon_j - \mu_j)}{KT} - 1}, \tag{2}$$

where ε_i and ε_j are the energies of molecules, μ_i and μ_j are their chemical potentials, and N_i and N_j are the number of molecules in the ith and jth states, respectively.

Representing

$$\varepsilon_i - \mu_i = \Delta U_i\,, \quad \varepsilon_j - \mu_j = \Delta U_j\,, \tag{3}$$

where ΔU_i and ΔU_j are the change in the potential energies of molecular vibrations due to different processes in the ith and jth states, respectively, we finally obtain

$$N_j = \frac{N_i \left[\exp \dfrac{\Delta U_i}{KT} - 1 \right]}{\exp \dfrac{\Delta U_j}{KT} - 1}. \tag{4}$$

In our case, as the ith state we assume the state of one H_2O molecule interacting with one molecular ion O_2^-, then $N_i = 1$, while as the jth state a set of the H_2O molecules interacting with one molecular ion O_2^- is assumed.

Thus, for calculating N_j it is necessary to know ΔU_i and ΔU_j.

TABLE 3. Dimensionless Coefficients $\eta_{ij\alpha}$ Determining the Approximate Values of the Matrix Elements of Interatomic Interaction

Coefficient	Theoretical values		Fitting values
	simple cubic structure	tetrahedral structure	
$\eta_{ss\delta}$	$-\pi^2/8 = -1.23$	$-9\pi^2/64 = -1.39$	–1.4
$\eta_{sp\delta}$	$\frac{\pi}{2}\sqrt{\frac{\pi^2}{4} - 1} = 1.9$	$\frac{9\pi^2}{32}\sqrt{1 - \frac{16}{3\pi^2}} = 1.88$	1.84
$\eta_{pp\delta}$	$3\pi^2/8 = 3.7$	$21\pi^2/64 = 3.24$	3.24
$\eta_{pp\pi}$	$-\pi^2/8 = -1.23$	$-3\pi^2/32 = -0.93$	–0.81

To determine ΔU_i, we employ the results from [10–12], where quantum chemical calculations of the structure of hydrated complex ions $O_2^- \cdot (H_2O)_n$ are carried out for $n = 1.4$.

In [10], it is established that in the cluster $O_2^- \cdot (H_2O)_n$ ($n = 1$) the valence angle in an H_2O molecule is $\alpha = 91.02^o$, while the length of the valence bond is $r = 0.998$ Å. Introducing corrections for the value of charge transfer in the cluster $O_2^- \cdot (H_2O)_n$ equal to 0.04 e [12], we obtain $\alpha = 90.679^o$ and $r = 1.0202$ Å. Then

$$\Delta U_i = K_r\,(r - r_0)^2 + 0.5K_\alpha\,(r\Delta\alpha)^2 = 7.2283\ \text{kcal/mole}\,.$$

We determine ΔU_j by the method described in [4]. The numerical values of $\Delta U_j = \Sigma\Delta U$ for different states of water are given in Table 2.

For the water filtered once through flint, $\Delta U_j = 0.1336$ kcal/mole (the first line in Table 2). Then for this state of water $\Delta U_j = 9.6\cdot 10^5$ kcal/mole and the ionic concentration of molecular oxygen is $N_{O_2^-} = 1.83$ mg/liter. In Table 2, column 13 gives the values of $N_{O_2^-}$ for different states of water. The maximum accumulation of the molecular ion O_2^- in water is established when the water is dissolved in the cognac spirit.

In order to take into account the distinctive features of the structure of "flint" water in determining the energy of interaction of its molecules with each other (the energy of hydrogen bonds), with the oxygen molecule, or with the other ions dissolved in water, it is necessary to have a simple and reliable calculation method that allows for the interaction of the off-center (not valence) forces between atoms. We suggest such a method, which is based on the ideas developed in [6]. And although [6] is concerned with quantum mechanical methods of study of the analysis of the electronic structure of solids, the results of these investigations can be used to study other systems as well, in particular, liquids.

In essence, the problem is reduced to determination of the energy of interaction between two atoms:

a) belonging to the same solid within the limits of an elementary crystal lattice;
b) one atom belongs to a solid, while the other is in the adsorbed (ionic) state;
c) belonging to two molecules in a liquid;
d) one atom belongs to a molecule in a liquid, while the other is in the ionic state in this liquid.

According to [6], for calculation of the electronic structure it is necessary to know the values of different matrix elements. In [6], it is shown that a good approximation for the matrix element of interatomic interaction can be obtained from the formula

$$V_{ij\alpha} = \eta_{ij\alpha}\,\hbar^2/(md^2)\,, \tag{5}$$

where d is the distance between the nuclei, m is the electron mass, and $\eta_{ij\alpha}$ is the parameter acquiring four universal constant values corresponding to matrix elements of the type $ss\delta$, $sp\delta$, $pp\delta$, and $pp\pi$ (where s, p, δ, and π are the symbols for the orbitals in an atom).

As is shown in [6], the coefficients $\eta_{ij\alpha}$ acquire the values given in Table 3.

To determine the energy of interaction between two atoms belonging to one or several systems, we employ the theory of chemical capture developed in [6] as well. The chemical capture is the event caused by the interatomic matrix elements of interaction; its energy is determined by the contributions of off-center (not valence) forces, and the formula for calculation of this energy can be represented as follows:

$$E_{\text{capt}} = \frac{2W_2^4}{|2W_3|^3} \sum_{\alpha > \beta} \cos^2 \theta_{\alpha\beta} , \tag{6}$$

where W_2 is the interaction corresponding to the matrix element $V_{ij\alpha}$.

$$W_3 = \varepsilon_s^{\text{c}} - \varepsilon_p^{\text{a}} . \tag{7}$$

The quantities $\theta_{\alpha\beta}$ are the angles between the vectors formed by the central ions and neighboring atoms. In our work, we consider the systems for which

$$\sum_{\alpha > \beta} \cos^2 \theta_{\alpha\beta} = 1 .$$

To substantiate the correctness of the chosen theoretical approach, we calculate at first the energy of the hydrogen bond in ordinary water. With this aim in view, we determine the electron energy level of the hydrogen and oxygen atoms in a water molecule. The electron energy level of a hydrogen atom in the free state is equal to 13.6 eV. According to [13], the total electronic charge on the oxygen atom in a water molecule is 8.35 *e*, while on one hydrogen atom it is equal to 0.8225 *e*. Then the electron energy level of the hydrogen atom in ordinary water (the zero variant) is

$$T_{\text{H(H}_2\text{O)}} = 13.6 \cdot (0.8225)^2 = 9.2005 \text{ eV} .$$

Now we pass to determination of the electron energy level of the oxygen atom in a molecule of ordinary water. For this operation we adopt the concept of [6], according to which, with account for the conditions of orthonormalization states of the wave functions of atomic (unhybridized) states, it is established that the wave functions of the hybridized states are orthonormalized. These hybridized orbitals are not the eigenfunctions corresponding to the states with a prescribed energy. The expected value of the energy is the mean and is called the hybridized state:

$$\varepsilon = (\varepsilon_s + 3\varepsilon_p)/4 . \tag{8}$$

A measurement of the electron energy in the state described by the hybridized wave function shows that for 25% of the time an electron has energy ε_s and for 75%, energy ε_p. The hybridized orbitals are oriented in the direction of the nearest neighbors and can be constructed for each species of atoms which form a molecule, a crystal, and a cluster.

To determine the electron energy level $T_{\text{O(H}_2\text{O)}}$ of an oxygen atom in a water molecule, we use the data of the Periodic Table of Elements [6] and the values of the electron energy level of a hydrogen atom in H_2O. Substituting these values into (8), we obtain $T_{\text{O(H}_2\text{O)}}$ = 11.9731 eV.

Now it is necessary to determine the dimensionless coefficient $\eta_{ij\alpha}$.

According to [13], the formation of a hydrogen bond in the dimer of a water molecule is possible if we take into account the low excited orbital 4_{a_1} (i.e., the configuration interaction). The $pp\pi$-matrix element of the tetrahedral structure corresponds to such an interaction, i.e., $\eta_{ij\alpha} = \eta_{pp\pi} = -0.93$.

The length of the hydrogen bond in liquid water is 1.825 Å. Substituting all the existing parameters into formula (6), we determine the energy of the hydrogen bond in the dimer of an H_2O molecule, $E_{\text{h.b}}$ = 5.536 kcal/mole. The experimental values of the energy of the hydrogen bond in water are 5–6 kcal/mole.

Now we pass to calculation of the electron energy level of the hydrogen atom in H_2O with a changed structure.

According to [13], the total atomic population of hydrogen in a water molecule is determined by the partial populations of the molecular orbitals $\tilde{\psi}_2(2a_1)$, $\tilde{\psi}_3(3a_1)$, and $\tilde{\psi}_5(1b_2)$. Analytical expressions for these orbital wave functions are written as follows:

$$\tilde{\psi}_2\,(2a_1) = (\psi_2 + \lambda\psi_4)\,\sqrt{1+\lambda^2}\,,\quad \tilde{\psi}_3\,(3a_1) = (\psi_3 + \lambda\psi_4)\,\sqrt{1+\lambda^2}\,,\quad \tilde{\psi}_5\,(1b_2) = (\psi_5 + \mu\psi_0)\,\sqrt{1+\mu^2}\,, \tag{9}$$

where $\psi_2 = a_1 2s$; $\psi_3 = a_1 2p_2$; $\psi_4 = a_1(1s_{H'} + 1s_{H''})$, $\psi_5 = b_2(1s_{H'} - 1s_{H''})$ are the linear combinations of atomic orbitals; λ and μ are the parameters of hybridization of atomic orbitals; $\lambda^2 = -\cos\alpha$; $\mu = \cos\frac{\alpha}{2}/\sqrt{-\cos\alpha}$.

According to [13], the orbitals a_1 and b_2, which have, respectively, the form $1s_{H'} + 1s_{H''}$ and $1s_{H'} - 1s_{H''}$, determine the partial population of hydrogen atoms.

For H_2O with $\alpha = 104.5^{\circ}$ and r = 0.96 Å, the numerical value of the partial population of hydrogen atoms for the molecular orbital $\tilde{\psi}_2(2a_1) \rightarrow 1s_{H'} + 1s_{H''}$ is 0.309; for $\tilde{\psi}_3(3a_1) \rightarrow 1s_{H'} + 1s_{H''}$ it is equal to 0.257; for $\tilde{\psi}_5(1b_2) \rightarrow 1s_{H'} - 1s_{H''}$ it is 1.080.

Consequently, the numerical values of Π_ψ, i.e., partial populations of hydrogen atoms for any values of the valence angle in a water molecule can be established, with a certain degree of accuracy, as follows:

$$\text{for}\quad \tilde{\psi}_2\,(2a_1) \rightarrow 1s_{H'} + 1s_{H''}\quad \Pi_\psi = 0.309\,\frac{\lambda_\alpha\sqrt{1+\lambda_\alpha^2}}{\lambda_0\sqrt{1+\lambda_0^2}}\,,$$

$$\text{for}\quad \tilde{\psi}_3\,(3a_1) \rightarrow 1s_{H'} + 1s_{H''}\quad \Pi_\psi = 0.257\,\frac{\lambda_\alpha\sqrt{1+\lambda_\alpha^2}}{\lambda_0\sqrt{1+\lambda_0^2}}\,,$$

$$\text{for}\quad \tilde{\psi}_5\,(1b_2) \rightarrow 1s_{H'} - 1s_{H''}\quad \Pi_\psi = 1.080\,\frac{\mu_\alpha\sqrt{1+\lambda_\alpha^2}}{\mu_0\sqrt{1+\lambda_0^2}}\,.$$

Taking different values of the valence angle, for instance, 100–115° with an interval of 1°, we obtain an empirical dependence that relates the total population of the hydrogen atom in H_2O, Π, to the valence angle α°:

$$\Pi = \exp\,[-\,0.0331\,(\alpha - 90)^{0.6641}]\,. \tag{10}$$

Then the electron energy level of the hydrogen atom in the water molecule with the changed molecular structure will be determined as

$$T_{H(H_2O)} = \left\{\exp\,[-\,0.0331\,(\alpha - 90)^{0.6641}]\right\}^2 \cdot 13.6\ \text{eV}\,. \tag{11}$$

Table 2 provides the values of the electron energy levels of the oxygen and hydrogen atoms in different states and also the energies $E(H_2O)$ of hydrogen bonds in water. As follows from the table, the energy of hydrogen bonds between water molecules in "flint" water in the blend prepared with "flint" water and the alcohol "Lux" is lower than in ordinary water, i.e., the water in these states becomes less viscous; in the cognac spirit and cognac, the energy of hydrogen bonds between water molecules is higher than in ordinary water, i.e., the water in these states becomes more viscous.

However, the following question arises: "why will the charge formed on water molecules as a result of adsorption be absorbed by molecular oxygen?" An answer to it follows from a number of publications where the authors report data on the energies of affinity of atoms, molecules, and radicals to an electron (generalized in [14]), from the publications on proton transfer (generalized in [15]), and from the articles devoted to investigation of the mechanism of adsorption of molecular oxygen on silver [16, 17].

As follows from [14], of many compounds, it is an oxygen molecule that possesses the lowest energy of electron affinity of molecules, and this energy is 0.43–0.05 eV or 10–11.5 kcal/mole.

It should be noted that the energy of dissociation of the most widely dispersed salts in water [18] is: NaCl, 4.30 eV; KCl, 4.37 eV; CsCl, 4.58 eV.

Thus, in "flint" water the charge source is the adsorbed water molecules, while the charge consumer is the oxygen molecules dissolved in water. What is the mechanism of charge transfer?

As follows from [15], the proton conduction in the chains of H_2O molecules held by hydrogen bonds is due to the fact that a proton can transfer H_3O^+ (hydroxonium) or OH^- (hydroxyl) in the form of ionic defects along a chain; H_3O^+ and OH^- are formed in dissociation of water molecules as a consequence of the transfer of one proton to a neighboring molecule according to the formula $2H_2O \rightarrow H_3O^+ + OH^-$.

Along with the transfer of ionic defects in the chain, the orientational positive D- and negative L-defects of Bjerrum formed in rotation of H_2O molecules can be transferred. With a positive Bjerrum defect, there are two protons between two hydroxyl ions, while in the case of a negative defect, none.

The orientational defects possess an electric charge: a D-defect has a positive charge, while an L-defect has a negative one. Within the framework of a rather simple electrostatic model of water, Bjerrum evaluated the energies of formation of such orientational defects. He has shown that the energy for defect formation is equal to 11.9–1.7 kcal/mole, while the activation energy necessary for the corresponding reorientation of molecules is 2.5 kcal/mole.

Thus, the total activation energy is 14.4–1.7 kcal/mole. Such an energy is responsible for the concentration of D- and L-defects in pure ice equal to, approximately, $7 \cdot 10^{15}$ cm^{-3} at a temperature of -10^oC.

Now we compare the results of our calculations with the published information.

The energy of electron affinity in formation of a molecular negative ion of oxygen is 10–11.5 kcal/mole. The potential vibration energy of a water molecule in its interaction with a negative molecular ion of oxygen is 12.5 kcal/mole. The energy of formation of a Bjerrum defect, i.e., a carrier of a charge from an adsorbed water molecule to an oxygen molecule, is 11.9 ± 1.7 kcal/mole. The total activation energy necessary for the reorientation of molecules is 14.4 ± 1.7 kcal/mole. The concentration of the D- and L-defects in pure ice at a temperature of -10^oC is $7 \cdot 10^{15}$ cm^{-3}. The maximum concentration of negative molecular ions in "flint" water is $6 \cdot 10^{15}$ cm^{-1}.

All these data indicate that the oxygen molecules dissolved in water acquire a charge from the adsorbed water molecules and create clusters of the $O_2^- \cdot (H_2O)_n$ type, thus becoming the nuclei of formation of a new structure of water. This modified structure of water is retained in a blend as well.

To prove this hypothesis, we can refer to [16], where in a cluster approximation a theoretical analysis is made of the properties of oxygen in a near-surface layer of silver. An oxygen molecule is placed in the octahedral cavity of a cubic Ag_{14} cluster. Optimization of the system O_2/Ag_{14} and the structural parameters are determined by the nonempirical Hartree–Fock method.

For three nonequivalent positions of O_2 in the Ag_{14} cluster, a possible stabilization of molecular forms of oxygen is shown. Calculations have demonstrated that the ground state of the system O_2/Ag_{14} system is a triplet, while the spin density is delocalized on silver atoms. Spin polarization leads to splitting till the $3G_g$-level. In its properties, an oxygen molecule has parameters intermediate between the superoxide O_2^{1-} and the peroxide O_2^{2-} with the bond length $R(O{-}O) = 1.41$ Å.

In [17], the forms of chemisorbed oxygen on the Ag(110) surface are established. Four stable positions are found. With respect to the equilibrium length of the $R(O{-}O)$ bond and its force constant, all the obtained structures are assigned to the peroxide O_2^{2-}.

The existence of the stable forms of negative ions of molecular oxygen interacting with the silver atoms of the Ag_{14} cluster confirms our hypothesis on the existence of stable forms of the cluster $O_2^{-}\cdot(H_2O)_n$ where negative ions of the molecular oxygen interact with the deformed molecules of "flint" water.

The nature (mechanism) of formation of the $O_2^{-}\cdot(H_2O)_n$ and O_2^{-}/Ag_{14} clusters is one and the same; everything is reduced to the magnitude of the transfer of an electronic charge to an oxygen molecule.

The practical value of the formulated problem is quite obvious. Use of the natural mineral flint for modification of the molecular structure of different liquids (water, ethyl alcohol, cognac spirit, and other liquids) makes it possible to obtain a wide variety of items with the best organoleptic properties or other useful characteristics.

But for scientific substantiation of new technologies it is necessary:

1) to study the processes of n-fold passing of liquids through columns filled with flint;

2) to evaluate the role of impurities, dissolved in the initial liquids (especially in water), in the processes of formation of new molecular structures;

3) to develop methods of calculation of the energy of the bond between the deformed molecules of "flint" water and the molecules of other liquids with the molecules of oxygen (its forms) dissolved in these liquids.

NOTATION

m_0, mass of the solid phase (flint); M, mass of the solid phase and water; T_1 and T_1^0, longitudinal relaxation time of the protons of water (contacting with the surface of the solid phase and in the absence of the solid phase) in NMR spectra; α, r, and b, valence angle, length of the valence bond, and distance between hydrogen atoms, respectively; M_0, dipole moment in a water molecule; $2a$, distance between the oxygen atoms of two neighboring water molecules; ΔU, change in the potential vibration energy of water molecules in their interaction with a molecular oxygen ion; R, length of the hydrogen bond; θ, angle of bending of the hydrogen bond; K_α, force constant of the valence angle (α) in a water molecule; K_r, force constant of the valence bond in a water molecule; ΔU_α, change in the potential vibration energy of a water molecule due to the change in the valence angle; ΔU_r, change in the potential vibration energy of an H_2O molecule due to the change in the length of the valence bond; k, Boltzmann constant; T, temperature; $\varepsilon_s^{\mathrm{c}}$, atomic term of the cation of the s-state; $\varepsilon_p^{\mathrm{a}}$, atomic term of the anion of the p-state; $T_{\mathrm{H(H_2O)}}$ and $T_{\mathrm{O(H_2O)}}$, electron energy levels of the hydrogen and oxygen atoms in a water molecule; e, electron charge; $\hbar$, Planck's constant.

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