liquid filtration coefficient; a_m, diffusion coefficient for moist bodies; a_m^T, thermal diffusion coefficient; $k_{b,n}$ filtration coefficient; h_n, specific enthalpy of vapor; h_b, specific enthalpy of liquid; S_{sp}, specific entropy of vapor; S_{sp}^b, specific entropy of liquid; c_p^n, specific heat of vapor; c_p^b, specific heat of liquid; σ_n, σ_b, saturation by vapor and liquid; V_n, V_b, specific volumes of vapor and liquid; ρ_n, vapor density; η_n, η_b, viscosity of vapor and liquid; k_n, k_b, permeability coefficients of vapor and liquid; μ, molecular weight of liquid; μ_n, μ_b, chemical potentials in vapor and liquid phases; β, mass transfer coefficient; α_n, heat-transfer coefficient.

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DENSITY OF ADSORBED WATER IN DISPERSE SYSTEMS

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UDC 541.182

On the basis of the existence of the effect of changing density of a dispersing medium and taking into account the crystal lattice deformation of the solid phase, the article determines the density of water adsorbed on kaolinite.

Among the wide-ranging investigations concerning the study of adsorbed water, there are relatively few works in which an attempt was made to determine the density of such water. This situation is due to the fact that the existing methods of experimentally measuring the density of adsorbed water, based on the use of various dispersing media (gases, liquids), did not take into account some phenomena (effects) originating in the surface layers of the disperse system. Among these effects are:

a) a change in the density of the dispersing medium under the effect of the solid phase and of the adsorbed water;

b) crystal lattice deformation of the solid phase under the effect of the water molecules and of the molecules of the dispersing medium;

c) the influence of the molecules of the dispersing medium on the structure of the adsorbed water.

We measured these effects and took them into account when devising a method of determining the density of adsorbed water.

The object of investigation was Glukhovetsk kaolin in its natural form.

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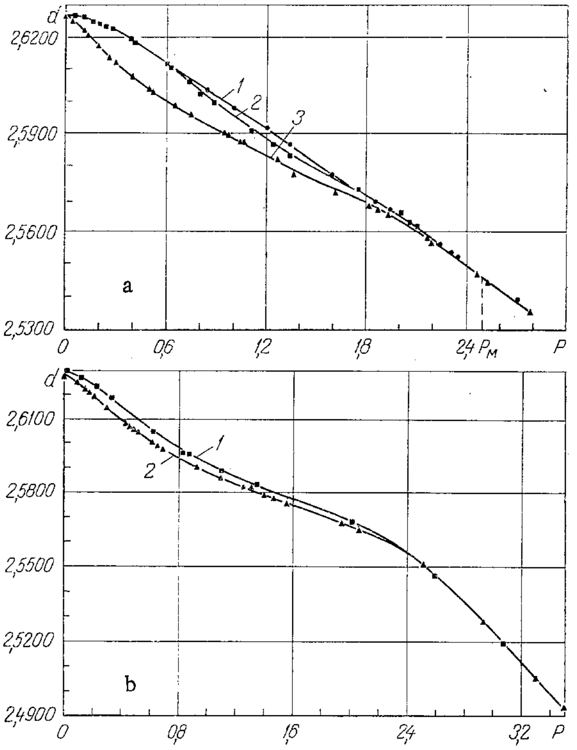

Fig. 1. Dependence of the density of the natural form of Glukhovetsk kaolin d (g/cm^3) measured in nitrobenzene (a) and toluene (b) on the amount of adsorbed water P(%) for different ratios m/V: for a) 1) m/V = 0.136 g/cm^3; 2) 0.205; 3) 0.027; for b) 1) m/V = 0.136 g/cm^3; 2) 0.027.

The first stage of the work consisted in determining the density of the dehydrated adsorbent d_0 in liquids having a zero effect of changing their density, which means that in such liquids, the density of the solid phase does not depend on its mass. For the natural form of kaolin we found that liquids with zero effect are nitrobenzene and toluene. According to the data of numerous measurements, the mean density of dehydrated kaolin in nitrobenzene was 2.6270, in toluene 2.630 g/cm^3.

At the second stage we determined the density of the hydrated adsorbent in dependence on the moisture content of the specimen and its mass. The method of the experimental measurements was explained in [1] but, like in [2], the interaction of the particles of the solid phase with the walls of the picnometer was taken into account. On the basis of curves of the change of the optical density of water dissolved in nitrobenzene and toluene and the relative density ρ_c/ρ_H of these systems vs. water content (ρ_c is the density of the dehydrated organic substance, ρ_H is the density of the substance with a certain water content), plotted with the aid of an IKS-22, we calculated the amount of adsorbed water passing from the kaolin into the liquid or from the liquid into the adsorbent. The results of the experimental investigations are presented in Fig. 1a, b. It can be seen from the figure that there is a clear division density for any concentration of the adsorbed water molecules in dependence on the mass of the adsorbent or on the ratio m/V (m is the mass of the dehydrated adsorbent; V is the volume of the disperse system).

On the other hand it was found that the ratio m/V = 0.027 g/cm^3 (weight of the powder 2 g, curve 3 in Fig. 1a and 2 in Fig. 1b) is the "critical" ratio for such division, i.e., with smaller values, m/V = 0.014 g/cm^3 (mass 1 g), there is no decrease in density of the hydrated specimen for any concentration of the water molecules.

The relative change of the density of the dispersing medium was calculated by the formula

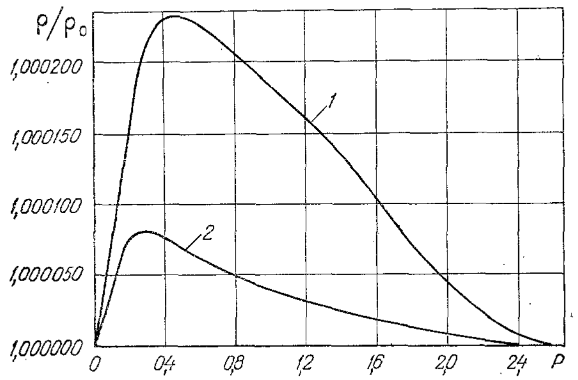

Fig. 2. Change of the relative density of the dispersing medium (1) nitrobenzene, 2) toluene) in dependence on the amount of water adsorbed on the natural form of Glukhovets kaolin.

$$\frac{\rho}{\rho_0} = \frac{\left(d - \frac{m}{V}\right) d_0'}{\left(d_0' - \frac{m}{V}\right) d}, \tag{1}$$

ρ/ρ_0 is the relative change of the density of the dispersing medium; d_0' is the density of the hydrated specimen, and ρ_0 is the density of the liquid corresponding to the mass of the solid phase, equal to the "critical" one; d is the density of the hydrated specimen, and ρ is the density of the liquid corresponding to the mass of the solid phase, larger than the "critical" one. The results of the calculation are presented in Fig. 2. Curves 1 and 2 merge at the point corresponding to 2.5% bound water. It can be demonstrated that this amount corresponds to the complete covering of the active centers of the surface with adsorbed water.

We will examine the possible mechanisms of adsorption of the dispersing medium explaining the origin of the second effect. As an example we take nitrobenzene with which this effect manifests itself more intensively.

The first boundary condition is P = 0. The surface is completely dehydrated. The distance between the active centers, i.e., the hydroxyl groups, and the oxygen atoms does not exceed 3 Å.

Because the nitrobenzene molecule contains the NO_2 group (a typical electron acceptor), the distribution of the electron density at all the six carbon atoms is not equal. The excess negative charge in the basic state of the molecule is concentrated at the carbon situated next to the NO_2 group, and at the other five carbon atoms this charge is positive. When all the free vacancies (active centers) are on the surface of the crystal lattice, the stablest state of the adsorbed nitrobenzene molecule is determined by the parallel orientation of the plane of the benzene ring relative to the plane of the spatial elementary kaolinite cell (the charge is transferred to the benzene ring as well as drawn back to the crystal lattice).

With such a state of the adsorbed molecules (according to the data of x-ray structural investigations [3]), six nitrobenzene molecules are located on the six elementary planes of the lattice.

At the first stage of hydration, moisture content is up to 0.4%. The water molecules are firmly attached to the surface which is situated directly on two centers, the hydroxyl groups and the oxygen atoms of the crystal lattice. The nitrobenzene molecules are adsorbed on the free OH-groups and oxygens, and they can orientate themselves only vertically by the plane of the benzene ring relative to the surface.

According to the data of x-ray structural investigations [3], to this state of absorption corresponds the disposition of 12 nitrobenzene molecules on one elementary spatial kaolinite cell. It can be seen from Fig. 2 that with a moisture content of 0.4%, the increase of the density of the dispersing medium attains its maximum.

The subsequent stages of hydration from 0.5 to 2.5% moisture content are determined by the sorption of water molecules on the free centers through single bonds, and also on the adsorbed water molecules. At these stages the nitrobenzene molecules are successively dislodged from the surface of the layer, and this also determines the gradual approach (degene-

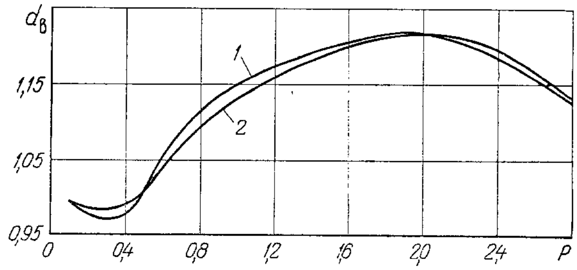

Fig. 3. Dependence of the density of water adsorbed on natural kaolinite d_B on its amount P, obtained with a view to the deformation of the crystal lattice under the effect of molecules of water and organic compounds (1) results with use of nitrobenzene, 2) with toluene).

ration of the second effect) of the density of the dispersing medium to the density of the pure liquid.

An analogous change in the second effect is obtained from an evaluation of the deformation of the crystal lattice under the influence of the water and nitrobenzene molecules [3].

The density distribution of the hydrated kaolin, obtained for the critical mass of the adsorbent (in this case a mass of 2 g), measured with the use of nitrobenzene and toluene, and also the found change in the volume of the elementary cell in the adsorption processes of water and toluene as well as of water and nitrobenzene, enabled us to calculate the density of the adsorbed water in the following way:

$$d_{\text{в}} = \frac{0.01Pd\, d_0 \dfrac{V_0}{V_i}}{0.01P\, d_0 \dfrac{V_0}{V_i} + d_0 \dfrac{V_0}{V_i} - d}, \qquad (2)$$

where d_B is the density of the adsorbed water; P, content of adsorbed water, %; d_0, density of the dehydrated adsorbent; V_i and V_0, volume of the elementary kaolinite cell measured with P and $P \to 0$, respectively, during the process of adsorption of nitrobenzene and toluene [3]. The results of the calculation are presented in Fig. 3. The maximum difference in the density of the water (with the same mass), determined with the use of toluene and nitrobenzene, was 0.9%.

On the graph of the function $d_B = f(P)$ we can distinguish two regions: the first one in the range of moisture contents 0-0.5, where $d_B \leqslant 1$ g/cm^3, with a minimum equal to 0.975 g/cm^3, and the second one in the range 0.5-2.5%, with the maximum 1.22 g/cm^3 for P = 2%.

To interpret the obtained results, we use the analysis of the diffractometric measurements to evaluate the deformations of the crystal lattice [3] and the data of IR spectroscopy of the adsorbed water [4].

According to the IR spectroscopic investigations, in the adsorption of water molecules on two active centers of the crystal lattice (the exchange cation (or hydroxyl group) and the oxygen atom), the sum of the projections of the lengths of the chemical bonds of the water molecule on the direction perpendicular to the line connecting the centers depends on the energy of the O–Me bond, and it is always somewhat larger than the sum of these same projections but with the weak hydrogen bond with an energy of 5 kcal/mole.

If we assume that the volume per adsorbed water molecule forming chains of asymmetric complexes on the crystal surface is proportional to the cube of the sums of the projections of the chemical bonds, it is easy to demonstrate that the density of the substance in such complexes is always somewhat smaller than the density of ordinary liquid water. Here it should be pointed out that the calculated density of bound water forming asymmetric complexes on the natural form of montmorillonite is equal to 0.96 g/cm^3.

However, it follows from an analysis of the deformations of the crystal lattice of kaolinite that together with the preferential sorption of water molecules on two centers within the first region (0.0-0.5%) of moisture content, it is also assumed that H_2O settles on one OH-group. According to the data of IR spectroscopy, the adsorption energy on one center is smaller than on two, and consequently, the degree of elongation of the valency bonds of H_2O and the volume taken up by it decrease in this case. Therefore already within the first region the density of the bound water, remaining below 1 g/cm^3 during the process of sorption, gradually increases.

The further sorption process is associated with the formation of dimers.

It was already noted in [4] that the exchange cations of the OH-group indicate the redistribution of the electron density in the system $(H_2O)_2$ in such a way that the hydrogen bond in it becomes stronger than a dimer isolated from a water molecule.

Knowing the oscillation frequencies of the O—H (or O—D) bonds in an isolated water molecule, in a water molecule in the dimer, being coordinated near the active centers of the adsorbent, calculating them for the isolated dimer and using the potential Morse function of interaction of two molecules, we calculated the distances between the oxygen atoms in the dimer being coordinated near the active centers. It is perfectly obvious that these distances have to be smaller than in ordinary liquid water.

The results of the calculations in the form of a summary projection of the lengths of the chemical bonds to the oxygen atom of the second molecule and of the density of the substance distributed throughout the bulk of the dimer are presented in [4].

For the natural form of montmorillonite the density of adsorbed water in such complexes was found to be equal to 1.06 g/cm^3, for the Fe-form it was 1.15 g/cm^3.

It should be pointed out that in determining the distances between molecules, the parameter n in the Morse function, in accordance with [5], was taken equal to 5, with smaller values of n (e.g., n = 3, as was done in [6]), the density values are somewhat larger. But it is clear in principle that the structure of the water adsorbed on Glukhovetsk kaolin in the range of moisture contents in the region of its maximum density is represented chiefly by dimers. Further sorption determining the lowering of the density is due to the locking of the water molecules on the adsorbed dimers.

Thus, as the active centers of the surface become filled, there is a gradual transition from the firmly locked molecules sorbed on two centers to water molecules adsorbed through single bonds, and later to dimers. It is perfectly obvious (and is always confirmed experimentally) that dimers are the least stable structure of water.

The notion of the formation of a "monolayer" of water adsorbed on the entire surface of a clayey mineral with nonexpanding crystal lattice is unrealistic. The actual monolayer are only the firmly locked molecules, and at the instant when all active centers are filled, a double layer forms.

At present it is diffucult to predict the possibility of using new notions on the structure of adsorbed water and information on its density. But at least we may point out two regions (problems) of using these results.

The first is the determination of the amount of adsorbed water covering all active centers of the crystal lattice, the calculation of the specific surface of the particles of the solid phase of the soils, and also an estimate of the number of layers of the liquid not taking part in the filtration.

The second is an estimate of the deformation of the soils during their freezing and thawing.

Thus, it may be assumed that another step was made toward understanding the structure of bound water and the mechanism of its sorption.

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COMPLEX OF METHODS, PROGRAMS, AND APPARATUS FOR AUTOMATING THERMOPHYSICAL INVESTIGATIONS

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The article describes a system of automating thermophysical experiments (SATPhE) devised at the Leningrad Institute of Precision Mechanics and Optics. It explains its possibilities as applied to problems of thermophysical investigations.

Systems of automating experimental investigations are at present widely used in various laboratories, among them also thermophysical laboratories. The appearance of these systems and their introduction into research practice was due to a number of causes, among them the increasing complexity of experimental investigations and the endeavors to extract more complete information from the experimental data. The systems of automating experiments develop and progress together with the development of computer and electronic techniques and with increasing complexity of experiments. Construction of these systems is effected in different ways; one of them is the main-line modular principle of construction, which to us seems the most promising one because of its flexibility, ease of adding on to the system and of programming [1]. Particularly convenient is this principle in automating a broad class of problems, when it is necessary to ensure ease of rearrangement of both the instrumental and the program part of the system.

At the Leningrad Institute of Precision Mechanics and Optics (LITMO) work has been carried out for years with automation of investigation of the thermophysical properties of substances, steady-state and pulsating thermal flows, contact thermal resistances, temperature fields, etc., and this led to the devising of a complex of methods, programs, and apparatus for automating thermophysical investigations whose abbreviated designation is SATPhE—LITMO. It is based on the main-line modular principle of construction and the use of Soviet-made desk computers; various programs were prepared to enable the users to process the results of a broad class of thermophysical experiments. The construction of the system by the main-line principle ensures that the system can be easily extended by adding on, or that its composition of the system can be changed during the experiments according to a program fed to the computer. The possibility of changing the composition of the system during experiments is attained by using commands of reference to the given external device, which may be an analog—digital converter (ADC) F-4221, a digital voltmeter F-30, an external memory (EM) with a capacity of 4 kbyte, a curve-drawing recorder PDP-4. The functions of selecting the hardware, and also the function of feeding the information to the computer and of obtaining it from it are realized with the aid of a controller based on microcircuits of the series K-155. A block diagram of the SATPhE—LITMO is shown in Fig. 1.

The basis of the system are two desk computers connected via a mainline expander with the hardware comprising the EM, a digital voltmeter F-30, the ADC F-4221, the curve-drawing recorder PDP-4, connected to the mainline by a digital-analog converter (DAC). The digital

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