Journal of Engineering Physics and Thermophysics, Vol. 69, No. 1, 1996

ON THE THEORY OF THE EFFECT OF INHIBITION OF RADIONUCLIDE AND HEAVY-METAL TRANSFER FROM SOIL TO PLANTS BY AMELIORANTS.
II. ESTIMATION OF THE CHANGES IN THE ION DIFFUSION COEFFICIENTS IN SOIL AT LOW CONCENTRATIONS OF FILTRATION SOLUTIONS. THEORY AND CALCULATIONS

P. P. Olodovskii

UDC 541.18:631.4

Relative ion diffusion coefficients in sandy-loam and loamy soils are calculated.

In [1] it is shown that when calcium oxide (quicklime) is introduced into a disperse system (soil), the relative ion-diffusion coefficients are smaller than unity at low concentrations of filtration solutions. In order to find an explanation of this effect, it seems useful to consider works in which processes of diffusion transfer have been studied for various types of compounds in solid-liquid or solid-gas systems. In particular, in [2] different transfer variants (schemes) are considered: a reagent is introduced into a liquid or gas containing a solid compound; the reagent approaches the external contour of a solid powder; and in a porous layer diffusion occurs towards the external contour of every grain. It is shown that in a solid-gas or solid-liquid system, the diffusion coefficient of the i-th compound can be defined as follows:

$$D = \frac{\Phi_i z}{\Delta c}, \tag{1}$$

where Φ_i is the absolute value of the flow (flow rate) of a diffusing compound passing through a unit area; Δc is the difference between the concentration of the diffusing compound on the solid surface and the concentration of the compound in the liquid or gas; z is the thickness of the boundary layer within which this concentration difference appears.

Consequently, in the present case

$$\frac{D_1}{D_2} = \frac{z_1}{z_2}\frac{\Delta c_2}{\Delta c_1} \tag{2}$$

(subscript 1 refers to ameliorant-modified systems; subscript 2, to the reference systems).

First, z_1/z_2 will be estimated. To do this, use will be made of the results given in [3], where a theory is presented for the changes in the filtration properties of disperse systems induced by physicochemical processes. Then, it follows that

$$\frac{z_1}{z_2} = \frac{P_{\mathrm{m}(1)}}{P_{\mathrm{m}(2)}} \times \left[\ln \frac{\overline{m}_0^{\,2} g_0 \rho_0}{d_{\mathrm{w}(1)} \overline{m}_1^{\,2} \left[1 + 2\cos\left(\frac{\alpha_{i(1)}}{2} + \beta_{i(1)} - \gamma_{i(1)}\right) + 2\cos\left(\frac{\alpha_{j(1)}}{2} + \gamma_{j(1)}\right)\cos\beta_{j(1)}\right]}\right] \times$$

$$\times \left[\ln \frac{\overline{m}_0^{\,2} g_0 \rho_0}{d_{\mathrm{w}(2)} \overline{m}_2^{\,2} \left[1 + 2\cos\left(\frac{\alpha_{i(2)}}{2} + \beta_{i(2)} - \gamma_{i(2)}\right) + 2\cos\left(\frac{\alpha_{j(2)}}{2} + \gamma_{j(2)}\right)\cos\beta_{j(2)}\right]}\right]^{-1}, \tag{3}$$

Central Research Institute of Integrated Water Management, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 69, No. 1, pp. 151-159, January-February, 1996. Original article submitted January 1, 1995.

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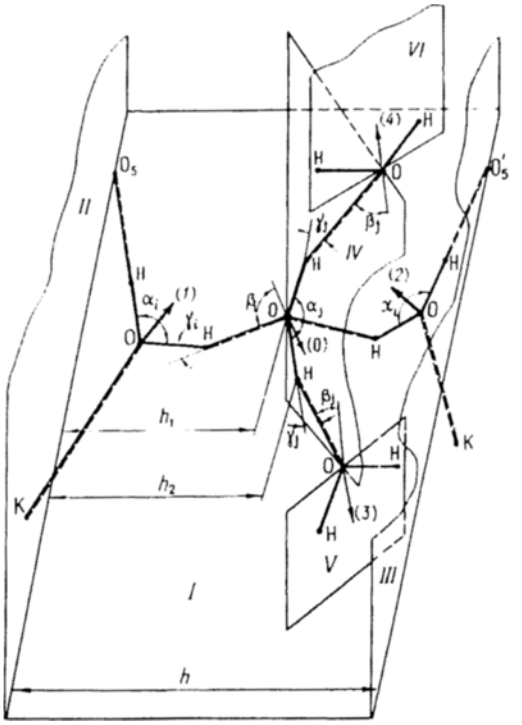


Fig. 1. Dipole moments in water molecules adsorbed in narrow capillaries.

where P_m is the mass of the double molecular layer of adsorbed water molecules; d_w is the density of absorbed water corresponding to the formation of a double molecular layer; $\overline{m}_0$ is the dipole moment of a water molecule in the bulk; $\overline{m}_1$ and $\overline{m}_2$ are the dipole moments of water molecules in the adsorbed state; g_0 is the correlation parameter in Kirkwood's equation for the bulk water; ρ_0 is the density of the bulk water. The other parameters in formula (3) will be explained using Fig. 1. According to the figure, the water molecule that forms a dimer in the process of sorption (its dipole moment, designated by (0), is located at the intersection of planes I and IV) is taken as the central molecule.

The oxygen atom of the central molecule is located on the axis of symmetry of a narrow slot capillary of width h bounded by planes II and III, and the molecule itself forms a tetrahedral environment of four water molecules, two of which (their dipole moments are designated by (1) and (2)) are adsorbed directly on the crystal lattice and located in plane I, while the other two are oriented along the axis of the slot capillary and located in planes V and VI. Bent hydrogen bonds are assumed. Consequently, in formula (3) α_i is the value of the valence angle in the water molecules designated by (1) and (2) in Fig. 1; α_j is the valence angle in the water molecule designated by (0); β_i is the angle between the dipole of the central molecule with subscript (0) and the direction of the hydrogen bonds forming dimers in plane I; γ_i is the bend angle of these hydrogen bonds; β_j is the angle between the dipole designated by (3) and (4) in Fig. 1 and the direction of the hydrogen bond forming the dimer and stretched along the slot capillary; γ_j is the bend angle of these hydrogen bonds. The procedure for calculation of the parameters in formula (3) is described in [4-6].

Proceeding from the scheme shown in Fig. 2, we have

$$\cos(\beta_i - \gamma_i) = \frac{h_2 - h_1}{r_j \cos\frac{\alpha_i}{2} \cos\varphi_i}. \tag{4}$$

Here h_1 is the sum of the projections of the lengths of the chemical bonds in the adsorbed dimer onto the direction perpendicular to the surface of the crystal lattice (in particular, onto the direction perpendicular to the straight line connecting the vertices of the tetrahedra of the structural layers) to the oxygen atom in the central molecule, i.e.,

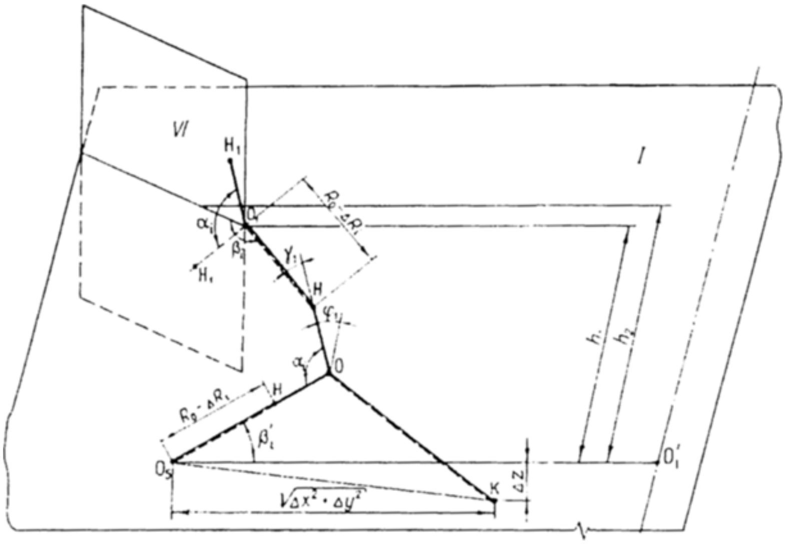


Fig. 2. Adsorbed dimer on active sites of argillaceous mineral.

$$h_1 = [(R_0 - \Delta R_i) + r_i] \cos \beta_i' + r_i \cos \varphi_i + (R_0 - \Delta R_i) \cos (\gamma_i + \varphi_i) \tag{5}$$

where R_0 is the length of the hydrogen bond between water molecules in liquid water; ΔR_i is the change in the length of the hydrogen bond induced by adsorption of a water molecule at active sites of the crystal lattice of the mineral; r_i is the length of the valence bond in water adsorbed on the crystal lattice.

The angles β_i' and φ_i are found as follows. In Fig. 1, O_5 and O_1 are the positions of oxygen atoms at the vertices of the tetrahedra of the crystal lattice of the mineral, K is the position of the exchange cation. Then,

$$O_5K = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2}$$

where Δx, Δy, and Δz are the differences of the coordinates between K and O_5; $\angle KOO_5 = 180^0 - (\alpha_i/2)$. Consequently, it is easy to determine all the angles and lengths of the sides in the triangle OO_5K. The angle $\varphi_i = 90^0 - \alpha_i + \beta_i$. If the density of the adsorbed water is assumed to be inversely proportional to h_i^3, then

$$h_2 = h_{0(2)} \sqrt[3]{\rho_0 / d_w}\ , \tag{6}$$

where $h_{0(2)}$ is the projection of the lengths of the chemical bonds in the dimer of liquid water onto the height of the tetrahedra from the center of its base formed by the plane passing through three oxygen atoms to the hydrogen atom in the molecule whose oxygen atom is the fourth vertex of the tetrahedron. In [4] $h_{0(2)}$ is found to be 3.88 Å.

Concrete calculations should be started from infrared spectra of the disperse systems studied. In Fig. 3 one can see IR spectra of water absorbed on the surface of the solid phase of sandy-loam soil. We studied soil samples modified by calcium oxide with contents of 0.083, 0.166, and 0.330% of the weight of the air-dry soil, soil samples modified by $CaCO_3$ with the same ameliorant content, and the control (without any ameliorant). In the additions indicated 0.083% is equivalent to introduction of 2.5 t/ha of the ameliorant, 0.166% to 5 t/ha, and 0.330% to 10 t/ha of the ameliorant.

In the region of deformation vibrations of water molecules (Fig. 3a), two frequencies (1635 and 1655 cm^{-1}) are observed, irrespective of the modification conditions. In the region of stretching vibrations of water molecules (Fig. 3b), three frequencies (3420, 3480, and 3555 cm^{-1}) are observed in the control; in the case of calcium oxide the following frequencies are observed: at 0.089%, 3420, 3480, and 3552 cm^{-1}; at 0.166% and 0.330%, 3420, 3480, and 3550 cm^{-1}; in the case of $CaCO_3$ in all the cases the following frequencies were observed: 3420, 3480, and 3555 cm^{-1}. Consequently, introduction of $CaCO_3$ does not bring about any changes in the frequency of stretching vibrations of H_2O as compared with the control, while introduction of CaO induces a 5 cm^{-1} change in one of the three frequencies at 0.330% and 0.166%, and a 3 cm^{-1} change at 0.083%.

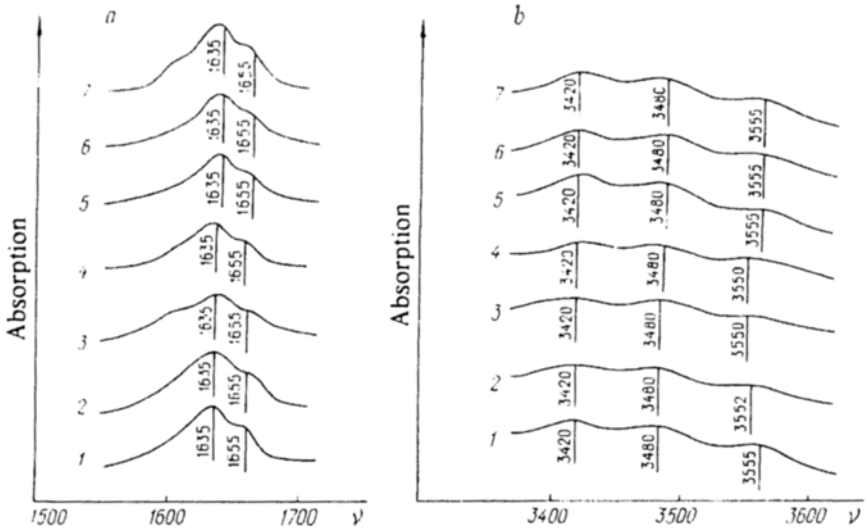


Fig. 3. IR spectra of water adsorbed on the surface of sandy-loam soil: 1) the soil without any ameliorant (control); 2, 3, 4) CaO introduced at 0.083, 0.166, 0.083, and 0.330%, respectively, of the weight of air-dry soil; 5, 6, 7) $CaCO_3$ introduced at 0.083, 0.166, and 0.330%, respectively, of the weight of air-dry soil. ν, cm^{-1}.

In further calculations the case with CaO will be referred to as variant 1 (the quantities have subscript 1), and the case of $CaCO_3$ and the control, as variant 2 (the quantities have subscript 2).

The presence of three frequencies in the region of stretching vibrations implies the formation of three types of adsorbed complexes: a symmetric complex with the frequencies 3420 and 3480 cm^{-1} and an asymmetric complex with frequencies of 3420 and 3550 cm^{-1} (variant 1) and 3420 and 3555 cm^{-1} (variant 2). With these frequencies, the force constants of the valence bonds, lengths of valence bonds, valence angles in absorbed water molecules (molecules with subscripts (1) and (2) in Fig. 1), changes in the potential energy of vibrations of these molecules, and changes in the lengths of hydrogen bonds with the central molecule as well as bend angles of these hydrogen bonds were determined. The calculated results are summarized in Table 1.

As follows from the table, introduction of CaO (quicklime) results in a 0.420^0 increase in the bend of the hydrogen bond.

For determination of the other parameters in formulas (2) and (3), it is insufficient to know the frequencies obtained from the IR specta. In determination of the angle φ_i, account was taken of the deformation of the crystal lattice of argillaceous minerals that results from adsorption of water molecules; in determination of h_2 data on the density of absorbed water [4] were used.

Formulas (2) and (3) also contain parameters of the central water molecule (see Fig. 1): α_j, r_j, γ_j, β_j. These quantities were estimated by NMR spectroscopy methods. The theory of the calculation is developed in [5]. The same paper gives the relative longitudinal relaxation times T_1/T_1^0 in the NMR spectra as functions of the ratio m/M (where m is the mass of the solid phase, M is the mass of the solid phase and water) for montmorillonite, hydromica, and koalinite. Experimental values of T_1/T_1^0 were used to determine r, α, ΔR and γ for water molecules in the bulk water in contact with the solid phase. For the central water molecule the quantities r_j, α_j, ΔR_j, and γ_j were found by interpolation of the parameters of the molecule in the bulk water to the parameters of adsorbed water at m/M corresponding to the structure shown in Fig. 1.

The quantities φ_i, α_j, γ_j, and $\beta_i - \gamma_i$ determined to fit the data on deformation of the crystal lattice of montmorillonite and keolinite as well as the values of $\overline{m}_j$ and d_w are given in Table 2.

The tables contain all parameters for determination of z_1/z_2. Assuming $P_{m1}/P_{m2} \simeq 1.0$ (this result follows from a series of experimental measurements), it is found that for sandy-loam soil with account of deformations of the crystal lattice of montmorillonite and kaolinite, $z_1/z_2 = 0.846$ and 0.735, respectively, and the average $z_1/z_2 =$ 0.79.

TABLE 1. Parameters of Water Molecules Adsorbed on the Surface of the Solid Phase of Sandy-Loam and Loamy Soils

Parameter	Soil type			
	sandy-loam		loam	
	(1)	(2)	(1)	(2)
Force constants of valent bonds in symmetric adsorbed complexes (cm^{-1})				
$K_{q_1q_1} \cdot 10^6$	10.97	10.97	10.97	10.97
$K_{q_1q_2} \cdot 10^6$	0.19	10.19	0.19	0.19
The same in asymmetric complexes				
$K_{q_1q_1} \cdot 10^6$	11.69	11.75	11.69	11.75
$K_{q_2q_2} \cdot 10^6$	11.02	11.04	11.02	11.04
Lengths of valence bonds (Å)				
r_{11}	0.991	0.990	0.991	0.990
r_{22}	1.011	1.010	1.011	1.010
Valence angles α_i (deg)	99.5	99.65	99.4	99.65
Change in potential energy of molecular vibrations ΔU (kcal/mole)	2.189	2.087	2.206	2.087
Changes in lengths of hydrogen bonds ΔR_i (Å)	0.096	0.093	0.097	0.093
Bend angle of hydrogen bonds γ_i (deg)	21.72	21.30	21.99	21.30

TABLE 2. Parameters of Water Molecules Calculated for Deformation of Crystal Lattices of Montmorillonite and Kaolinite in Absorption on the Surface of Solid Phase of Sandy-Loam and Loamy Soils

Parameter	Soil type			
	sandy-loam		loam	
	(1)	(2)	(1)	(2)
For defomations of montmorillonite				
φ_i (grad)	5.44	5.37	5.52	5.37
α_j (grad)	99.503	99.653	99.403	99.653
γ_j (grad)	21.621	21.201	21.90	21.201
$\beta_i - \gamma_i$ (grad)	40.68	42.40	38.867	41.340
$\overline{m}_j$ (D)	1.793	1.796	1.793	1.796
Density of adsorbed water d_w (g/cm^3)	1.153	1.153	1.153	1.153
For deformation of kaolinite				
φ_i (grad)	4.35	4.32	4.48	4.32
α_j (grad)	99.52	99.67	99.42	99.52
γ_j (grad)	21.65	21.14	21.93	21.65
$\beta_i - \gamma_i$ (grad)	35.04	37.11	37.97	40.23
$\overline{m}_j$ (D)	1.793	1.796	1.793	1.796
Density of adsorbed water d_w (g/cm^3)	1.177	1.177	1.177	1.177

In Fig. 4 IR spectra of water adsorbed on the surface of the solid phase of loamy soil are presented. Samples modified by calcium oxide at 0.166, 0.330, and 0.496% of the weight of the air-dry soil, samples modified by

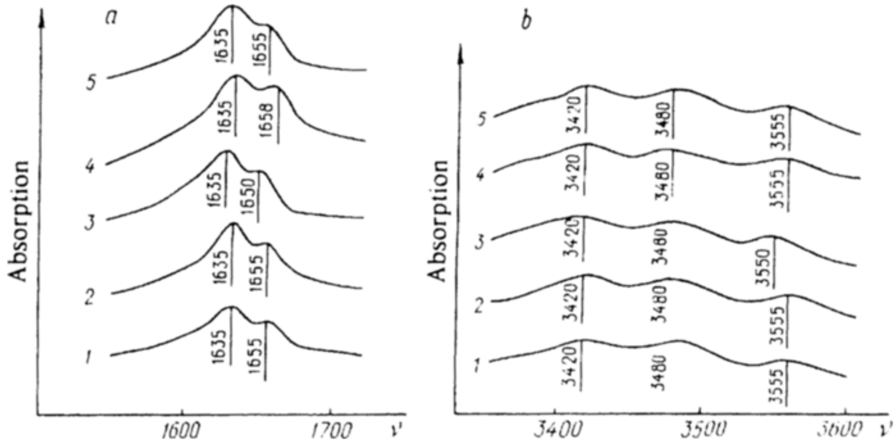


Fig. 4. IR spectra of water adsorbed on the surface of loamy soil: 1) the soil without any ameliorant (control); 2) $CaCO_3$ introduced at 0.166% of the weight of air-dry soil; 3, 4, 5) CaO introduced at 0.083, 0.166, and 0.330%, respectively, of the weight of air-dry soil.

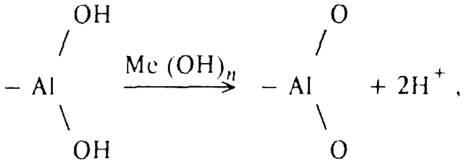
$CaCO_3$ at 0.166%, and control samples were investigated. In the region of stretching vibrations of water molecules (Fig. 4b) the three frequencies 3420, 3480, and 3555 cm^{-1} are observed for the control; the three frequencies 3420, 3480, and 3555 cm^{-1} are observed in the case of calcium oxide at 0.166%, and the three frequencies 3420, 3480 and 3555 cm^{-1} at 0.330 and 0.496%; in the case of introduction of $CaCO_3$, the frequencies 3420, 3480, and 3555 cm^{-1} are observed.

In the region of deformation vibrations of water molecules (Fig. 4a), two frequencies (1635 and 1655 cm^{-1}) are observed in all experimental variants except the case of calcium oxide introduced with a content of 0.330%. Consequently, introduction of calcium oxide with the 0.25% content causes the frequency 3550 cm^{-1} (instead of 3555 cm^{-1}) in the region of stretching vibrations and the frequency 1658 cm^{-1} (instead of 1655 cm^{-1} in the region of deformation vibrations.

Basically, only a frequency difference in the region of deformation vibrations caused a difference in some other parameters of water molecules adsorbed on the loamy soil. All parameters are presented in the tables and used to obtain the average $z_1/z_2 = 0.70$.

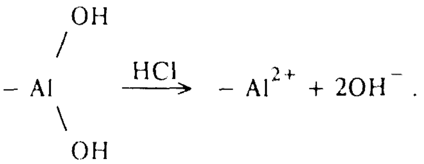
Now, the ratio $\Delta c_1/\Delta c_2$ will be determined. Estimation of this ratio will be based on the principle (mechanism) of ion adsorption on the surface of the solid phase of the soil upon introduction of calcium oxide.

It is known that in argillaceous minerals of soils, the most active hydroxyls are unsaturated paired OH-groups linked with Al atoms at the boundary of the octahedral layer as well as OH-groups linked with silicon at the boundary of the tetrahedral layer. The OH-groups of the first structural unit exhibit amphoteric properties, i.e., in an alkaline medium they dissociate following the acid type:



$$-\mathrm{Al}\begin{matrix}/\,\mathrm{OH}\\ \backslash\,\mathrm{OH}\end{matrix} \xrightarrow{\mathrm{Me\,(OH)}_n} -\mathrm{Al}\begin{matrix}/\,\mathrm{O}\\ \backslash\,\mathrm{O}\end{matrix} + 2\mathrm{H}^+,$$

and in an acid medium they dissociate following the alkaline type:



$$-\mathrm{Al}\begin{matrix}/\,\mathrm{OH}\\ \backslash\,\mathrm{OH}\end{matrix} \xrightarrow{\mathrm{HCl}} -\mathrm{Al}^{2+} + 2\mathrm{OH}^- .$$

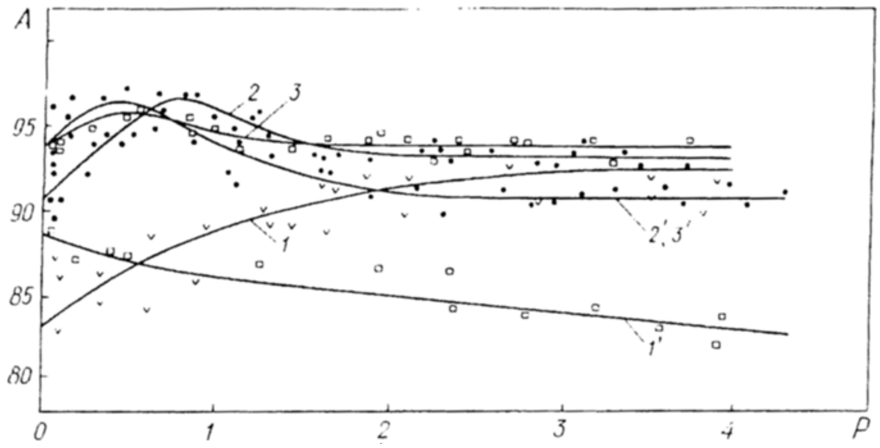
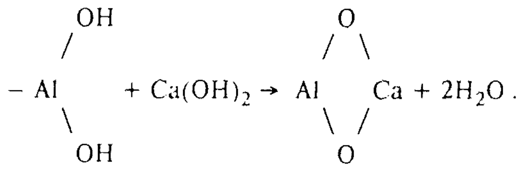


Fig. 5. Constants of hyperfine interaction in EPR spectra of the Mn^2 ion (*A*, e) in loamy soil (*P*, %, moisture content of the soil): I) position of the Mn^{2+} ion on the base and lateral faces of montmorillonite; 1) the same, but on the base; 2) position of the Mn^{2+} ion on the base and lateral faces of hydromica; 2') but same, only on the bases; 3) position of the Mn^{2+} ion on the base and lateral faces of kaolinite; 3') the same, but on the bases.

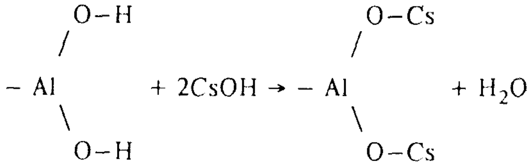
In view of this, it is possible to suggest that in an alkaline medium absorption of H$^+$ and OH$^-$ ions (in excess of the Donnan absorption) is caused by an increase in the exchange capacity of soils due to substitution of H$^+$ for Me^{n+} ions from OH-groups.

In the case of CaO introduction

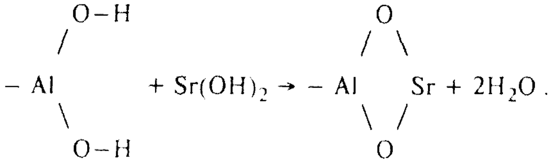


$$-\mathrm{Al}{<}^{\mathrm{OH}}_{\mathrm{OH}} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{Al}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Ca} + 2\mathrm{H_2O}\,.$$

But the other ions are simultaneously bound to calcium following the same scheme:



$$-\mathrm{Al}{<}^{\mathrm{O-H}}_{\mathrm{O-H}} + 2\mathrm{CsOH} \rightarrow -\mathrm{Al}{<}^{\mathrm{O-Cs}}_{\mathrm{O-Cs}} + \mathrm{H_2O}$$



$$-\mathrm{Al}{<}^{\mathrm{O-H}}_{\mathrm{O-H}} + \mathrm{Sr(OH)_2} \rightarrow -\mathrm{Al}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Sr} + 2\mathrm{H_2O}\,.$$

In this work it appeared possible to show that in particular ranges of soil moisture content, the bond energy of some exchange cations adsorbed on oxygen atoms following the schemes presented here (these oxygen atoms are located on the lateral faces of the crystal lattice) is higher than the bond energy of the same cations located on the basal surfaces. This was proved by EPR methods. Loamy soil was studied in which argillaceous fraction consisted of montmorillonite, hydromica, and kaolinite. Two samples were prepared simultaneously. In the first sample Mn^{2+} ions were fixed to the basal surfaces and lateral faces and in the second sample, only to the basal surfaces.

For the two kinds of samples, the constants of the hyperfine structure in the EPR spectra of Mn^{2+} ions were determined following the procedures used in [4, 7-9]. The results are shown in Fig. 5.

It is known that in the EPR spectra of transient ions the constant of hyperfine interaction is proportional to $<1/r^3>$, characterizing the position of the maximum of electron density, i.e., as the constant grows, the binding energy of the central ion with the field of ligands decreases. Consequently, the decrease in the constants of hyperfine interaction observed at zero moisture content for the first sample relative to the constant of hyperfine interaction for the second sample for montmorillonite and hydromica indicates that the binding energy of the Mn^{2+} ion adsorbed due to destruction of the side OH-groups with oxygen atoms in the crystal lattice is higher than the binding energy of the same ion fixed to the basal surfaces. It is this fact that explains the effect of a decrease in the concentration of some ions in a pore solution in soil into which quicklime has been introduced as well as the effect of a decrease in the ion diffusion coefficients in the soil. Then, it is possible to write:

$$\frac{\Delta c_1}{\Delta c_2} = \frac{A_2}{A_1} = \frac{E_1}{E_2}, \tag{7}$$

where A_1, A_2, E_1, and E_2 are the constants of hyperfine structure and bond energies of ions adsorbed on the modified and unmodified argillaceous mineral.

According to the data shown in Fig. 5, at a moisture content close to zero, the ratio of the constants of hyperfine structure is 0.93 for montmorillonite and 0.97 for hydromica. The average ratio $A_2/A_1 = 0.95$. Then, for sandy-loam soil the predicted ratio is $D_1/D_2 = 0.75$ and the experimental ratio is 0.76. For loamy soils the predicted value is $D_1/D_2 = 0.66$ and the experimental value is 0.61.

It should be noted that in the case of quicklime introduction into the soil, the decrease in the ion diffusion coefficients can be explained by a more rigid attachment of ions to the solid phase surface and, as a result, by changes in the parameters of water molecules adsorbed on the soil surface. It should be noted that the introduction of powdered dolomite, a conventional ameliorant, at least into neutral soils, cannot decrease the diffusion coefficients or, consequently, ion accumulation in plants.

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