the crater (Fig. 3). Near the walls and on the tank bottom the velocity components are small, with a strong attenuation from the free surface to the bottom.

The results of the calculations show that the velocity distribution agrees with the experimental data [3].

## NOTATION

$a$, tank radius; h, tank height, crater depth; F, mass force; v, V, velocities; P, pressure; $Re_T$, turbulent analog of the Reynolds number; r, z, coordinates; $\delta$, boundary-layer thickness; $\rho$, density; $\nu_T$, turbulent analog of the viscosity; $\psi$, stream function; $\omega$, vorticity. Indices: g, gas; $l$, liquid; c, crater; (i, j), node of the rectangular mesh; i1, node corresponding to $h_c$; j1, node corresponding to $r_c$.

## LITERATURE CITED

1. A. N. Kolmogorov, Dokl. Akad. Nauk SSSR, 30, No. 4 (1941).
2. A. V. Tonkonogii, A. V. Ul'yanov, and D. B. Kozhakhmetov, in: Problems in Heat Engineering and Applied Thermophysics [in Russian], No. 2, Izd. Nauka Kazakh SSR, Alma-Ata (1965).
3. V. I. Yavoiskii, G. A. Dorofeev, and I. L. Povkh, Theory of Cooling of Steel Melt Tanks [in Russian], Metallurgiya, Moscow (1974).
4. J. F. Elliot et al., Thermochemistry for Steelmaking, Addison-Wesley (1960).

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# INFLUENCE OF THE PROPERTIES OF HYDRATED SOLID PHASE SURFACES ON THE EFFECT OF A DENSITY CHANGE IN A DISPERSED MEDIUM

P. P. Olodovskii

UDC 541.18.051

The role of exchange cations in the formation of the structure of a dispersed medium on hydrated surfaces of montmorillonite is shown.

Results of experimental investigations associated with the proof of the existence of an effect of a density change in a dispersed medium in a solid—adsorbed water—liquid system and an interpretation of these results on the basis of a mechanism of adsorption of the dispersed medium molecules on active centers of clayey mineral surfaces are presented in [1].

Taking account of this effect permitted a more confident estimation of the density distribution of the adsorbed water and giving a foundation to methods of computing the adsorption characteristics of dispersed systems. But it is interesting to extend the investigation and to establish the influence of the active center configuration in the solid phase on both the change in structure of the dispersed medium on the boundary with this phase and on the density of the adsorbed water.

The natural form of montmorillonite (Crimean kill) was taken as the subject of the study, it being selected also because it was necessary to establish the role of the specific surface of different sections of the crystal lattice in the formation of the filtration properties of a mineral modified by water-soluble polymers.

The first step in the research was to determine the density of the dehydrated adsorbent $d_0$ in a fluid possessing a zero effect of a change in its density, i.e., the density of the solid phase in such a fluid is independent of its mass. As for Na-montmorillonite, nitrobenzene is a fluid with zero effect for the natural form of bentonite. According to the

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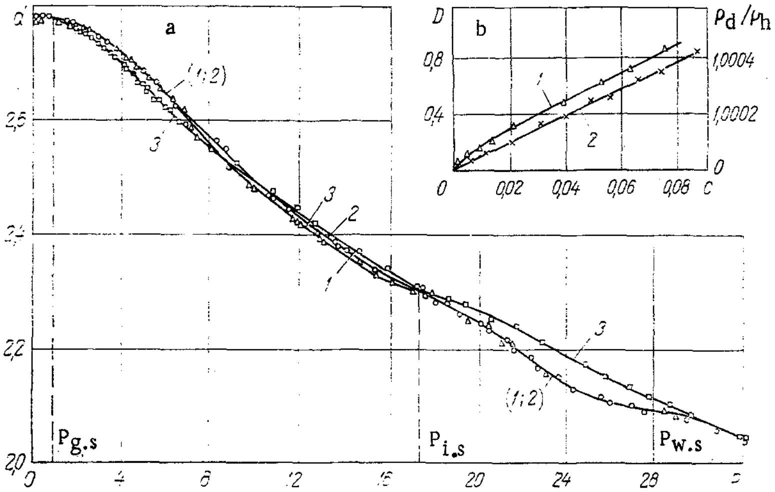


Fig. 1. Dependence of the density of the natural form of Crimean kill (montmorillonite) d, g/cm$^3$, measured in nitrobenzene, on the quantity of adsorbed water P, %, for different ratios m/V [1) m/V = 0.223 g/cm$^3$; 2) 0.133; 3) 0.013] (a) and change in the optical density of water D dissolved in nitrobenzene (curve 1) and relative density of such a system $\rho_d/\rho_h$ on the water content c, % (curve 2) (b).

results of numerous measurements, the mean density of dehydrated Crimean kill turned out to equal 2.7740 g/cm$^3$.

The second step is the determination of the density of the hydrated adsorbent as a function of the specimen moisture and its mass.

The methodology for the experimental measurements is elucidated in [2], but, as in [1], the interaction between the solid phase particles and the pycnometer walls is taken into account. The process of measuring the liquid mass terminated with the cessation of nitrobenzene penetration (diffusion) into the interpacket space of the bentonite. On the basis of curves (constructed by using an IKS-22 device) for the change in the optical density of water dissolved in nitrobenzene and the relative density of such a system $\rho_d/\rho_h$ on the water content ($\rho_d$ is the density of dehydrated nitrobenzene, and $\rho_h$ is the density of nitrobenzene with a specific water content, Fig. 1), the quantity of adsorbed water which has gone from the clay into the liquid or from the liquid into the adsorbent was computed. The results of experimental investigations are represented in Fig. 1, and as is seen from the figure, a clear separation in the density is observed for an arbitrary concentration of adsorbed water molecules (starting from 0.9%), depending on the mass of adsorbent or the relationship m/V (m is the mass of dehydrated adsorbent, and V is the volume of the dispersed system).

As in the investigation of natural kaolinite and Na-montmorillonite, it turns out that the ratio m/V = 0.035 g/cm$^3$ (3 g mass of powder, curve 3 in Fig. 1) is "critical" for such a separation, i.e., there is no decrease or increase in the density of the hydrated specimen (with the admissible error) for any water molecule concentration for lesser values of m/V.

The relative change in the density of the dispersed medium was computed as follows:

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

for the moisture interval when $d > d_0'$ and

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

in the interval $d_0' > d$.

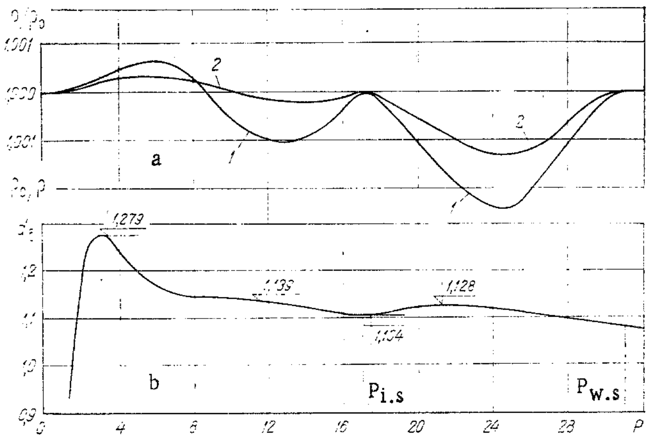


Fig. 2. Change in the relative density of nitrobenzene $\rho/\rho_0$ and $\rho_0/\rho$ as a function of the quantity of adsorbed water P, %, for different values of m/V [1) m/V = 0.223 g/cm$^3$; 2) 0.133] (a) and the distribution of the adsorbed water density $d_w$, g/cm$^3$, as a function of its content (b).

The results of the computation are represented in Fig. 2.

By merging in the 0-0.9% moisture range obtained during desorption, curves 1, 2, and 3 (Fig. 1) form a horizontal plateau, i.e., conditions occur when the volume of adsorbent is measured during dehydration and is somewhat higher than the true volume of the solid phase. These conditions are due to the presence of micropores, the hexagonal vacancies of adjacent packets accessible to water molecules, but where the nitrobenzene molecules do not penetrate. The quantity of moisture associated with the presence of micropores ($P_{g.s}$) was taken into account in computations of the adsorbed water density, which was defined as

$$d_w = \frac{0.01\,(P - P_{g.s})\,d_0\,d_0'}{0.01Pd_0 + d_0 - d_0'}\,. \tag{2}$$

It must be noted that the possible deformation of the structural layers of the crystal lattice of the mineral under the influence of the adsorbed water was not taken into account in the definition of $d_w$.

Three domains can be isolated on the curves of the change in density of the dispersed medium (Fig. 2). The first domain in the 0.9-(8.5-10)% moisture range corresponds to an elevated concentration of nitrobenzene molecules ("compression") in the surface layers of the solid phase, while the second in the 10-17% range and the third in the 17-32% range correspond to a reduced molecule concentration ("expansion") of the dispersed medium. As is known [1], only "compression" of nitrobenzene was detected on hydrated Na-montmorillonite. These peculiarities of the natural form of Crimean kill can be explained by the specifics of exchange-cation adsorption ($Ca^{2+}$ ions in this case), by their concentration, the character of the hydration, and, in sum, by the location (orientation) of the adsorbed molecules of the dispersed medium on the hydrated surfaces of montmorillonite. In the subsequent interpretation we shall carry out a comparison with the results in [1] and with other known data obtained for Na-montmorillonite.

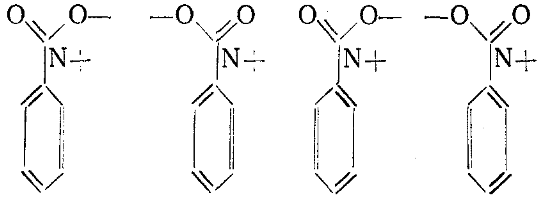
The mean spacing between the adsorbed cations can be calculated to a certain approximation as follows:

$$D_c = \sqrt{\frac{S\cdot 10^{23}}{N\Sigma\,\frac{c_*}{n}}}\,. \tag{3}$$

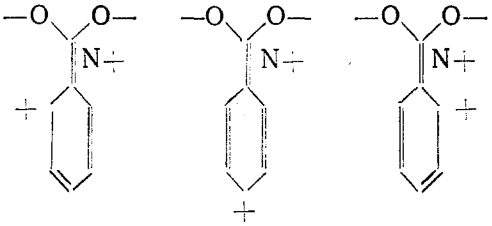
According to the results in [3], the quantity of basic potential-determining ions for the natural form of Crimean kill is $Ca^{2+}$ = 0.65; $Mg^{2+}$ = 0.15 meq/g, while for Na-montmorillonite [4] it is $Na^+$ = 0.5; $Ca^{2+}$ = 0.13 meq/g. The quantity of the total specific surface (as will be shown later) is 877 m$^2$/g for the natural form and 720 m$^2$/g for the Na-form. Then $D_c$ (natural form) = 19.1 Å and $D_c$ (Na-form) = 14.5 Å.

The length of the O—O edge in silicon oxide tetrahedral layers of montmorillonite is approximately 2.98 Å [5]; therefore, we can finally take $D_c$ (natural form) = 21 Å and $D_c$ (Na-form) = 14.9 Å.

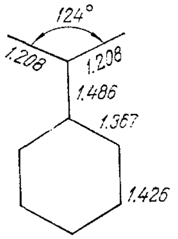
X-ray measurements show that the nitrobenzene molecule is planar. Resonance theory describes nitrobenzene by the superposition of four Kekulé structures



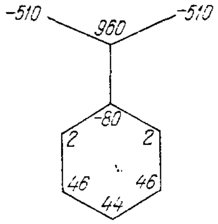
and three ion structures



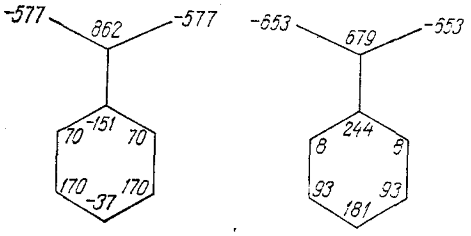
The following bond lengths in the molecule were taken in [6]:



and the π-electron distribution (in e/1000 units) in the ground state



and in the first two excited n—π-states of nitrobenzene



As is seen from [6], the maximum linear dimension of the nitrobenzene molecule is 8.6 Å.

Let us consider the possible location (orientation) of nitrobenzene molecules in sequence in the interpacket space and on the external basal surfaces of the mineral during the dehydration and hydration of Ca- and Na-montmorillonite.

It has been proved experimentally that the nitrobenzene molecule concentration in the surface layers of completely dehydrated bentonites does not differ from their concentration in the volume of a dispersed medium. It should be assumed that a parallel arrangement of the benzene ring to the plane of the packets (horizontal orientation) is energetically favorable for this state of the solid phase. Exchange cations bind to the $NO_2$ groups, while the positively charged CH centers of the benzene ring partially cancel the negative charges of the oxygen atoms of the silicate layers. Two nitrobenzene molecules are stacked in the gap between two $Ca^{2+}$ exchange cations in such an orientation, and two molecules between the $Na^{+}$ cations (taking account of the possible curvature of the bonds in the $NO_2$ group).

A number of successive stages, due to the filling or rupture of the cation coordination sphere, can be extracted during hydration or desorption. If one water molecule appears in the gap between the $Ca^{2+}$ cations, then just one nitrobenzene molecule occupies the horizontal position in the remaining space, and two free (vacant) positions (oxygen atoms of the silicate layers) may be centers of adsorption for two nitrobenzene molecules whose benzene rings occupy the vertical position to the plane of packets. An elevated concentration of molecules of the dispersed medium on the boundary with the solid phase corresponds to such a hydration stage. But if two water molecules appear in the gap between $Ca^{2+}$ cations, then just one nitrobenzene molecule, which cancels all the rest of the vacancy, occupies the energetically favorable horizontal position. A reduced concentration of molecules of the dispersed medium in the surface layer corresponds to this hydration stage.

It is known that the $Na^{+}$ exchange cations which drop into the interpacket space will interact with just one active center in contrast to the divalent ($Ca^{2+}$, $Mg^{2+}$) cations which are simultaneously coupled to two, shrinking adjacent surfaces of tetrahedral and octahedral layers. This difference specifies another position of the nitrobenzene molecules in the interpacket space. An edge orientation, i.e., rotation of the plane of the benzene ring 90° around the C—C bond, is energetically favorable, and in this case the oxygen atoms of the $NO_2$ group bind simultaneously with two $Na^{+}$ cations located on adjacent structural layers.

If a water molecule appears in the gap between the $Na^{+}$ cations, then two nitrobenzene molecules with mutually perpendicular orientations of the planes of the benzene rings are arranged in the remaining space, where one of these molecules can occupy the vertical position (the maximum dimension along the c axis is the vertical edge orientation). An elevated concentration of the molecules of the dispersed medium on the boundary with the solid phase corresponds to such a hydration stage.

The adsorption of two water molecules between $Na^{+}$ cations specifies the conservation of the minimum of two vacant positions (the oxygen atoms of the silicate layers), which is the center of the bond of two nitrobenzene molecules also but with an identical vertical edge orientation. It is clear that an elevated concentration of the dispersed medium in the surface layer corresponds to such a hydration stage.

It must be noted that the schemes represented do not reflect, by far, all the modifications of nitrobenzene molecule stackings in the surface layer, but permit a conception of the density changes in a dispersed medium observed in experiment, depending on the composition, concentration of exchange cations, and the degree of their hydration.

As follows from Fig. 2, the domain of elevated fluid molecule concentration in the surface layer corresponds to the initial hydration stage (0.9-10% moisture). It can be assumed that this stage will be determined by the preferred appearance of single water molecules in the interpacket space in the gaps between the $Ca^{2+}$ cations, the coordination sphere of the cation is formed from the minimum number of molecules, and the electrostatic binding strength becomes a maximum. The density of the adsorbed water takes on the maximum value 1.27 $g/cm^3$ (see Fig. 2) in the first stage of the hydration, i.e., conditions actually occur when the first groups of water molecules being adsorbed on the available most active centers of the solid phase particles are "rigidly attached" to the surface by tetrahedral bonds, and the density of the material distributed in the volume of the separate mutually unconnected island should be greater than that for ordinary liquid water. It can be assumed that termination of the first stage of the hydration (10% moisture) and its associated passage from the domain of "compression" of the dispersed medium to its "expansion" domain specify formation of the first "layer" of water molecules in the interpacket space of natural montmorillonite.

The second stage of hydration, which is characterized by the preferred appearance of two water molecules in the interpacket space in the gaps between $Ca^{2+}$ cations, specifies a reduction in the concentration of molecules of the dispersed medium in the surface layer. As is seen in Fig. 2, the domain in the 10-17% moisture range can correspond to this stage. The maximum value of the effect of a 0.1% density change in the dispersed medium in this range occurs for a 13% water content, i.e., the vacant oxygen atoms of the silicate layers for such a quantity of adsorbed water produce the most favorable conditions of the horizontal orientation, and a gradual passage to the vertical edge position of the nitrobenzene molecules occurs with the growth of the degree of hydration in this domain until they disappear completely from the interpacket space.

It is clear that the total degeneration of the effect observed in experiments at 17% moisture is related to termination of the process of hydration of the interpacket space, and the computation of the interplanar spacings in montmorillonite and of the adsorbed water density for this moisture content indicates the formation of a completed two-layer structure with the minimum density 1.104 g/cm³. The parameters obtained at the minimum point of the change in density of the dispersed medium permit computation of the specific surface of the basal planes of the montmorillonite.

The third stage in the hydration of natural Crimean kill (the 17-32% moisture range) is related to water molecule adsorption by the outer basal planes of montmorillonite.

It must be noted that the $Ca^{2+}$ exchange cations, located on these planes, interact in contrast with those in the interlayers, with just one active center of the mother surface. It should be noted that hydration in this domain, i.e., the formation of a coordination sphere of a cation, will occur more intensively because of the bonds originating additionally between the cation and the water molecules. The abrupt change in the density of the dispersed medium observed in experiments, the "fluid expansion" ($\rho_0/\rho = 1.0025$), is related to the preferred plane orientation of the nitrobenzene molecules, and the total and final degeneration of this effect for a 31.8% moisture, which is due to the filling of all vacant positions by water molecules, permits the computation of the specific surface of the outer basal planes of montmorillonite.

## COMPUTATION OF THE SPECIFIC SURFACE OF NATURAL BENTONITE PARTICLES

The curves of the change in density obtained for a dispersed medium and of the density of the adsorbed water permit computation of the specific surfaces of different sections of the crystal lattice of the mineral.

a) The interlayer surface of bentonite

$$S_{in} = \frac{2P_{i.s}}{d_{i.s} D_S} . \qquad (4)$$

As is seen from Fig. 2, $P_{i.s} = 17\%$, $d_M = 1.104$ g/cm³. According to the results of an x-ray diffraction analysis performed on the DRON-1 diffractometer, $D_S$ turned out to equal 5.437 Å. Therefore, $S_{in} = 566.4$ m²/g.

b) External surface of bentonite,

$$S_{ex} = \frac{P_{w.s} - P_{i.s}}{d_{w.s} D_H} . \qquad (5)$$

As is seen from Fig. 2, $P_{w.s} = 31.8\%$; $d_{w.s} = 1.087$ g/cm³. On the basis of the model constructed for the arrangement of water molecules at active centers of the surface, the quantity $D_H$ was estimated as 4.08 Å. Thus, $S_{ex} = 311.2$ m²/g.

c) Total surface of particles of the natural form of Crimean kill,

$$S_{tot} = S_{in} + S_{ex} = 877.6 \text{ m}^2/\text{g}.$$

It is interesting to note that the magnitude of the specific surface of Ca-montmorillonite determined by means of water vapor adsorption for $p/p_S = 0.55$ turned out to equal 910 m²/g in [4].

Therefore, the investigations performed on natural kaolinite, the Na-form of montmorillonite, and the natural form of montmorillonite, which are related to the study of the effect of a density change in the dispersed medium, permit the development of a method to compute a number of adsorption characteristics of comparatively highly dispersed systems and to produce a more rigorous method of estimating the adsorbed water density. However, the possible deformation of the crystals under the influence of the adsorbed water was not taken into account in these computations. At the same time, the necessity to take such deformations into account is indicated in a number of published papers and, hence, we have already started to investigate the structure of adsorbed water as a function of its mass by the IR spectroscopy method, and an attempt is made to estimate the possible deformations of the crystal lattice of different clayey minerals during hydration or dehydration on the basis of an x-ray diffraction analysis, and thereby to refine the distribution obtained for the adsorbed water density.

## NOTATION

$\rho/\rho_0$ and $\rho_0/\rho$, relative changes in the density of the dispersed medium; $d_0'$, density of the hydrated solid phase with a mass equal to the lower "critical" value; $\rho_0$, fluid density corresponding to this mass; d, density of the moist specimen; $\rho$, fluid density corresponding to the mass of solid phase greater than the lower "critical" value; $d_w$, density of adsorbed water; P, content of adsorbed water, %; $d_0$, density of dehydrated adsorbent; $D_c$, spacing between exchange cations; S, specific surface of solid phase particles; n, cation valency; $c_*$, quantity of adsorbed cations of a given valency; N, Avogadro number; $P_{i.s}$, quantity of adsorbed water corresponding to complete filling of interpacket space; $d_{i.s}$, density of this water; $D_S$, spacing between packet inner surfaces; $P_{w.s}$, quantity of adsorbed water corresponding to total covering of the whole surface; $d_{w.s}$, density of this water; $D_H$, projection of the length of the chemical bond on a plane perpendicular to the adsorbent surface from the active center (Ca ion) for the second adsorbed layer of water.

## LITERATURE CITED

1. P. P. Olodovskii, Inzh.-Fiz. Zh., 27, No. 4 (1974).
2. P. P. Olodovskii and M. G. Murashko, Inzh.-Fiz. Zh., 11, No. 5 (1971).
3. I. A. Briling, Bound Water in Dispersed Systems [in Russian], Izd. Mosk. Gos. Univ. (1972).
4. R. I. Zlochevskaya, G. G. Il'inskaya, G. A. Kuprina, V. I. Osipova, N. N. Skoblinskaya, and M. M. Chekhovskikh, Bound Water in Dispersed Systems [in Russian], Izd. Mosk. Gos. Univ. (1972).
5. B. B. Zvyagin and Z. G. Pinsker, Dokl. Akad. Nauk SSSR, Nov. Ser. No. 3 (1949).
6. J. G. Wagner, Chemistry of the Nitro and Nitroso Groups [Russian translation], Mir (1972).

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# WETTING ANGLES CLOSE TO CRITICAL TEMPERATURE

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and Yu. V. Tarlakov

UDC 532.61

Information available in the literature on the temperature dependence of the wetting angle in various systems is generalized for a wide range of temperatures. The dependence $\theta = f(T)$ obtained experimentally is compared with theoretical results.

The wetting of solid surfaces by liquids is a process of considerable importance in engineering practice. The characteristics of wetting determine the operation of capillary evaporators, heat tubes, etc. Wetting is particularly important under conditions of weightlessness. Under these conditions, the Bond number is considerably less than unity ($Bo \ll 1$), since the surface-tension forces predominate over the inertial forces and the form of the liquid surface depends exclusively on the equilibrium conditions at the solid–liquid–gas phase interfaces. This lends particular importance to information on wetting angles for various systems and their dependence on a number of factors, in particular, temperature.

The aim of the present paper is to generalize the known experimental results on the dependence of the wetting angle on the temperature and saturation pressure over a broad temperature range, extending to values close to the critical temperature $T_{cr}$, and to compare the experimental data with theoretical results.

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