ROLE OF THE ADSORBED-WATER STRUCTURE IN THE FORMATION OF THE FILTRATIONAL PROPERTIES OF DISPERSE SYSTEMS (CLAY SOILS). I

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Relations are obtained between the characteristics of the adsorbed water and the change in water permeability of disperse systems arising under the influence of physicochemical processes.

A physicochemical model of water-saturated clay as a system of plane infinite parallel slits (pores) is proposed. Analogous models have been considered in earlier works, especially [1, 2].

Suppose that there are 2n slits of width h in such a system in some state. The water flow rate through a slit is slight if the slit is narrow while the water viscosity in such capillaries, according to [3], is

$$\eta = \eta_0 \exp\left(\frac{cd}{\varepsilon d''}\right), \tag{1}$$

where η_0 is the water viscosity in the volume; c is a constant; ε is the porosity coefficient; d is the density of the solid phase; d'' is the water density; or

$$\eta = \eta_0 \exp\left[\frac{1-2nh}{2nh}\right]\frac{cd}{d''}. \tag{2}$$

With increase in porosity, when slits of width H are formed from n slits of width h, the mean viscosity of the water may be determined as

$$\eta = \eta_0 \exp\left[\frac{1-n(H+h)}{n(H+h)}\right]\frac{cd}{d''}. \tag{3}$$

Using the solution in [4], it is simple to show, from the definition of the mean flow velocity of incompressible viscous liquid between two infinite parallel planes, that the "filtration" coefficient of water through a system of nH slits may be defined as

$$K_{(1)} = \frac{H^3 \exp\left[-c_{0(1)}\frac{1-n(H+h)}{n(H+h)}\right]}{12\eta_0(H+h)}. \tag{4}$$

Suppose that, on account of any physicochemical processes arising in surface layers of the solid phase, there is an increase in the width h (weakly conducting slits) by an amount Δ. Then, while retaining the overall porosity of the system, the width H (conducting slits) is reduced by Δ. The filtration coefficient of the new state of the system is written as follows:

$$K_{(2)} = \frac{(H-\Delta)^3 \exp\left[-c_{0(2)}\frac{1-n(H+h)}{n(H+h)}\right]}{12(H+h)\eta_0}, \tag{5}$$

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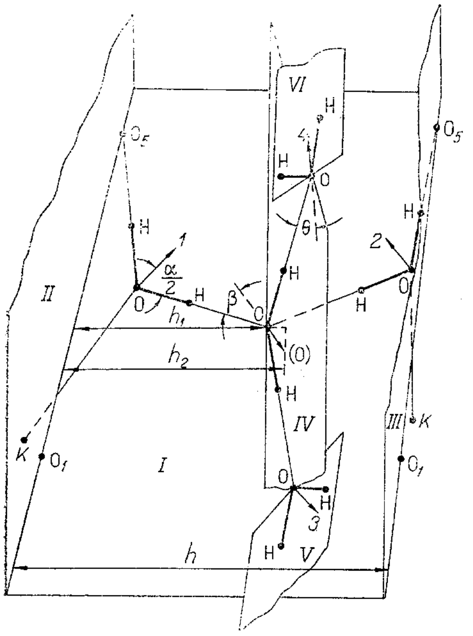

Fig. 1. Configuration of dipole moments in water molecules adsorbed in narrow capillaries.

where

$$c_{0(1)} = \frac{c_{(1)}d_{(1)}}{d''}; \quad c_{0(2)} = \frac{c_{(2)}d_{(2)}}{d''},$$

or

$$\frac{K_{(1)}}{K_{(2)}} = \frac{H^3 \exp\left[-c_{0(1)}\frac{1-n(H+h)}{n(H+h)}\right]}{(H-\Delta)^3 \exp\left[-c_{0(2)}\frac{1-n(H+h)}{n(H+h)}\right]}. \tag{6}$$

Expanding the exponents in Eq. (6) in series and retaining the first two terms (which is valid at real values of $cd/\varepsilon d''$), one polynomial is divided systematically by the other and, neglecting terms making a small correction to $K_{(1)}/K_{(2)}$ in the result, it is found that

$$\frac{K_{(2)}}{K_{(1)}} = \frac{c_{0(1)}+1}{c_{0(2)}+1}\left[1+\sum_{t=1}^{\infty}\left(\frac{3\Delta}{h}\right)^t+\sum_{t=1}^{\infty}\left(\frac{3\Delta}{H}\right)^t\right]. \tag{7}$$

Next, $c_{0(1)}$ and $c_{0(2)}$ are determined. According to [3],

$$\frac{c}{p} = \frac{E_a - E_a^0}{RT},$$

where E_a is the activational energy of translational mobility of water molecules in narrow capillaries; E_a^0 is the activational energy of the same process but in a volume of water; R is the gas constant; T is the absolute temperature of the system; p is the wetness of the clay.

With reduction in wetness of the system, when a structure similar to that in Fig. 1 is created inside the slit capillary, it must be assumed that

$$\frac{E_1 - E_a^0}{RT} = \frac{c_1}{1.5P_{M(1)}}, \quad \frac{E_2 - E_a^0}{RT} = \frac{c_2}{1.5P_{M(2)}},$$

where E_1 and E_2 are activational energies, but this time of the translational mobility of molecules in dimer absorption; $P_{M(1)}$ and $P_{M(2)}$ are the masses of the absorbed double molecular layers in the initial and modified states of the system, respectively.

The final result is

$$\frac{K_{(2)}}{K_{(1)}}=\frac{1.5P_{M(2)}(E_2-E_a^0)d_{(2)}+RTd''}{1.5P_{M(1)}(E_1-E_a^0)d_{(1)}+RTd''}\left[1+\sum_{t=1}^{\infty}\left(\frac{3\Delta}{h}\right)^t+\sum_{t=1}^{\infty}\left(\frac{3\Delta}{H}\right)^t\right]. \tag{8}$$

It will be shown in a forthcoming work that, for real values of Δ/h, it is sufficient to take account of the first 5-7 terms of the series in Eq. (8). The method of determining E_1, E_2, and E_a^0 is given in [5].

From experimental data relating to the influence of the structural-adsorption characteristics of natural and ion-exchange forms of clay minerals on the permeability coefficients of these systems in the filtration of water and aqueous solutions of inorganic salts and organic compounds, it is found that [6]

$$K=\frac{(\varepsilon-\varepsilon_0)(\varepsilon+1)^2\varphi}{S^2d^2L^3}, \tag{9}$$

where $L=\varepsilon_0 d''/(P_M d)$; K is the permeability coefficient; ε_0 is the porosity coefficient as $K\to 0$; S is the specific surface of unit mass of solid phase; L is the number of liquid layers corresponding to ε_0; φ is a dimensionless constant.

In Eq. (9), the characteristics S, P_M, ε_0, L reflect both the mineralogical composition and the composition of the exchange ions, while ε_0 and L also reflect the properties of the liquid being filtered.

The change in the permeability coefficient under the influence of various physicochemical processes, but corresponding to the same porosity, may be expressed in the following form on the basis of Eq. (9):

$$\frac{K_{(2)}}{K_{(1)}}=\frac{(\varepsilon-\varepsilon_{0(2)})L^3_{(1)}d^2_{(1)}}{(\varepsilon-\varepsilon_{0(1)})L^3_{(2)}d^2_{(2)}}. \tag{10}$$

For the given model of plane slits, Eq. (10) takes the form

$$\frac{K_{(2)}}{K_{(1)}}=\frac{(H-h)(h+\Delta)^3[1-2n(h+\Delta)]P^3_{M(1)}d^2_{(1)}}{(1-2nh)h^3(H-2\Delta-h)P^3_{M(2)}d^2_{(2)}}. \tag{11}$$

It is taken into account here that $L_{(1)}=h/P_{M(1)}\lambda$, $L_{(2)}=(h+\Delta)/P_{M(2)}\lambda$ and $S_{(1)}=S_{(2)}$ (λ is the mean effective projection of the chemical-bond lengths in dimers of water molecules within the limits of the whole capillary width, in the direction perpendicular to the surface of the solid phase). Systematic division of one polynomial by the other, neglecting the terms in the result which introduce small corrections to $K_{(2)}/K_{(1)}$, leads to the final result:

$$\frac{K_{(2)}}{K_{(1)}}=\frac{P^3_{M(1)}d^2_{(1)}}{P^3_{M(2)}d^2_{(2)}}\left[1+\frac{4\Delta}{h}+\frac{6\Delta^2}{h^2}+\frac{4\Delta^3}{h^3}+\frac{\Delta^4}{h^4}+\frac{2\Delta}{H}+\frac{4\Delta^2}{H^2}+\frac{8\Delta^3}{H^3}\right]. \tag{12}$$

The results for $K_{(2)}/K_{(1)}$ obtained from Eqs. (8) and (12) and directly from experimental data for various ion-exchange forms of Chasov-Yarskii monothermite clay are similar; they will be presented in a forthcoming publication. In Eqs. (8) and (12), however, the basic parameters are Δ/h and Δ/H. It may be shown that these parameters are determined by elements of the adsorbed-water structure.

According to the theory of the stability of disperse systems, the distance between solid-phase particles h (or H) in the chosen model of water-saturated clay is determined by the disjoining liquid pressure in thin layers (pores).

The generalized Deryagin–Landau–Ferveya–Overbek (DLFO) theory considers three components of the disjoining pressure [7, 8]

$$\Pi(h)=\Pi_m(h)+\Pi_e(h)+\Pi_s(h), \tag{13}$$

where $\Pi(h)$ is the overall disjoining pressure; $\Pi_m(h)$ is the molecular component due to dispersional-interaction forces between particles separated by a liquid layer; $\Pi_e(h)$ is the ionic-electrostatic component of the disjoining pressure; $\Pi_s(h)$ is the structural component of the disjoining pressure due to overlap of the liquid boundary layers with a structure changed in comparison with the volume phase.

In the first approximation, the components of the disjoining pressure are assumed to be additive; therefore Δ/h may be written in the form

$$\frac{\Delta}{h} = \frac{\Delta_{1(m)}}{h} + \frac{\Delta_{2(e)}}{h} + \frac{\Delta_{3(s)}}{h}. \tag{14}$$

The quantities $\Delta_{1(m)}/h$, $\Delta_{2(e)}/h$, $\Delta_{3(s)}/h$ are determined from the relations $\Pi_{(m)} = \Pi_{(m)}'$, $\Pi_{(e)} = \Pi_{(e)}'$, $\Pi_{(s)} = \Pi_{(s)}'$, where $\Pi_{(m)}'$, $\Pi_{(e)}'$, and $\Pi_{(s)}'$ are components of the disjoining pressure resulting from modification of the solid phase under the influence of various physicochemical processes.

The interface between the solid and liquid is taken to be the external surface of the double molecular layer consisting of adsorbed water molecules.

Consider the distribution of the molecular component of the disjoining pressure. For two identical solids separated by a thin liquid layer with $h < \lambda_0$ (λ_0 denotes the basic wavelengths appearing in the absorption spectra), the attractive force between solids is rigorously defined according to the formula [9]

$$\Pi_{(m)} = \frac{\hbar}{8\pi h^3} \int_0^{\infty} \frac{[\varepsilon_1(i\omega) - \varepsilon_2(i\omega)]^2 \, d\omega}{[\varepsilon_1(i\omega) + \varepsilon_2(i\omega)]^2}, \tag{15}$$

where $\varepsilon_1(i\omega)$, $\varepsilon_2(i\omega)$ are the imaginary components of the complex dielectric permittivity for the solid and liquid, respectively. On the basis of [10], $\varepsilon(i\omega) = 1 + \varepsilon''(\omega)$ and, according to [11],

$$\varepsilon_1''(\omega) = \frac{4\pi a_{0(1)} \omega \tau_1 N_1}{1 + \omega^2 \tau_1^2}, \qquad \varepsilon_2''(\omega) = \frac{4\pi a_{0(2)} \omega \tau_2 N_2}{1 + \omega^2 \tau_2^2}, \tag{16}$$

where $a_{0(1)}$ and $a_{0(2)}$ are the static orientational polarizabilities of the molecules; τ_1 and τ_2 are their relaxation times; N_1 and N_2 are the numbers of molecules in unit volume in the adsorbed double molecular layer and in the liquid, respectively.

The static orientational polarizability of the molecule in [11] is defined as $a_0 = m^2/3kT$, where m is the dipole moment of the molecule; k is the Boltzmann constant.

Following [12-14], it may be shown that $m_1/N_2 = m_2/N_1$ for water molecules but, since $m_2 = 1.87 \cdot 10^{18}$ cgs charge units·cm and $N_2 = 0.33 \cdot 10^{23}$

$$\varepsilon_1''(\omega) = \frac{10\tau_1\omega}{1 + \omega^2\tau_1^2}, \qquad \varepsilon_2''(\omega) = \frac{10\tau_2\omega}{1 + \omega^2\tau_2^2}. \tag{17}$$

Substituting Eq. (17) into Eq. (15) and performing appropriate manipulations, it is found that

$$\Pi_{(m)} = \frac{\hbar}{8\pi h^3} \int_0^{\infty} \frac{\left[\omega\tau_1 - \dfrac{\omega\tau^2(\tau_2^2 + \omega^2\tau_1^2\tau_2^2)}{\tau_2(\tau_1^2 + \omega^2\tau_1^2\tau_2^2)}\right]^2 d\omega}{\left[\dfrac{1}{5}(1 + \omega^2\tau_1^2) + \dfrac{\omega\tau_1^2(\tau_2^2 + \omega\tau_1^2\tau_2^2)}{\tau_2(\tau_1^2 + \omega\tau_1^2\tau_2^2)} + \omega\tau\right]^2}. \tag{18}$$

Note that τ_2 (relaxation time of molecules in liquid water) depends on the temperature and is 10^{-11} sec at T = 293°K [14], but in narrow capillaries τ_2 is determined also by the viscosity; τ_1 (the relaxation time of adsorbed water molecules) also depends on the temperature, but is also determined by the adsorption energy and varies in the range 10^{-5}-10^{-8} sec [15]. Denoting the integrand in Eq. (18) by $f(\omega)$, this equation is rewritten in the form

$$\Pi_{(m)} = \frac{\hbar}{2\pi h^3}\left[\int_0^{1/\tau} f(\omega)\,d\omega + \int_{1/\tau_1}^{1/\tau_2} f(\omega)\,d\omega + \int_{1/\tau_2}^{\omega_3} f(\omega)\,d\omega + \int_{\omega_3}^{\infty} f(\omega)\,d\omega\right], \tag{19}$$

where ω_3 is taken to be 10^{13} sec^{-1}.

In the first integral of Eq. (19), the factor $[(\tau_2^2 + \omega^2\tau_2^2\tau_1^2)/(\tau_1^2 + \omega^2\tau_1^2\tau_2^2)]$ at all values of ω, within the limits of integration of 0 and $1/\tau_1$, tends to zero; in the second integral, its mean value is 0.25; in the third, 0.75; in the fourth, 1. Using these values, the general solution of Eq. (18) is obtained:

$$\Pi_{(m)} = \frac{\hbar}{8\pi h^3}\left[\frac{0.4}{\tau_1} - \frac{2.6\tau_2}{\tau_1^2} + \frac{3.6}{\tau_2}\right]. \tag{20}$$

But since $\tau_1 >> \tau_2$,

$$\Pi_{(m)} = \frac{\hbar}{8\pi h^3}\,\frac{3.6}{\tau_2}. \tag{21}$$

In modifying the solid phase under the influence of physicochemical processes,

$$\Pi'_{(m)} = \frac{\hbar}{8\pi (h+\Delta_1)^3}\,\frac{3{,}6}{\tau'_2}.$$

Then

$$\frac{\Delta_{1(m)}}{h} = \sqrt[3]{\frac{\tau_2}{\tau'_2}} - 1.$$

According to [11], the relaxation time in liquids is related to the viscosity η approximately as follows:

$$\tau = \frac{4\pi\eta a^3}{kT}, \tag{22}$$

where a is the molecular radius. Hence,

$$\frac{\Delta_{1(m)}}{h} = \sqrt[3]{\frac{\eta_1}{\eta_2}} - 1. \tag{23}$$

But, according to [3],

$$\frac{\eta_1}{\eta_2} = \exp\left(\frac{c_{(1)}}{P_{(1)}} - \frac{c_{(2)}}{P_{(2)}}\right). \tag{24}$$

In estimating Δ/h, P corresponds to the porosity ε_0.

Substituting Eq. (24) into Eq. (23), and replacing $c_{(1)}$ and $c_{(2)}$ by the above expressions, the final result is

$$\frac{\Delta_{1(m)}}{h} = \sqrt[3]{\exp\left[\frac{1{,}5P_{\text{M}(1)}d_{(1)}(E_{(1)} - E_{\text{a}}^0)}{PT\varepsilon_{0(1)}d''} - \frac{1{,}5P_{\text{M}(2)}d_{(2)}(E_2 - E_{\text{a}}^0)}{RT\varepsilon_{0(2)}d''}\right]} - 1. \tag{25}$$

Consider the contribution of the ionic–electrostatic component of the disjoining pressure to Δ/h.

According to [8, 16], when $\psi_s > 100\ Z$ (mV) or $ZF\psi_s/RT >> 1$ and $\chi h << 1$ (the parameters ψ_s and χh of the systems considered here satisfy these inequalities), the ionic–electrostatic component of the disjoining pressure may be calculated from the formula

$$\Pi_{(e)} = \frac{\pi}{2}\,\varepsilon'_{0(1)}\left(\frac{RT}{FZ_{(1)}}\right)^2 \frac{1}{h^2}, \tag{26}$$

where ψ_s is the total potential of the surface (substrate layer); F is the Faraday number; $Z_{(1)}$ is the valence of the counterions in the double electric layer; $\varepsilon_{0(1)}'$ is the static dielectric permittivity of the liquid; χ is the inverse Debye radius of ionic atmospheres.

In the modification of the solid phase under the influence of physicochemical processes

$$\Pi'_{(e)} = \frac{\pi}{2}\,\varepsilon'_{0(2)}\left(\frac{RT}{FZ_{(2)}}\right)^2 \frac{1}{(h+\Delta_2)^2}. \tag{27}$$

Then

$$\frac{\Delta_{2(e)}}{h} = \frac{Z_{(1)}}{Z_{(2)}}\sqrt{\frac{\varepsilon'_{0(2)}}{\varepsilon'_{0(1)}}} - 1. \tag{28}$$

In many cases $Z_{(1)} = Z_{(2)}$ in the modification of the solid phase of disperse systems and, therefore,

$$\frac{\Delta_{2(e)}}{h} = \sqrt{\frac{\varepsilon'_{0(1)}}{\varepsilon'_{0(2)}}} - 1. \tag{29}$$

Consider the change in static dielectric permittivity of water in modification processes. It has been established experimentally that the dielectric permittivity of water in thin layers enclosed between mineral surfaces is considerably reduced [17, 18]. In [17], for Na-montmorillonite at 288°K, the following results were obtained: at 9.6, 22, 38.6, and 55% water contents, the static dielectric permittivities are 5, 15, 25, and 30, respectively.

In [18] it was shown that, at 281°K, depending on the thickness of the water layer between mica plates (0.07, 0.1, 0.3, 1.6, 2.9, and 3.7 μm), the corresponding values of the dielectric permittivity are 4.5, 8, 35, 75, 79, and 80, respectively. This sharp change in dielectric permittivity is explained by the features of the water structure in thin layers.

According to the Kirvud equation [14]

$$\varepsilon'_0 = \frac{2\pi N^* m^2 g}{kT}, \tag{30}$$

where m is the mean dipole moment of the molecule in the material; N^* is the number of dipoles per unit volume; g is the correlation parameter characterizing the degree of angular correlation of the dipole moments of adjacent molecules with the dipole moment of an arbitrary central molecule. In liquid water, the correlation parameter g is determined as follows: $g = 1 + N_1 < \cos\gamma >$ (N_1 is the number of nearest-neighbor molecules; $<\cos\gamma>$ is the mean cosine of the angles between the dipole moments of the adjacent and central molecules).

The change in g in the adsorbed complex shown in Fig. 1 is now estimated. A water molecule forming a dimer in the sorption process is taken as the central molecule [its dipole moment is denoted by (0) and is at the intersection of planes I and IV].

The oxygen atom of the central molecule is at the symmetry axis of the narrow slit capillary of width h bounded by planes II and III, while the molecule itself forms tetrahedral coordination consisting of four water molecules, of which two (with dipole-moment indices 1 and 2) are directly adsorbed on the crystal lattice and lie in plane I, while the other two are oriented along the axis of the slit capillary and lie in planes V and VI. All the hydrogen bonds are assumed to be linear.

It is simple to show that

$$g = 1 + 2\cos\left(\frac{\alpha}{2} + \beta\right) + 2\cos\frac{\alpha}{2}\cos\theta, \tag{31}$$

where α is the angle HOH in the water molecule; β is the angle between the dipole of the central molecule and the direction of the hydrogen bonds forming the adsorbed dimers in plane I; θ is the angle between the dipole denoted by 3 or 4 in Fig. 1 and the direction of the hydrogen bond forming the dimer elongated along the axis of the slit capillary.

On the basis of Fig. 1,

$$\cos\beta = \frac{h_2 - h_1}{\mathrm{OH}\cos\frac{\alpha}{2}}, \tag{32}$$

where h_1 is the sum of the projection of chemical-bond lengths in the adsorbed dimer on the direction perpendicular to the surface of the crystal lattice (in particular, on the direction perpendicular to the straight line connecting the vertices of tetrahedra of the structural layers) to the oxygen atom of the central molecule; h_2 is the sum of the same projections and a supplementary term from the length of the OH bond of the central molecule.

Supposing that the density of the adsorbed water is inversely proportional to h_2^3, it follows that $h_2 = L_0\sqrt[3]{d''/d_W}$, where d_W is the density of the adsorbed water in the formation of the double molecular layer; L_0 is the projection of the chemical-bond length in the liquid-water dimer onto the height of the tetrahedron from the center of its base formed by the plane passing through the three oxygen atoms to the hydrogen atom of the molecule whose oxygen atoms form the fourth vertex of the tetrahedron. For liquid water, L_0 = 3.88 Å. Hence,

$$\cos\beta = \frac{3.88\sqrt[3]{d''/d_W} - h_1}{0.96\cos\frac{\alpha}{2}}.$$

According to [19], where a detailed review of work relating to the structure and properties of water associated was given, the angle θ may be estimated with great confidence at 57 ± 10°.

The results of determining g for adsorbed complexes coordinated close to exchange cations are now given. Data on h_1 and d_W were given in [20].

For the Li, Na, Mg, Ni, Ca, Mn, Co, Fe, and Al forms of montmorillonite, g is 0.422, 0.423, 0.404, 0.395, 0.375, 0.374, 0.372, 0.370, and 0.372, respectively. For liquid water at 293°K, g = 2.78 [14]. Hence, the sharp decrease in static dielectric permittivity of water in narrow capillaries may be understood.

To estimate the change in static dielectric permittivity of water in clay soils as a function of the water content, the Low principle is used [21]. According to this principle, a series of characteristics of water in disperse systems vary exponentially:

$$J = J_0 \exp\left(\frac{c}{P}\right), \tag{33}$$

where J_0 is a characteristic of volume water; c is a constant.

Hence, the change in static dielectric permittivity may be written as follows:

$$\begin{aligned} \varepsilon'_{0(1)} &= \varepsilon'_0 \exp\left(\frac{c'_{(1)}}{P_{(1)}}\right), \\ \varepsilon'_{0(2)} &= \varepsilon'_0 \exp\left(\frac{c'_{(2)}}{P_{(2)}}\right), \end{aligned} \tag{34}$$

or

$$\frac{\varepsilon'_{0(2)}}{\varepsilon'_{0(1)}} = \exp\left(\frac{c'_{(2)}}{P_{(2)}} - \frac{c'_{(1)}}{P_{(1)}}\right). \tag{35}$$

The values of $c_{(1)}'$ or $c_{(2)}'$ are calculated from the conditions under which the water structure corresponding to that in Fig. 1 is created inside the slit capillary. Then Eq. (34) takes the form

$$\begin{aligned} N^*_{(1)} m^2_{(1)} g_{(1)} &= N^*_0 m_0^2 g_0 \exp\left(\frac{c'_{(1)}}{1.5P_{M(1)}}\right), \\ N^*_{(2)} m^2_{(2)} g_{(2)} &= N^*_0 m_0^2 g_0 \exp\left(\frac{c'_{(2)}}{1.5P_{M(2)}}\right). \end{aligned} \tag{36}$$

Using the equation obtained for the water molecules – $(N_{(1)}^*/m_{(2)} = N_{(2)}^*/m_{(1)})$ – and Eqs. (31) and (36), the final result obtained is

$$\begin{aligned} \frac{\Delta_{2(e)}}{h} = \Biggl\{\exp\Biggl[\frac{1.5P_{M(2)}d_{(2)}}{d''\varepsilon_{0(2)}} \ln\Biggl\{\frac{d_{W(2)}}{d''}\left(1 + 2\cos\left(\frac{\alpha}{2} + \beta_2\right) + \right. \\ \left. + 2\cos\frac{\alpha}{2}\cos\theta\right)\Biggr\} - \frac{1.5P_{M(1)}}{d''\varepsilon_{0(1)}} \ln\Biggl\{\frac{d_{W(1)}}{d''}\left(1 + 2\cos\left(\frac{\alpha}{2} + \beta_1\right) + 2\cos\frac{\alpha}{2}\cos\theta\right)\Biggr\}\Biggr]\Biggr\}^{1/2} - 1, \end{aligned} \tag{37}$$

where

$$\cos\beta_1 = \frac{L_0\sqrt[3]{d''/d_{W(1)}} - h_{1(1)}}{0.96\cos\frac{\alpha}{2}}; \quad \cos\beta_2 = \frac{L_0\sqrt[3]{d''/d_W} - h_{1(2)}}{0.96\cos\frac{\alpha}{2}}.$$

Consider the contribution of the structural component of the disjoining pressure to Δ/h. This entails Using Eq. (38) [7]:

$$\Pi_s(h) = \frac{\varepsilon'_{0(1)}P^2_{0(1)}}{2a_0}\exp\left(-\frac{h}{l}\right), \tag{38}$$

where P_0 is the polarization of the dielectric at the layer surface due to the orientation of its dipoles by the field of surface forces; ℓ is a constant characterizing the correlation length of the liquid molecules. For water layers, ℓ is estimated at 10 Å [7].

With modification of the solid phase under the influence of physicochemical processes

$$\Pi_s'(h) = \frac{\varepsilon_{0(2)}' P_{0(2)}^2}{2a_0} \exp\left(\frac{-h - \Delta_{3(s)}}{l}\right). \tag{39}$$

Hence

$$\frac{\Delta_{3(s)}}{h} = \frac{l}{h} \ln \frac{\varepsilon_{0(2)}' P_{0(2)}^2}{\varepsilon_{0(1)}' P_{0(1)}^2}, \tag{40}$$

or

$$\frac{\Delta_{3(s)}}{h} = \frac{l}{h} \ln \frac{\varepsilon_{0(2)}' \chi_{0(2)}^2}{\varepsilon_{0(1)} \chi_{0(1)}^2}, \tag{41}$$

where $\chi_{0(1)}$ and $\chi_{0(2)}$ are the dielectric susceptibilities of the solid phase.

Following [22], it may be shown that the dielectric susceptibility is proportional to the characteristic bond length in the crystals. Then $\chi_{0(2)}^2/\chi_{0(1)}^2 = [(b + \Delta_{(2,b)})/(b + \Delta_{(1,b)})]^2$ (b is the characteristic bond length in the crystals, $\Delta_{(b)}$ is the deformation of this bond).

The final result obtained is

$$\frac{\Delta_{3(s)}}{h} = \frac{l}{h} \ln \left\{\left[\frac{b + \Delta_{(2,b)}}{b + \Delta_{(1,b)}}\right]^2 \exp\left\{\frac{1.5P_{M(2)}d_{(2)}}{d''\varepsilon_{0(2)}} \ln\left[\frac{d_{W(2)}}{d''}\left(1 + 2\cos\left(\frac{\alpha}{2} + \beta_2\right) + 2\cos\frac{\alpha}{2}\cos\theta\right)\right] - \right.\right.$$
$$\left.\left. - \frac{1.5P_{M(1)}d_{(1)}}{d''\varepsilon_{0(1)}} \ln\left[\frac{d_{W1)}}{d''}\left(1 + \cos\left(\frac{\alpha}{2} + \beta_1\right) + 2\cos\frac{\alpha}{2}\cos\theta\right)\right]\right\}\right\}. \tag{42}$$

Thus, the change in filtrational properties of disperse systems (clay soils and minerals) under the influence of physicochemical processes is determined by the change in volume of the nonconducting and conducting pores and also by the change in the following structural parameters of the adsorbed water; the mass of the double molecular layer; the activation energy of translational mobility of water molecules in the formation of this layer (the activation energy is found from the potential energies of molecular oscillation [5]); the density of the adsorbed water; the sum of the projections of the chemical bond lengths in the adsorbed dimer on the direction perpendicular to the surface of the crystal lattice (in particular, on the direction perpendicular to the straight line connecting vertices of the structural-layer tetrahedra), taking account of lattice deformation.

The experimental results estimating the contribution of the structural parameters of the adsorbed water to the change in filtration coefficients of the disperse systems under the influence of various physicochemical processes will be presented in a forthcoming publication.

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INFLUENCE OF THE AQUEOUS-PHASE PRESSURE ON THE FREEZING AND THAWING OF PORE MOISTURE IN HIGHLY DISPERSE MEDIA

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The freezing and thawing of sandy (frozen) rock is considered, taking account of the temperature and pressure correlation at the phase-transition front.

To ensure reliable construction and operation of boreholes in extreme northerly regions, it is necessary to know the laws of rock freezing. In some models of highly disperse media, for example sandy loam, sand, sandstone, thawing and freezing are described by the Stefan problem [1, 2], in which the existence of a smooth frontal surface between two phases of pore water – liquid and solid – is assumed. The temperature at the front is usually assumed to be constant throughout the whole period of development of the process. However, in situations that are of practical interest, it is common to determine the pressure in the liquid phase, which is transmitted there from outside or created there because the front displaces the water excess as a consequence of the density difference between the two phases. In a limited volume of water phase, the pressure arising on freezing may contort the borehole

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