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 \( \pi \) 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.

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/cm³ (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/cm³ (mass 2 g) and m/V = 0.0137 g/cm³ (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

\[
\frac{\rho}{\rho_0} = \frac{(d - \frac{m}{V})d_0}{(d_0 - \frac{m}{V})d}.
\]

(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