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Abstract

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THE NATURE OF HYDRATION OF EXCHANGE CATIONS IN CLAY MINERALS

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The role of exchange cations and of the surface of clay minerals in the binding of water has been studied in detail and widely discussed (1-3). However, up to the present time there are no experimental data that would make it possible to decide, with justification, the question of the degree and nature of this influence. The influence of cations on the total amount of adsorbed water in clays, on its energetic nonuniformity, mobility (4), and swelling (5) has been demonstrated. Meanwhile, the nature of the influence of cations is still insufficiently clear: whether it is only a manifestation of the hydration of the cations themselves, or the result of a change in the molecular nature of the surface of the clay particles and in the microstructure of the clay.

In the present work experimental material is presented on the study of differential heats of wetting, dehydration curves, and nuclear magnetic resonance spectra of monomineral clays saturated with ions Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}. It is known (6) that the selected cations have different hydration character.

Dehydration curves of askangel, Polozhsk kaolinite, and Chasov-Yar montmorillonite were obtained on an apparatus providing dehydration of the sample under isothermal conditions in the interval from 60 to 300°, in steps of 20°. Transfer to the next heating stage was carried out when the dehydration rate became less than 0.001 mg/min. The accuracy of recording the weight loss was 0.05 mg.

Consideration of the obtained dehydration curves leads to the conclusion that, on all curves, against the background of continuous water evolution, at a certain temperature T_i, characteristic for each cation (independently of the mineral), there occurs a substantial increase in the rate of water removal. By the magnitude of this characteristic temperature the cations can be arranged in the following series: $Mg^{2+} \gg Ca^{2+} > Na > K$, which differs from the usual series of cations arranged by the total amount of water removed, $Mg^{2+} \approx Ca^{2+} > Na^{+} \approx K^{+}$. It is precisely in this sequence that the cations are arranged by the value of ΔE (6), which characterizes the change, under the action of the ion, of the potential barrier for water molecules nearest to the ion, in contrast to the usual series by total hydration energy. This suggests that the temperature T_i is determined by the onset of removal of water molecules that constitute the nearest environment of the cations. The probability of transition of molecules across the potential barrier $E + \Delta E$ at temperature T is proportional to $\exp((E + \Delta E)/kT)$. Starting from the experimental value of T_i for Mg samples ($t_{\text{Mg}} \approx 280^\circ$) (for Mg minerals the effect is most distinct, since it lies in the region of high temperatures where other categories of water have been removed), T_i was calculated for Ca^{2+}, Na^+, K^+ cations:

$$t_{\text{Ca}} \approx 114^\circ, \qquad t_{\text{Na}} \approx 80^\circ, \qquad t_{\text{K}} \approx 60^\circ.$$

The obtained temperature values are close to the experimental ones.

The amount of water removed at $t^\circ = 260$—280° in Mg-montmorillonite and kaolinite, referred to the adsorption capacity of these minerals, is 1–2 molecules.

The heats of wetting of preliminarily moistened Ca- and K-Askangel samples were obtained on a microcalorimeter making it possible to record an amount of heat greater than 0.02 cal with an accuracy of 2%. Table 1 gives experimental data on the dependence of the heat of wetting Q of the samples on the degree of their preliminary moistening W (%) and the differential heats of wetting $q(W)$, obtained by graphical differentiation of the experimental dependence $Q(W)$.

Table 1

Ca-Askangel	Ca-Askangel	Ca-Askangel	K-Askangel	K-Askangel	K-Askangel
W, %	Q, cal/g	q, kcal/mol	W, %	Q, cal/g	q, kcal/mol
0	30.8		0	10.2	
8.3	22.2	1.9	1.1	10.6	0.7
13.5	13.1	3.1	2.4	5.3	7.3
15.0	9.3	4.6	2.9	4.1	4.3
19.8	6.3	1.1	3.2	3.9	1.2
23.2	4.5	1.0	5.1	2.0	1.8
27.0	3.6	0.5	8.0	0.8	0.7
30.0	2.6	0.6			
42.2	1.1	0.3			

The difference in the differential heats for Ca- and K-Askangel at low moisture content fully corresponds to the different character of hydration of the ions Ca^{2+} and K^+. Indeed, if one assumes that, upon binding of the first portions of water, its molecules hydrate the exchange cations, entering their nearest environment, then we must take into account not the full hydration energy of these cations, but only ΔE, whose value is positive for Ca^{2+} and negative for the K^+ ion. In this case hydration of K-Askangel must proceed with an additional loss of energy, which is what we observe (see Table 1).

Fig. 1. Recording of the derivative of the proton absorption signal of bound water in Ca- and K-montmorillonite

Figure 1: Fig. 1. Recording of the derivative of the proton absorption signal of bound water in Ca- and K-montmorillonite

The nuclear magnetic resonance spectra were obtained on a TsLA NMR spectrometer (^{7}). A check showed that the OH groups of the lattice make no contribution to the observed spectra.

Figure 1 presents the spectra of bound water in samples of Ca- and K-montmorillonite kept in a desiccator at $P/P_s = 0.01$. The asymmetry of the spectrum of the K sample is noteworthy.

Below are given the results of calculating the third moment $\overline{\Delta H^3}$ of the spectra of montmorillonite, the magnitude of which characterizes the degree of asymmetry of the signal caused by the shift of its components.

Ion	Mg^{2+}	Ca^{2+}	Na^{+}	K^{+}
$\overline{\Delta H^3}$ (G^3)	1.8	0.5	0.2	0.1

The asymmetry is not connected with the presence of paramagnetic impurities, since its degree depends entirely on the composition of the exchange cations. The magnitude of the component shift is considerable: ~ 0.1 G for the K sample. The degree of asymmetry and the character of its dependence on the type of exchange cation can be explained if it is assumed that part of the molecules of adsorbed water hydrate the OH groups of the lattice, while another part constitutes the nearest environment of the exchange cations. Indeed, for a field equal to 5000 G, the shift upon hydration of OH groups, relative to liquid water in electrolyte solutions, is $\approx 5 \cdot 10^{-2}$ G (^{8}), which is close to the observed value. The difference in the magnitude of the asymmetry for cation-substituted samples can qualitatively be explained (by analogy with the spectra of electrolyte solutions) by the different magnitude of the shift of the other component, caused by hydration of ions. In electrolyte solutions the ions Mg^{2+}, Ca^{2+} only slightly disturb the structure of water, while being strongly hydrated themselves, which leads to displacement of the signal toward

of the weaker field. Na^{+} and K^{+} ions destroy hydrogen bonds in the structure of water, themselves being only weakly hydrated; this leads to a shift toward the stronger field (^{8}). In our case, however, the difference is considerably larger in magnitude. This is understandable, since in electrolyte solutions we obtain an averaged picture from water molecules forming the immediate surroundings of the ions and from more remote molecules (near and far hydration—

Fig. 1. Recording of the derivative of the proton absorption signal of bound water in Ca- and K-montmorillonite

tion) (^{6}). In the adsorbed water of clays, apparently, only the near hydration of exchange cations occurs. Therefore, for the same directions of shifts, their magnitude in the second case may be considerably greater.

The very fact that, in the spectrum of bound water of clays, a given ion causes the same direction of shift as in the spectrum of solutions, with a simultaneous increase in the magnitude of the shift, may be interpreted as the absence of far hydration of the exchange ions of clays at the humidities studied.

In the spectra of water adsorbed by kaolinite, asymmetry is absent; this indicates the relatively small role of cations in the binding of water by kaolinite minerals.

The results of studying adsorbed water in monomineral, monoionic clays by a combination of methods lead to the conclusion that there are water molecules bound directly to the exchange cations and belonging to their nearest environment.

Indeed, the presence, for each ion, of a characteristic temperature during clay dehydration; the dependence of the course of the curve of differential heats of wetting on the type of ion; and the dependence of the magnitude of the anisotropy of the NMR signal of adsorbed water on the type of ion indicate hydration of exchange cations by molecules of adsorbed water. The influence of exchange cations on the mobility of the water molecules closest to them corresponds to the character of their nearest hydration in electrolyte solutions (6).

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Note: Figure translations are in progress. See original paper for figures.

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