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EVALUATING THE STRUCTURAL CHANGE IN ADSORBED WATER IN DISPERSED SYSTEMS DURING THEIR HYDRATION BY THE METHOD OF INFRARED SPECTROSCOPY

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UDC 541.182

On the basis of an analysis of the vibration frequency of D_2O molecules adsorbed on different ionic forms of montmorillonite, a method is proposed for evaluating the change in the density of this water in different groups.

Infrared spectroscopy was used in [1] to detect the existence of two types of groups of molecules of combined water and to evaluate their stability during dehydration.

This article carries the study to a second stage, investigating the effect of exchange cations on the change in the frequencies and force constants of water molecules adsorbed on montmorillonite.

The equipment and procedure used to obtain the measurements were detailed in [1].

Figures 1 and 2 show the change in the infrared spectra of deuterated Al- and Fe-forms of montmorillonite in the cases of desorption in the regions 1200-1500, 2500-2700, and 3500-3700 cm^{-1}. Similar spectra for the natural form are presented in [1].

It is known that the region 1200-1300 cm^{-1} corresponds to deformational vibrations of D_2O molecules, while the 1400-1450 cm^{-1} region corresponds to deformational vibrations of HDO. Thus, analysis of the resulting spectra is most conveniently begun by calculating the frequencies of these vibrations.

As was shown in [1], the greatest degree of hydration of the natural form of montmorillonite corresponds to a broad range, with a maximum of 1300 cm^{-1}; in the region of valence vibrations, the maximums of the corresponding ranges are 2680, 2610, and 2523 cm^{-1}. A relatively narrow band at 1264 cm^{-1} is distinguished on the general contour of the deformational vibration band as desorption proceeds, but it disappears at a low moisture content.

On the basis of calculation of the deformational vibration frequencies of H_2O molecules, we showed that the most stable molecules during desorption are those which interact with the exchange cation and an oxygen atom on the surface of the mineral, or with two oxygen atoms on the mineral surface [1].

Taking the values of the force constants characteristic of weak hydrogen bonds [2], we used our calculated data to obtain the frequency of the deformational vibrations of a symmetrical group – 1206 cm^{-1}. This frequency was not observed in the experiments. Calculation of the frequency for an asymmetrical group at the same force constants yielded a value of 1250 cm^{-1}.

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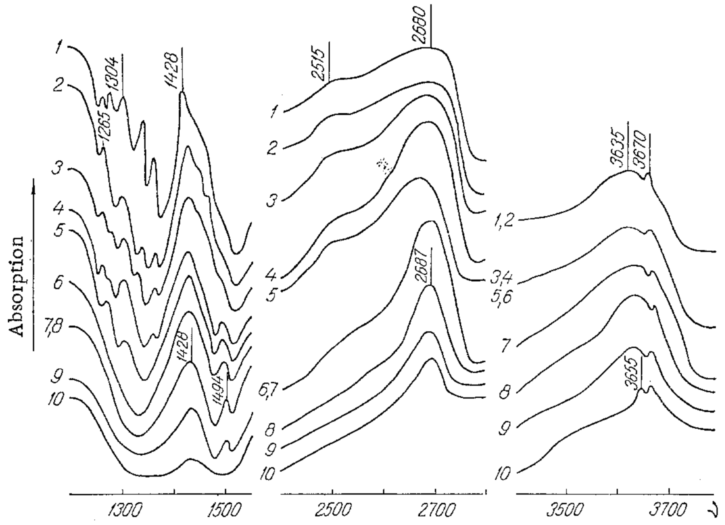

Fig. 1. Change in infrared spectra of deuterated Al-montmorillonite during desorption: 1) moisture content 11.8%; 2) 10.1; 3) 9.5; 4) 7.3; 5) 5.0; 6) 4.5; 7) 3.9; 8) 1.7; 9) 0.6; 10) about 0%.

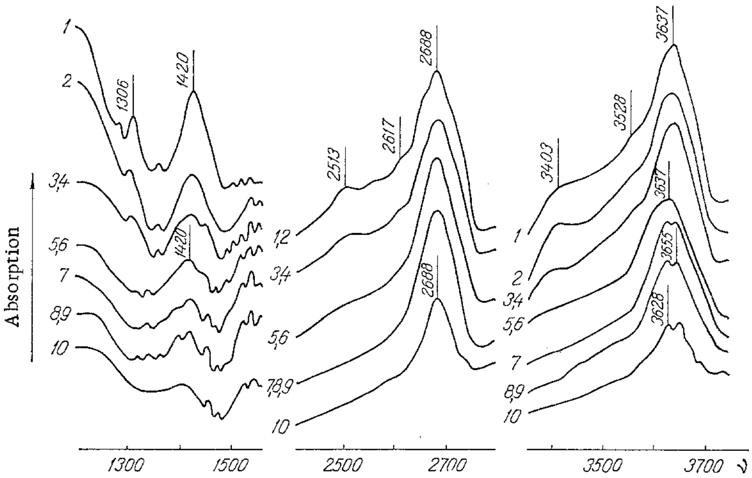

Fig. 2. Change in the infrared spectra of deuterated Fe-montmorillonite during desorption: 1) moisture content 5.4%; 2) 6.3; 3) 4.5; 4) 3.6; 5) 3.3; 6) 2.9; 7) 1.4; 8) 1.3; 9) 0.79; 10) about 0.1%.

However, it must be noted that, in selecting the force constants, we took their probable mean values. These values in part determine the energy of the hydrogen bond. The value selected for the force constant of the hydrogen bond itself, $0.22 \cdot 10^6$ cm^{-2}, corresponds to a bond energy of 5 kcal/mole. At the same time, the differential heat of adsorption of water observed experimentally on Ca-montmorillonite [3] and on the hydrated surfaces of several oxides (TiO_2, SiO_2) [4] at low values of surface coverage is close to 20 kcal/mole. Such an increase in adsorption energy is usually explained by the interaction of water molecules with exchange cations or coordination-unsaturated atoms of Si or Al of the crystalline lattices. According to [2], this bond energy corresponds to a force constant of $0.9 \cdot 10^6$ cm^{-2}, and a force constant for the bond angles of $0.06 \cdot 10^6$ cm^{-2}. Calculations showed that the deformational vibration frequency of D_2O molecules in an asymmetrical group is equal to 1262 cm^{-1} at the new force constants, which is close to the values seen in experiments. It was shown in [1] that only a frequency of 1300 cm^{-1} is seen on infrared spectra 1, 2, and 3 in the deformational vibration region in the initial periods of dehydration of the natural form of montmorillonite (change in moisture content from 13 to 10%). This frequency results in the presence of associations of water molecules coordinated around exchange cations or other active centers on the surface. The calculated deformational vibration frequency of D_2O in such symmetrical groups at force constants corresponding to a hydrogen bond energy of 5 kcal/mole was 1300 cm^{-1}, which agrees exactly with the frequency seen in experiments. It must be noted that the calculations were based on the same principles as outlined in [1].

Frequencies of 1264 and 1304 cm^{-1} are observed for the Al-form of montmorillonite (Fig. 1). By analogy with the natural form, these frequencies correspond respectively to asymmetrical and symmetrical groups of D_2O molecules. However, together with these frequencies, there is a relatively intense and stable (with respect to dehydration processes) band in the region of 1428 cm^{-1}. It is easily shown that this frequency corresponds to deformational vibrations of HDO molecules, and that the appreciable energy of interaction with the surface of the solid phase (final desorption occurs in a deep vacuum and at a temperature of 350°C) results in the presence of asymmetrical adsorption bonds.

Knowing the analytical formulas for elements of the kinematic coefficient matrix [1] and taking as a first approximation for the valence-angle and valence-bond force constants the values obtained for an isolated water molecule, we may obtain the experimental deformational vibration frequency by varying the force constants for the donor-acceptor bond between the oxygen atom of the water molecule and active centers on the surface of the solid phase—particularly Al^{+3} exchange cations. For the Al-form of montmorillonite, the bond force constant turns out to have a value of $4.1 \cdot 10^6\ \mathrm{cm}^{-2}$. For Fe-montmorillonite, the mean statistical frequency of the HDO deformational vibrations corresponds to 1420 cm^{-1} (Fig. 2) and the bond force constant is $3.3 \cdot 10^6\ \mathrm{cm}^{-2}$.

Let us return to the frequencies observed in the region of valence vibrations of water molecules.

For the natural form of montmorillonite (as was shown in [1]), in the region 2500-2700 cm^{-1}, the frequencies 2680 and 2610 cm^{-1} are the most stable during dehydration processes.

It is logical to assume that these frequencies determine the vibrations of the OD group in an isotopic water molecule in asymmetrical associations and the appearance of the second maximum in the range 3500-3700 cm^{-1} (frequency 3534 cm^{-1}) indicates the presence of HDO molecules in the latter.

The main idea behind analyzing the frequencies of valence vibrations is determining the force constants of OD- and OH-bonds.

The force constants of these bonds in a molecule are calculated from the formula (complete analogy with the calculation of the frequencies of deformational bonds)

$$\nu^2_{q_nq_n} = D_{q_nq_n} + \sum_{n \neq m} \frac{D_{q_nq_m} D_{q_mq_n}}{D_{q_nq_n} - D_{q_mq_m}}, \tag{1}$$

where $D_{q_nq_m}$, $D_{q_nq_n}$; $D_{q_mq_n}$, $D_{q_mq_m}$ are the coefficients of the total interaction; Eq. (1) was obtained by El'yashevich [5] on the basis of the properties of the secular equation under the condition that $[D_{q_nq_m}] \ll [D_{q_nq_n} - D_{q_mq_m}]$.

The coefficients of the total interaction were found as follows:

$$\begin{gathered} D_{q_mq_n} = \sum_{\lambda=1}^{r} A_{q_nq_\lambda} K_{q_\lambda q_n};\ D_{q_nq_m} = \sum_{\lambda=1}^{r} A_{q_nq_\lambda} K_{q_\lambda q_m}; \\ D_{q_mq_n} = \sum_{\lambda=1}^{r} A_{q_mq_\lambda} K_{q_\lambda q_n};\ D_{q_mq_m} = \sum_{\lambda=1}^{r} A_{q_mq_\lambda} K_{q_\lambda q_m}, \end{gathered} \tag{2}$$

where $A_{q_nq_\lambda}$, $A_{q_mq_\lambda}$ are elements of the matrix of kinematic interaction coefficients; $K_{q_\lambda q_n}$, $K_{q_\lambda q_m}$, elements of the force-constant matrix.

The force constants of OD bonds of D_2O molecules in an asymmetrical group can also be calculated on the basis of Eq. (1), but (as shown by analysis) the absolute difference between the quantities $D_{q_1q_1}$ and $D_{q_2q_2}$ is close to $D_{q_1q_2} \cdot D_{q_2q_1}$. Thus, in the present case, the frequencies and force constants should be determined on the basis of the solution of the simple secular equation

$$\begin{vmatrix} D_{q_1q_1} - \nu^2 & D_{q_2q_1} \\ D_{q_2q_1} & D_{q_2q_2} - \nu^2 \end{vmatrix} = 0, \tag{3}$$

ignoring the contribution of the diagonal and nondiagonal total-interaction coefficients of other bonds.

In determining the total-interaction coefficients, we did not take into account the products of force constants and kinematic bond coefficients which yielded trivial corrections.

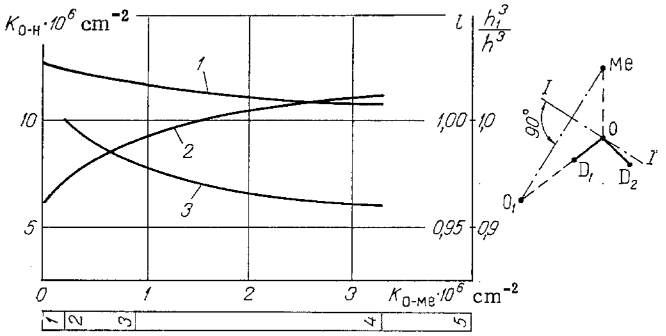

Fig. 3. Dependence of the force constant of a valence bond K_{OD_2} or K_{OH_2} (curve 1), the length of this bond l (Å) (curve 2), and the relative density of the substances h_1^3/h^3 distributed in the volume of adsorbed molecules forming asymmetrical groups on the surface of a clay mineral (curve 3) on the force constant of a donor-acceptor bond K_{O-Me}: 1) parameters corresponding to isolated molecules of H_2O; 2) isolated dimers of H_2O; 3) adsorbed molecules of H_2O on natural (Ca-form) montmorillonite; 4) same, on Fe-form montmorillonite; 5) same, on Al-form montmorillonite.

Varying certain values of the diagonal and nondiagonal force constants for the frequencies found experimentally, we computed values of these constants that simultaneously satisfy the existence of asymmetrical HDO and D_2O groups. These values turned out to be as follows: natural form $K_{q_1q_1} = 12.38\cdot 10^6$ cm^{-2}, $K_{q_2q_2} = 11.8\cdot 10^6$ cm^{-2}; $K_{q_1q_2} = 0.1\cdot 10^6$ cm^{-2}; Fe-form $K_{q_1q_1} = 12.45\cdot 10^6$ cm^{-2}; $K_{q_2q_2} = 10.9\cdot 10^6$ cm^{-2}; $K_{q_1q_2} = 0.1\cdot 10^6$ cm^{-2}. The absence of a maximum in the region of 3500 cm^{-1} on the contour of the band of valence vibrations made it impossible to calculate the force constants of valence bonds of HDO and D_2O molecules adsorbed on Al-montmorillonite.

Figure 3 shows the dependence of the force constant of a valence bond (hydrogen which does not react with other atoms) and the length of this bond on the force constant of a donor-acceptor bond of an oxygen atom of a water molecule with an active center on the surface of the clay mineral. The change in bond length was evaluated on the basis of the following equation, obtained from [6]:

$$\frac{K(O-D)}{K(O-D)_0} = \frac{l_0^3}{l^3}, \qquad (4)$$

where $K_{(O-D)_0}$ is the force constant and l_0 is the length of the O–D bond in an isolated water molecule ($K_{(O-D)_0} = 12.87\cdot 10^6$ cm^{-2}, $l_0 = 0.96$ Å).

Further analysis of the results of the infrared spectrometric studies were connected with an attempt to prove the existence of the effect of a change in the density of adsorbed water in different groups. It is readily seen (Fig. 3) that the change in volume associated with a single molecule of water adsorbed on two active centers on the surface of a clay mineral such as O_1–Me (Me represents the position of any exchange cation or other active center) depends on the change in projections of the lengths of the chemical bonds in a direction perpendicular to lines connecting the O_1–Me centers, i.e., is proportional to the change in the value of h_1^3/h^3 where h_1 is the projection of the length of the chemical bonds of a water molecule with a force constant equal to $0.22\cdot 10^6$ cm^{-2}, i.e. (in accordance with [2]), a bond energy equal to 5 kcal/mole. The O–Me spacing is 1.77 Å. This corresponds to the structure of liquid water with a density of 1.0 g/cm^3.

It can be seen from Fig. 3 that the density of combined water, forming asymmetrical groups, adsorbed on the natural form of montmorillonite corresponds to 0.96 g/cm^3. It must be noted here that we have yet to obtain data on the distribution of the density of adsorbed water in such a system with allowance for deformation of the crystalline lattice under the influence of both the water molecules and molecules of organic compounds.

However, measurements made for the natural form of Glukhov kaolinite using nitrobenzene and toluene with allowance for lattice strains established that the density of adsorbed water at low values of surface

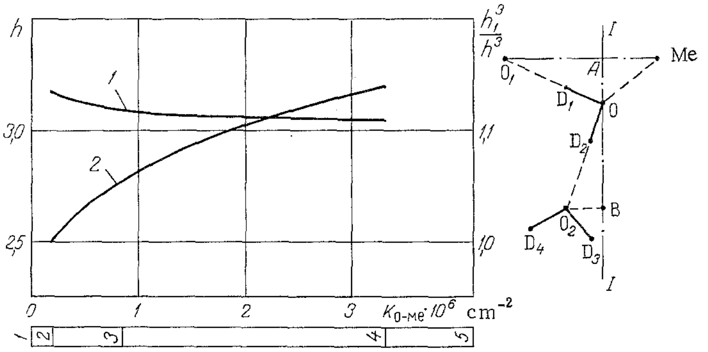

Fig. 4. Dependence of projection of lengths of chemical bonds in the direction I–I h (Å) to the second layer of adsorbed molecules (curve 1) and the relative density of the substance distributed in the volume of the dimers (2) on the force constant of a donor-acceptor bond K_{O-Me}: 1-5) same as in Fig. 3.

coverage (to 0.4% moisture content) was 0.96 g/cm^3. This moisture content corresponds to the formation of asymmetrical groups.

Let us examine the case of the interaction of a water molecule with an already-adsorbed molecule (Fig. 4). A similar problem was solved for the example of an Li^+ ion. It was shown that for the structure depicted in Fig. 4, the $O-O_2$ spacing in the group $(H_2O)_2$ decreases compared to the free dimer (from 3.0-2.7 Å) and the energy of the hydrogen bond increases from 5-8 kcal/mole.

For an $F^- 2\cdot H_2O$ system, the change in the length of the $O-O_2$ bond in the $(H_2O)_2$ dimer under the influence of the F^- ion amounts to about 8%, while the hydrogen bond energy increases by 8 kcal/mole, i.e., in both cases the ions induce a redistribution of electron density in the $(H_2O)_2$ system such that the hydrogen bond within is made stronger compared to the case of an isolated water-molecule dimer.

We propose a somewhat different method for evaluating the change in the energy and length of the $O-O_2$ bond (Fig. 4) in dimers coordinated near exchange ions adsorbed on clay minerals.

According to [7], the hydrogen bond energy in the interaction of two water molecules may be represented as follows:

$$U_{H-O} = D\{1 - \exp[-n(r - r_0)]\}^2 - D, \tag{5}$$

where r_0 is the D_2-O_2 spacing (Fig. 4); $-D$ is the energy corresponding to the minimum of the potential curve (Morse curve).

According to the data in [2] and other works, $r_0 = 1.77$ Å, the force constant of the bond is $0.22\cdot 10^6$ cm^{-2}, and $D \approx 5$ kcal/mole.

Let us change Eq. (4) over to such a form:

$$\frac{U_{H-O}}{-D} = -\{1 - \exp[-n(r - r_0)]\}^2 + 1.$$

But $U_{H-O}/(-D)$ can be replaced by the ratio $(\nu - \nu_0)/(-\nu_1 + \nu_0)$, where ν_0 is the frequency of the vibrations of the O–H (or O–D) bonds in an isolated water molecule; ν_1, frequency of the vibrations of the O–H (or O–D) bonds of a water molecule in a dimer coordinated close to active centers on the adsorbent. Then we write Eq. (5) in the final form:

$$\frac{\nu - \nu_0}{\nu_0 - \nu_1} = -\{1 - \exp[-n(r - r_0)]\}^2 + 1. \tag{6}$$

To select parameter n, the authors of [7] examined a linear configuration of two water molecules (similar to the case in Fig. 4) and averaged the energy of the electrostatic interactions with the rotation of one of the molecules about the $O-O_2$ axis. The charges on the atoms were chosen by breaking down the dipole moment

(0.323e for H and 0.646e for O). Comparing the family of Morse curves corresponding to different values of n with the curve obtained by averaging the electrostatic interactions, the authors showed that satisfactory agreement is obtained at $n = 5$.

This value will also be used here in subsequent calculations. In these calculations, we used the cophasal frequencies of water molecules in different groups: ν_0 for D_2O, in accordance with [2], was assigned a value of 2671 cm^{-1}; ν_0 was determined from the solution of Eq. (3), and the force constant K_{O-D_2} was found from curve 1 (Fig. 3) at $K_{O-Me} = 0.22\cdot10^6$ cm^{-2}; K_{O-D_2} corresponds to a value of $12\cdot10^6$ cm^{-2}; $K_{O-D_1} = 12.40\cdot10^6$ cm^{-2}.

Thus, we determined all of the values needed to calculate r from Eq. (6) (this is the D_2-O_2 spacing in Fig. 4).

The results of the calculations are shown in curve 1 in Fig. 4 in the form of the total projection of the lengths of the chemical bonds (A–B) to the oxygen atom O_2 of the second molecule. Curve 2 shows the density of the substance distributed within the volume of dimers of water molecules coordinated close to active centers on the surface of the mineral.

The density of adsorbed water in such groups turns out to be 1.06 g/cm^3 for the natural form of montmorillonite and 1.15 g/cm^3 for the Fe-form. Here, it is necessary to note that for the measurements made for the natural form of Glukhov kaolinite using nitrobenzene and toluene with allowance for lattice deformation, the density of the combined water (with surface coverage from 0.4 to 2% of the moisture content, i.e., to complete blockage of the active centers) was determined in the form of a monotonic function with the maximum 1.22 g/cm^3.

Thus, calculations for model structures of two types of groups have confirmed that there exists a density of adsorbed water which differs appreciably from the density of water in the liquid state.

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MASS-TRANSFER CHARACTERISTICS OF BULK ORGANIC MATERIALS BY MASS-SPECTROMETRIC ANALYSIS

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and F. D. Braterskii

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The mass-spectrometric method was used to analyze the mass transfer characteristics of bulk materials, using seed being subjected to heat treatment as an example. The resulting data are used to propose temperature limits for the safe heating of seed while preserving its sowing qualities.

Complex, multicomponent gaseous systems are analyzed by the mass-spectrometric method, which makes it possible to investigate all classes of organic compounds. A small amount of the substance is needed

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