CHANGE IN THE DENSITY OF THE DISPERSION MEDIUM IN A SOLID-ADSORBED WATER– LIQUID SYSTEM. CALCULATION OF THE ADSORPTION CHARACTERISTICS OF DISPERSED SYSTEMS

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The influence of adsorbed water molecules on the structure formation of liquids in the surface layers of the solid phase in finely-dispersed systems is considered. A method of calculating the masses of the adsorbed water monolayers and the specific surface areas of particles in various parts of the crystal lattices of minerals is presented.

It was shown in our earlier paper [1] that, during the interaction of finely-dispersed dehydrated solids with various liquids, a change occurred in the density (and hence the structure, i.e., the stacking of the molecules) of the dispersion medium in the surface layers by virtue of a variety of adsorption mechanisms. Thus the adsorption of amines, water, alcohols, and ethers, i.e., oxygen- and nitrogen-containing compounds, on surfaces carrying concentrated positive charges (cations of small radius protonized by the hydrogen atoms of hydroxyl groups, uncompensated charges on parts of the cleavages of mineral-crystal lattices) is a result of the formation of a donor—acceptor bond, and in certain special cases a hydrogen bond, basically representing the interaction of the unshared electron pairs of the oxygen and nitrogen atoms in the adsorbate molecules with the active surface centers. This adsorption mechanism in general creates a compression of the dispersion medium. The interaction of aromatic hydrocarbons, aromatic halogen derivatives, halide alkyls, and alkanes with the surface of the solid phase, however, is mainly determined by the associative or dissociative mechanism of π complex adsorption, and creates an expansion of the dispersion medium. We discovered that liquids with a zero density-change effect could be found for any arbitrary finely-dispersed dehydrated solid. We proposed using these liquids for measuring the density of the adsorbed water, but found that when the liquids interacted with the hydrated surface new phenomena developed; due allowance for these phenomena nevertheless enabled a method of calculating the adsorption characteristics of the systems to be developed. All the experimental and analytical investigations were carried out for natural Glukhovetsk kaolin and the Na form of Crimean fuller's earth. The first stage lay in determining the density of the dehydrated adsorbent in liquids possessing the zero effect. For Glukhovetsk kaolin such liquids included toluene, benzene, ethyl benzene, and paracymene; for the Na form of Crimean fuller's earth nitrobenzene had the same effect. According to the results of many measurements the mean density of dehydrated kaolin equaled 2.6170 g/cm^3, and that of the Na form of Crimean fuller's earth 2.7560 g/cm^3. The second stage lay in determining the density of the hydrated adsorbent in these liquids as a function of the moisture content and mass of the sample.

The method employed for the experimental measurements was analogous to that set out in [1], but allowance was also made for the interaction of the solid-phase particles with the walls of the pyknometer; in every experiment the infrared spectra of the dispersion medium (toluene, nitrobenzene) were recorded in an IKS-22 spectrophotometer, together with the spectra of the same liquids taken from pyknometers not in contact with the solid phase, so as to determine possible absorption due to the adsorbed water.

The experimental results were analysed separately for minerals with expanding and nonexpanding crystal lattices.

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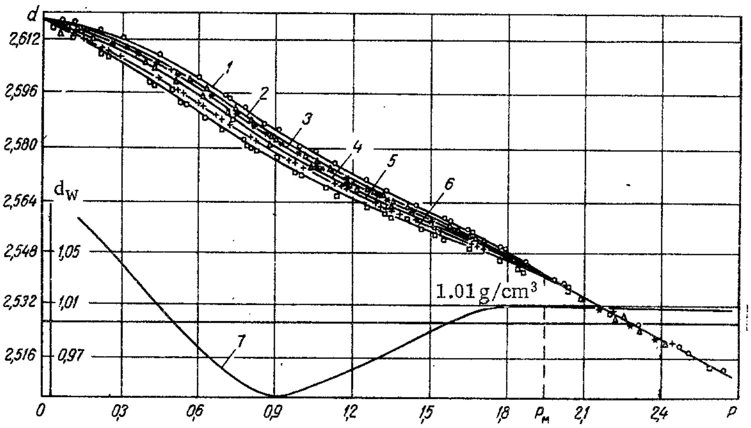

Fig. 1. Density d of natural Glukhovetsk kaolin determined in toluene as a function of the adsorbed water content P for various ratios of the solid phase to the volume of the dispersion system m/V: 1) m/V = 0.158 g/cm^3; 2) 0.105; 3) 0.211; 4) 0.0684; 5) 0.0548; 6) 0.041, 0.0274, 0.0137 g/cm^3; 7) density distribution d_W of the adsorbed water as a function of its mass; d, g/cm^3; P, %.

Minerals with Nonexpanding Crystal Lattices. The results of the experimental investigations are presented in Fig. 1. We see that there is a sharp division in the density of the hydrated kaolin for an arbitrary concentration of adsorbed water molecules, according to the mass of the adsorbent or the m/V ratio (where m is the mass of the dehydrated adsorbent; V is the volume of the dispersion system, the dispersion medium in the present case being toluene). At the same time it was found that the ratio m/V = 0.041 g/cm^3 (mass of powder 3 g, curve 6 in Fig. 1) was "critical" in relation to this division, i.e., for the smaller values m/V = 0.027 g/cm^3 (mass 2 g) and m/V = 0.0137 g/cm^3 (mass 1 g) there was no reduction in the density of the hydrated sample for any concentration of the water molecules. This experimental result is extremely important for calculating the density of the adsorbed water, since there is then no need for extrapolating the values of d to m/V → 0.

Using the results of the measurements presented in Fig. 1, we calculated the relative values of the density of the dispersion medium (toluene) as a function of the mass of adsorbed water in the following way

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

The results of the calculation are presented in Fig. 2.

It should be noted that, for all the kaolin masses studied, the density distribution was obtained for a range of moisture contents exceeding the equilibrium value. Samples with known initial water content were

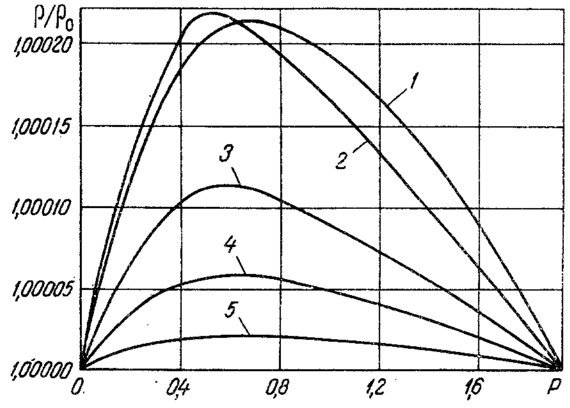

Fig. 2. Change in the relative density ρ/ρ_0 of toluene as a function of the amount of adsorbed water P for various values of m/V: 1) m/V = 0.158 g/cm^3; 2) 0.211; 3) 0.105; 4) 0.0684; 5) 0.0548 g/cm^3.

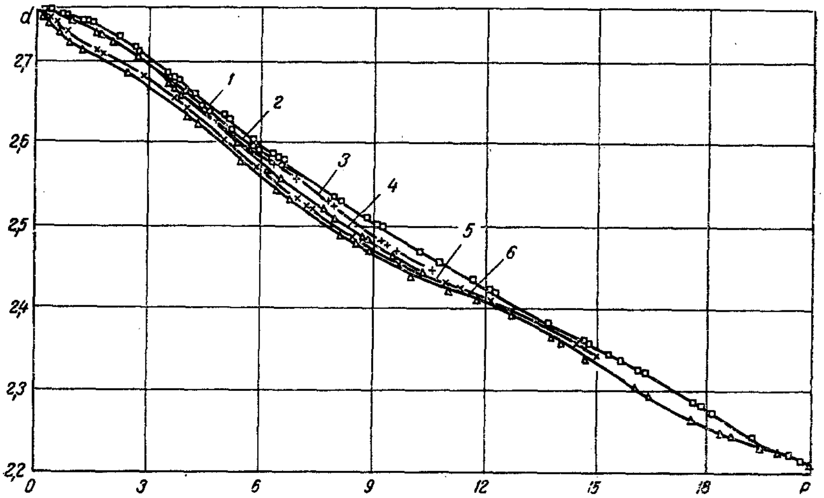

Fig. 3. Density of the Na form of Crimean fuller's earth, determined in nitrobenzene, as a function of the content of adsorbed water P for various ratios of the solid phase to the volume of the dispersion system m/V: 1) m/V = 0.144 g/cm^3; 2) 0.120; 3) 0.020; 4) 0.299; 5) 0.0480; 6) m/V = 0.039, 0.026, 0.013 g/cm^3.

humidified in a pressure chamber with an atmosphere of moist air at vapor pressures of up to 2 atm. We operated the pressure chamber under oscillatory conditions. These results are also presented in Fig. 1.

We thus find a clearly-expressed loop of density separation for the hydrated adsorbent on considering this as a function of the mass of the powders. Curves 1-6 merge at the point corresponding to 1.94% or 0.349 mmole/g of bound (combined) water. It may be shown that this quantity also corresponds to the complete coverage of the active centers on the surface with adsorbed water, i.e., to the capacity of a "monolayer" P_M.

Let us consider a possible mechanism for the adsorption of the dispersion medium in order to explain the origin of the second effect.

The first boundary condition is P = 0. This corresponds to a completely dehydrated surface. The distance between the active centers (hydroxyl groups or oxygen atoms) is no greater than 3 Å). The effective diameter of the toluene molecule is about 6 Å. In this case the interaction of the dispersion medium with the surface of the solid phase is determined by the associative mechanism of π-complex adsorption [2], in which the molecule is oriented with the plane of its benzene ring parallel to the surface, forming a bond with several (or at least two) active centers. Figure 2 shows that the equation $\rho/\rho_0 = \varphi(P) = 1$ corresponds to this condition.

As the surface becomes filled with water, the water molecules, blocking the active centers, create different concentrations of these at every act of sorption or desorption. If the distance between the free centers l_N exceeds the diameter of the toluene molecule D, the interaction process will be determined by the dissociative mechanism of π-complex adsorption. The π-bond will transform into a σ-bond, and the horizontal position of the plane of the benzene ring with respect to the surface will transform into an inclined or vertical position. Such orientations essentially arise from the fact that the toluene molecule is coupled to the hydroxyl group of the surface by means of one of its CH groups or the CH_3 group, while the remaining groups are coupled to the hydrogens of the adsorbed water molecules separated from the surface by a distance of at least 4 Å. The transverse dimension of the toluene molecule is no greater than 1.6 Å, and hence the inclined or vertical position of the benzene rings produces a higher concentration of such molecules in the surface layer of the adsorbent (relative to the horizontal position), and this determines the compression of the dispersion medium on the hydrated kaolin surface.

We see from Fig. 2 that the maximum relative density of toluene is $\rho/\rho_0 = 1.00025$, i.e., the maximum value of the second effect observed in kaolin is no greater than 0.025%, and arises when the distance l_N between any centers is greater than the diameter of the liquid molecule, while the number of free centers $N_N > N_H$ where N_H is the number of centers occupied by the water. The condition for the attenuation of the effect is when $l_N > D$.

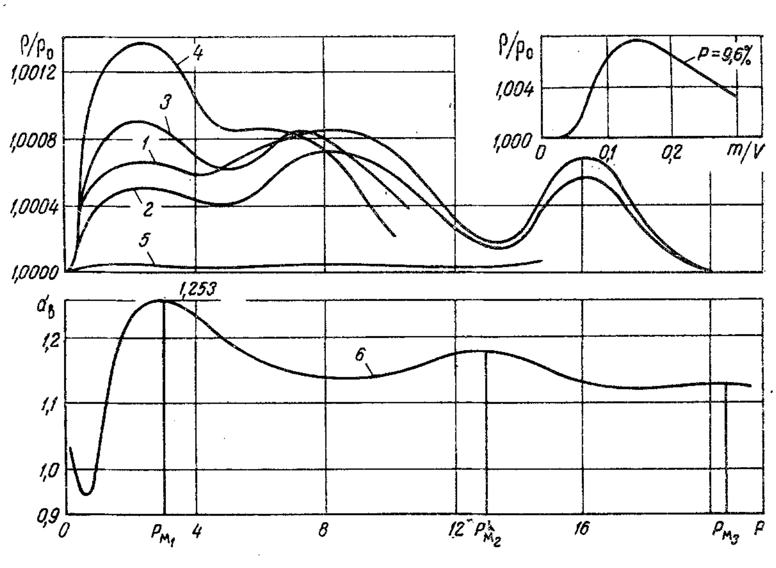

Fig. 4. Relative density ρ/ρ_0 of nitrobenzene in relation to the content of adsorbed water P for various values of m/V: 1) m/V = 0.144 g/cm^3; 2) 0.120; 3) 0.20; 4) 0.299; 5) 0.048; 6) density d_W of the adsorbed water as a function of its mass.

It is quite clear that, for a complete coverage of the active centers ($N_N = 0$), the bond between the molecules of the dispersion medium and the adsorbed water molecules is again essentially determined by the associated mechanism of π-complex adsorption. The conditions corresponding to the complete attenuation of the second effect are accordingly operative; as indicated by Figs. 1 and 2, this condition amounts to 1.94% for Glukhovetsk kaolin. Thus the calculation of the mass of adsorbed water completely screening the surface of the adsorbent, i.e., the mass of a "monolayer" essentially reduces to a solution of the equation $\rho/\rho_0 = \varphi(P) = 1$ (Fig. 2). The density distribution of the hydrated kaolin (curve 6, Fig. 1) obtained for the lower critical mass of adsorbent (in the present case mass less than 3 g) enables us to calculate the density of the adsorbed water with due allowance for the second effect (involving a change in the density of the dispersion medium) in the following way:

$$d_W = \frac{0.01\,Pd_0'd_0}{0.01Pd_0 + d_0 - d_0'}. \tag{2}$$

The results of the calculation are represented by curve 7 in Fig. 1, and may be interpreted in the following way. The maximum values of the density of the combined water are no greater than 10% of the normal value and occur for a low degree of surface coverage, when the first groups of water molecules, adsorbed on the most active, closely-disposed centers existing on the surface of the particle, are "rigidly fixed" to the surface by tetrahedral bonds. The density of the material distributed in the interior of individual, mutually unconnected islets should be greater than that of ordinary liquid water.

The development of a hollow on curve 7, with a minimum density of 0.9400 g/cm^3, may be explained by the formation of a network of water molecules with partial breaks in the interior; this minimum corresponds to the maximum density of the dispersion medium (toluene), i.e., the maximum number of free centers surrounded by water molecules. The second extremum on curve 7 (Fig. 1) equals 1.01 g/cm^3 and arises at the P value corresponding to the merging of curves 1-6 (the end of the loop), i.e., the complete attenuation of the second effect, the formation of continuous networks on the surface of the adsorbent, and the development of a "monolayer". Thus a second method of calculating P_M for systems with nonexpanding crystal lattices lies in finding the maximum on the density distribution curve of the adsorbed water. The smooth transition from the maximum to the normal density corresponds to the filling of the pore space of the adsorbent.

Minerals with an Expanding Crystal Lattice (Na Form of Crimean Fuller's Earth). The results of our experimental investigations are shown in Fig. 3. As in the case of kaolin, there is a sharp distinction in the density of the hydrated montmorillonite for an arbitrary concentration of adsorbed water molecules when considered in relation to the mass of the solid phase. In the same way as in the case of minerals

TABLE 1. Crystallographic Properties and Structural and Spectral Characteristics of Various Forms of Ice at −175°C and 1 atm

Ices	1 *n*	1*c*	II	III	V	VI	VII	VIII
Crystal symmetry	Hexagonal	Cubic	Rhombohedral	Tetragonal	Monoclinic	Tetragonal	Cubic	Cubic
Space group	$P6_3$ *nmc*	*F*43/*m*	*R*3	*P*4, 2, 2	*A*2/*a*	$P4_2$/ *nmc*	*Im*3*m*	*Im*3*m*
No. of molecules in the unit cell	4	8	12	12	28	10	2	3
Density, g/cm^3	0,94	—	1,17	1,14	1,23	1,31	—	1,5
Distance from nearest neighbors Å	2,74	2,75	2,75—2,84	2,76—2,8	2,76—2,87	2,81	2,86	2,86
Distance from neighbors not connected by a hydrogen bond Å	4,49	4,50	3,24	3,47	3,28—3,46	3,51	2,86	2,86
Valence vibration in the infrared spectrum cm^{-1}	3220	3220	3225	3250	3250			
In the Raman spectrum cm^{-1}	3085		3194	3159	3181	3204	3348	
Deformation (shear) vibrations in the infrared spectrum, cm^{-1}	1650		1690	2225	2210			

with nonexpanding lattices, we find that the ratio m/V = 0.039 g/cm^3 (mass of powder 3 g, curve 6 in Fig. 3) is "critical" for this distinction, i.e., for smaller values, such as: m/V = 0.028 g/cm^3 (mass 2 g) and m/V = 0.013 g/cm^3 (mass 1 g), there is no reduction in the density of the hydrated sample for any concentration of water molecules.

Figure 4 illustrates the relative changes taking place in the density of the dispersion medium (nitrobenzene) calculated by means of Eq. (1) and the distribution of effective adsorbed water density as a function of mass calculated by means of Eq. (2).

On the distribution curves we find three maxima; these special features of the Na form of montmorillonite may be explained by the existence of empty space between individual packs (packets) of the material (interpack space) and by the character of the interaction between the water and nitrobenzene molecules on the inner surfaces of the expending crystal lattice of the mineral.

It should be noted that in many investigations associated with the study of adsorbed water its structure is compared with the structure of ice. It is thus rather interesting at this point to indicate certain data regarding the crystallographic properties and structural and spectral characteristics of various forms of ice; these are presented in Table 1 (taken from [3]).

Let us consider the part of the adsorbed water density-distribution curve between 0 and 3% moisture content, obtained in the process of desorption. In a number of respects this distribution is analogous to that found for hydrated kaolin, but the maximum water density of 1.25 g/cm^3 corresponds to the maximum (and not the minimum) compression of the dispersion medium. The comparatively large compression of nitrobenzene ($\rho/\rho_0 = 1.0014$) for P = 3% is due to the vertical orientation of its molecules, by virtue of the interaction of the nitrogroups with the active centers of the inner surface; corresponding to this state we have the closest packing of water molecules lying on the opposite inner surface of the interpack space, and forming a structure similar to that of monoclinic ice. The desorption of the water from 3 to 0.7% moisture content is clearly associated with a transition from the monoclinic to the hexagonal structure, involving the breakdown of the framework of water molecules and the adsorption of nitrobenzene on the free active centers.

The last group of water molecules (adsorption range 0.7-0.02%) are "rigidly fixed" to the surface, i.e., fixed with all free tetrahedral bonds, forming a structure similar to that of tetrahedral ice. The density of the material distributed in the interior of these (individual and mutually disconnected) islets should be greater than ordinary liquid water.

Thus the first maximum on the density curve of the adsorbed water essentially determines the mass of a monolayer on the inner surface of the crystal lattice.

The section of the distribution curve from 3 to 13.2% moisture content was also obtained in the course of desorption.

The transition from the maximum values of d_W to the second water density maximum is associated with the filling of the intrapack space, i.e., with the formation of a second layer of water molecules. This process is accompanied by a gradual screening of the active centers. Whereas, in the region of 9% moisture content, the concentration of free centers is still quite high and largely determines the vertical orientation of the nitrobenzene molecules, in the region of $P = 13\%$ conditions are created for the π-complex adsorption of nitrobenzene on the "fixed" water molecules. Corresponding to this condition we have a minimum in the density variation of the dispersion medium and the complete occupation of the intrapack space by the combined water. Thus the second maximum on the adsorbed-water density-distribution curve, together with x-ray structural data regarding the interplane spacing, enable us to calculate the internal surface area of the montmorillonite.

The part of the distribution curves between 13 and 21% moisture content was obtained during the sorption of the water. The montmorillonite particles were humidified in the same way as the kaolin. The transition from the second maximum ($d_W = 1.186$ g/cm^3) to the third ($d_W = 1.126$ g/cm^3) is associated with the filling of the outer surfaces, and the mechanism underlying the interaction of the water and nitrobenzene molecules is analogous to that arising on the surface of minerals with a nonexpanding crystal lattice, while the mass of water corresponding to the complete degeneracy of the second effect determines the total capacity of the monolayer (in the present case this equals 20.4%) and the total surface area of the particles.

It should be noted that the existence of the second effect is determined by four limitations: 1) $\rho/\rho_0 = 1$ for $P = 0$; 2) $\rho/\rho_0 = 1$ for m below critical; 3) $\rho/\rho_0 = 1$ for P greater than the total capacity of the "monolayer", and 4) the fact that, as indicated in Fig. 4, there is a fall in ρ/ρ_0 with increasing m/V, starting from certain quantities of adsorbed water, i.e., there is an upper "critical" mass of adsorbent, the existence of which is due to a diminution of the part played by the interaction of the solid phase with the liquid, by virtue of an increase in the collective interaction between the particles as their concentration increases inside the dispersed system.

Calculation of the Surface Area of the Mineral. The surface area of the solid-phase particles may be determined during the adsorption of the molecules of any particular substance as follows:

$$S = \frac{P_M S_0}{d_W^c V_0}. \tag{3}$$

The most indeterminate parameter in Eq. (3) is S_0. The S_0 values of various authors for water fluctuate from 9 to 30 Å^2. Usually the surface area is determined by the BET method, using nitrogen, and the capacity of a monolayer is found from the adsorption of water; on the basis of these data the settling area associated with one water molecule is determined.

We here propose a slightly different method. The quantity V_0/S_0, a linear dimension of the adsorbate molecules, is essentially the length of the chemical bond from an active center on the surface to the second adsorbed layer.

On the basis of well-known data regarding the distribution of the charges, the distances between the atoms, and the valence angles, we constructed a model of the disposition of the water molecules on the surface of the adsorbent, and estimated the length of the chemical bond for kaolin was 3.49 Å and the specific surface area of the particles as 55 m^2/g. The inner surface of the crystal lattice of the Na form of Crimean fuller's earth was calculated in the following way

$$S_i = \frac{P_{M_2}}{d_W^0 D_{i[Na]}} = 380 \text{ m}^2/\text{g}$$

According to [4, 5] the value of $D_{i[Na]}$ for the Na form of montmorillonite with a moisture content close to P_{M_2} equalled 2.9 Å. The outer surface area of the crystal lattice of the Na form of Crimean fuller's earth was found as follows

$$S_e = \frac{P_{M_3} - P_{M_2}}{d_W^0 D_{t[Na]}} = 164 \text{ m}^2/\text{g}$$

The total surface area of the particles is

$$S_t = S_i + S_e = 544 \text{ m}^2/\text{g}$$

Thus the foregoing investigations have enabled us to develop a method of calculating the adsorption characteristics of dispersed systems and of refining the method of determining the density of the adsorbed water; however, fresh investigations are still required in this field in connection with determining the mechanisms underlying the interaction of the dispersion medium with the adsorbed water molecules, both theoretical and on the basis of infrared spectroscopy.

NOTATION

ρ/ρ_0 relative change in the density of the dispersion medium; d, density of the hydrated solid phase; d'_0, density of the hydrated solid phase equal to the lower "critical" value; d_w, density of adsorbed water; d_0, density of the dehydrated solid phase; S, specific surface area of the particles; P_M, mass of a "monolayer" of adsorbed material; S_0, area associated with one adsorbate molecule; V_0, volume of the surface layer associated with one adsorbate molecule; d_w^0, mean density of the adsorbed liquid in the "monolayer"; D_i, distance between the internal surfaces of the packs (packets); P_{M_2}, mass of adsorbed water corresponding to the complete occupation of the intrapack space; P_{M_3}, mass of adsorbed water corresponding to the total capacity of the "monolayer"; D_t, projection of the length of the chemical bond from an active surface center (Na ion) to the second adsorbed layer.

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