dimensionless complex; $r_s = q/(v_s\rho)$, heat of sublimation; c_p, specific heat at constant pressure; T_s, temperature at the subliming surface; $T = T^*/T_s$, dimensionless temperature; $a = \lambda/(c_p\rho)$, thermal diffusivity; λ, thermal conductivity; ν, kinematic viscosity.

LITERATURE CITED

1. P. A. Novikov and B. M. Smol'skii, "Influence of mass transfer on the heat transfer during sublimation in a rarefied gaseous medium for Couette flow," Inzh.-Zh. 12, No. 4, 433-439 (1967).
2. V. F. Getmanets and R. S. Mikhal'chenko, "Heat and mass transfer in plane channels in conditions of gas injection from a subliming surface," in: Hydrodynamics and Heat Transfer in Cryogenic Systems [in Russian], Naukova Dumka, Kiev (1977), pp. 24-36.

DENSITY OF ADSORBED WATER IN DISPERSED SYSTEMS.
II. MONTMORILLONITE

P. P. Olodovskii

UDC 541.123.31

The density has been determined for water adsorbed on montmorillonite from the changes in density in the dispersion medium and in the lattice deformation in the solid phase.

The density distribution has been derived for hydrated montmorillonite (Fig. 1) for critical mass of the adsorbent (here 2 g) as measured with nitrobenzene, and the change in volume of the unit cell during adsorption has also been measured in water and nitrobenzene (given in [1]), which enables one to calculate the density d_w of the adsorbed water as follows:

$$d_w = \frac{0.01\,(P - P_0)\,d_0 d \dfrac{V_0}{V_i}}{0.01 P d_0 \dfrac{V_0}{V_i} + d_0 \dfrac{V_0}{V_i} - d}, \tag{1}$$

where P is the water content in %; P_0, amount of water corresponding to the first adsorbed molecules, where the density change in the dispersion medium has not yet occurred, and in our case $P_0 = 1\%$; d_0 and d, densities of the adsorbent measured at P_0 and P correspondingly; and V_i and V_0, unit-cell volumes measured at P and P_0 in the adsorption of water and organic compounds.

An essentially new situation is introduced with P_0 into the calculation of the adsorbed-water density. It should be noted that $P_0 = 0$ for some adsorbents. For example, this parameter was not introduced in [2] in estimating the density of water adsorbed on kaolinite, although in an earlier study [3] concerned with the density of water adsorbed on montmorillonite, the estimates were made without allowance for the lattice deformation, and the total mass of water was reduced by P_0 (it was there denoted by P_h), but no adequate basis for this was given.

In fact, the density of the adsorbed water in (1) is referred to the mass $(P - P_0)$, i.e., it assumed that all the water is divided into two separate components at any level of content; 1) the initial groups firmly bound molecules with mass P_0, which are not adsorption centers for the subsequent molecules, and 2) all subsequent molecules with mass $(P - P_0)$, which form a single ensemble in the sorption.

Central Research Institute for Comprehensive Water-Resource Use, Ministry of Water of the USSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 6, pp. 938-942, June, 1984. Original article submitted Februrary 3, 1983.

0022-0841/84/4606-0676$08.50

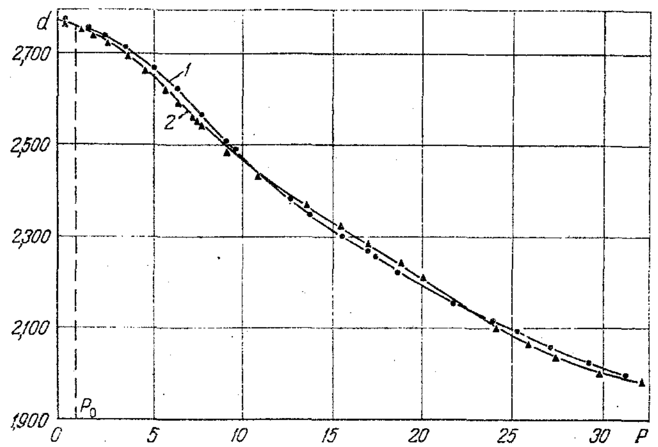

Fig. 1. Dependence of the density d (g/cm³) of a natural form of montmorillonite (Crimean fuller's earth) measured in nitrobenzene on the amount of adsorbed water P (%) for various m/v ratios: 1) m/v = 0.0131 g/cm³; 2) 0.133.

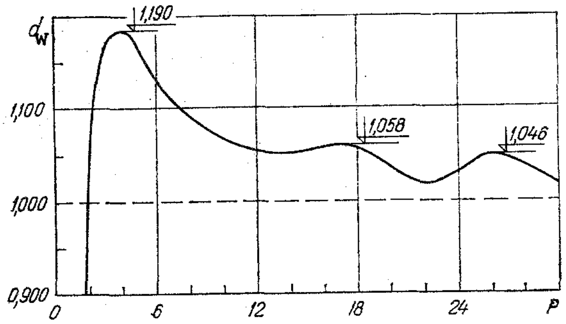

Fig. 2. Dependence of the density d_W of water adsorbed on a natural form of montmorillonite on the amount P.

The existence of two unrelated groups has been demonstrated in various ways.

The IR spectra of water adsorbed on varion ion-substituted forms of montmorillonite reveal several types of complex [4]. The deformation vibrations indicate the structure of these complexes, which varies during hydration or dehydration, and at low degrees of surface filling there are always at least two ways in which the molecules are attached to the active centers.

Calculations on montmorillonite lattice deformation [1] have shown that dimers are formed at 2/3 of the active centers in the adsorption of water (these centers are oxygen atoms and OH groups), which lie in (100) planes, while rigidly bound single water molecules are attached at 1/3 of these centers. However, the most reliable evidence for two unrelated groups of water molecules has been derived from estimates of the activation energies and correlation times provided by nuclear magnetic resonance.

These results for γ-Al_2O_3 will be presented in forthcoming papers.

Figure 2 shows how the density of water adsorbed on a natural form of montmorillonite varies with the amount. There are three distinct regions: the first at 1.0-11% water content with its maximum at 1.19 g/cm³, the second in the range 11-22% with its maximum at 1.058 g/cm³, and the third at 22-32% with its maximum at 1.046 g/cm³.

We used diffractometer data to estimate the lattice deformations and IR data in order to interpret these results.

Consider the first region. According to the IR data [4], the energy of the O—Me bond affects the sum of the projections of the lengths of the bonds in the water molecule on the direction perpendicular to the line joining the centers when a water molecule is adsorbed at two active centers: an exchangeable cation (or hydroxyl group) and an oxygen atom, and it is always somewhat greater than the sum of these projections for a weak hydrogen bond of energy 5 kcal/mole.

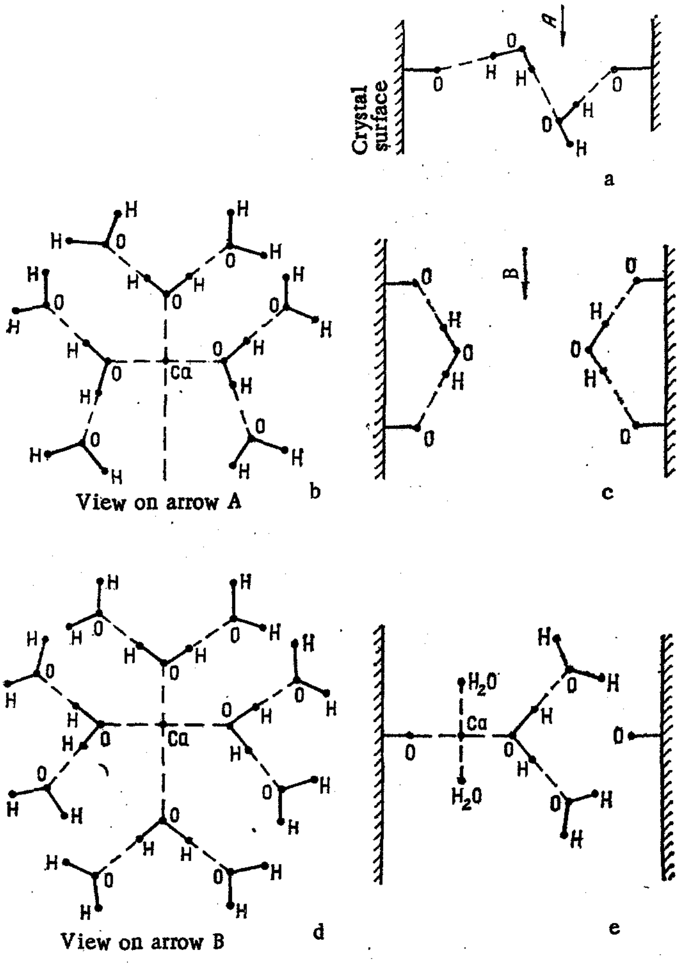

Fig. 3. Schemes for the adsorption of water molecules on montmorillonite.

If we assume that the cube of the sum of the bond length projections is proportional to the volume taken up by the adsorbed molecules forming chains of unsymmetrical complexes, it is readily shown that the density in these complexes will always be somewhat less than the ordinary density of liquid water. Here we should note that the calculated density for the bound water forming unsymmetrical complexes on montmorillonite is 0.98 g/cm^3 [4], while the average measured density is 0.975 g/cm^3 in the range 1.5-3% water, where the water molecules are sorbed mainly at OH groups and oxygen atoms. However, at 3% content the value is d_W = 1.167 g/cm^3, as is evident from the lattice deformations, which show that the preferred sorption at two centers in the range 1.5-3% is accompanied by the deposition of H_2O at single OH groups.

The IR data indicate that the energy of adsorption at a single center is less than that at two centers, and therefore there is a reduction in the stretching of the H_2O bonds and also a reduction in the volume occupied. The subsequent sorption involves dimers. The exchangeable cations or OH groups induce a shift in the electron-density distribution in the $(H_2O)_2$ system [4] such that the hydrogen bond in it is strengthened by comparison with an isolated dimer.

The vibration frequencies of the O–H or O–D bonds in isolated water molecules have been used together with the values for water molecules in the dimers coordinated near active centers and the values calculated for isolated dimers on the basis of a Morse potential for the interaction between the two molecules, and this was given the distance between the oxygen atoms in a dimer coordinated near active centers. It is obvious that the distance should be less than that in ordinary water.

Calculations have been reported [4] on the sum of the projections of the bond lengths to the oxygen atom in the second molecule and on the density of the material distributed as dimers.

The density of the adsorbed water in such complex in the natural form of montmorillonite is 1.06 g/cm^3, while it is 1.15 g/cm^3 for the Fe form.

The maximum adsorbed density found by experiment corresponds to 4% content and is 1.19 g/cm^3, and at this water content the molecules form dimers in (100) planes [1].

Further uptake (over 5%) reduces the density and arises because the water molecules are attached to oxygen atoms in the spaces between the packets. The lattice deformations indicate that various water-molecule ensembles are formed in the interpacket spaces in montmorillonite.

At contents of 6-9%, the water molecules are adsorbed as shown in Fig. 3a, and the water structure is represented by dimers, but of a type different from those in the (100) planes.

Each molecule forms a single hydrogen bond to each of the oxygen atoms in the lattice, and it is evident that the bond energy between the molecules in such a dimer is substantially less than that in the dimers on (100) planes, and consequently the distance is larger than in the latter. This accounts for the fairly marked shift in the density for water adsorbed on (100) and (001) planes.

At contents of 9-18%, the water molecules are coordinated near exchangeable cations, and at the end of this range (18%) they form complexes as in Fig. 3b, where the density attains a second maximum. Here in essence one again has dimers, but now of a third type. The oxygen atoms in the water molecules form donor—acceptor bonds with the lattice exchangeable cations. The bond energy and distance between the water molecules take intermediate values (by comparison with dimers of the first and second types).

At contents of 19-23%, a second stage in the adsorption at the oxygen atoms sets in (Fig. 3c), i.e., each of the additionally adsorbed molecules forms two hydrogen bonds to the lattice. The lattice deformation indicates that in this stage there is a sudden increase in the interplanar distance. Consequently, the distances between the water molecules along a line perpendicular to the (001) planes joining the oxygen atoms will be larger than the distances between the oxygen atoms in the dimers. It is clear that this circumstance is responsible for the second minimum of 1.019 g/cm^3 on the density curve in the region of 22% water content.

In the range 23-30%, the additionally adsorbed water molecules are again coordinated near the exchangeable cations and constitute the complexes shown in Fig. 3d and e. The density in the complexes formed as in Fig. 3d represents the third maximum of 1.046 g/cm^3 (in the region of 26.5%).

One assumes that the energy gradually decreases in the successive formation of the coordination bonds between the water molecules and the exchangeable cations, which means that the hydrogen bonds weaken and the distances between the molecules in the dimers increase. This explains the gradual decrease in the water density for complexes formed in the succesive stages of cation hydration, and in particular on passing from adsorption as in Fig. 3d to that as in Fig. 3e (in the range from 26 to 32%).

Therefore, the density data for water adsorbed on montmorillonite can be interpreted from estimates of the changes in the energies of the hydrogen bonds between the molecules within adsorbed complexes and from the energies of the bonds between the complexes and the active centers.

These results provide a better understanding of the lattice deformation and of the bound-water structure.

LITERATURE CITED

1. P. P. Olodovskii and L. A. Malkova, "A study of the structural parameters in surface layers in dispersed systems from estimates of the lattice deformation and dispersion-medium density. Part 1," Inzh.-Fiz. Zh., 46, No. 5, 746-754 (1984).
2. P. P. Olodovskii, "The density of adsorbed water in a dispersed system," Inzh.-Fiz. Zh., 40, No. 4, 711-716 (1981).
3. P. P. Olodovskii, "The effects of surface properties in a hydrated solid phase on the density change in the dispersion medium," Inzh.-Fiz. Zh., 32, No. 3, 449-457 (1977).
4. P. P. Olodovskii, "Evaluating the structure changes in adsorbed water in dispersed systems during hydration by means of IR spectoscopy," Inzh.-Fiz. Zh., 40, No. 3, 447-454 (1981).