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STUDY OF INTERLAYER WATER ON THE ACTIVE SITES OF MINERAL SORBENT
Thermal analysis

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Abstract

The programmed heating of montmorillonite samples is accompanied by their dehydration and dehydroxilation, this being registered by means of Derivatograph. The form of the endothermal effects within the 80–250°C interval can be of simple or double character depending on the nature of exchange cations. Though this phenomenon has been known for a long time, no satisfactory explanation has been provided so far. The herewith paper contains the results of bound water researches at various forms (Na, Ca, Al, Fe) of montmorillonite by means of thermal analysis as well as other physico-chemical methods. It has been found that the form of dehydration endoeffects depends on the state of the active centers of the mineral. In certain conditions, by means of thermal analysis one can determine corresponding quantities of bound water that are in agreement with various kinds of active centers of the mineral sorbent.

Keywords: active centers of mineral sorbent, bound water of montmorillonite, cationexchangeable montmorillonite, thermal analysis, X-ray

Introduction

Investigation of montmorillonite samples, conducted by thermal analysis, have demonstrated that independently of their origin, they display similar behavior while being heated. First their dehydration occurs (80–250°C), followed by dehydroxilation (occuring in one or two steps, 450–800°C) and, finally, there is the process of recrystallisation and amorphing accompanied by formation of new phases (850–950°C) [1–6].

Even during the first thermal investigations, it was observed that at various homoiones samples of mineral the dehydration process is marked by the appearance of a simple or double endothermal effect [1], the form of which depends on the nature of the exchangeable cation and on the degree of sample hydration. Various hypothe-

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ses have been advanced for explaining this phenomenon – from the one that saying that water molecules are fixed only on the interlaminary exchangeable cations (in case of the appearance of the simple endoeffect [7]), up to the one that admits the existence of various active centers (groups Si–OH, Me–OH), energetically non-homogenous, on the surface of the sorbent. They bind the water molecules in various ways thus bringing about a complex thermal effect [8]. However, this problem hasn't been fully resolved. It is still not known which active sites the water molecules, at the elimination of which these endothermal effects of various maxima appear, belong to. It is only known that the interlaminary exchangeable cations can have one, two or more strata of H_2O molecules that play an important role in the process of organic substances adsorption on montmorillonite. These molecules serve as linking rings between the molecules of the adsorbed organic substance and the active centers – exchangeable cations of montmorillonite [9–13]. A more profound knowledge of the state of the water that is sorbtively bound on the sorbent's active centers would explain some aspects of the mechanism for adsorption and catalysis on the surface of this mineral, this being both of theoretical and practical interest. The purpose of this paper was to study the bound water of montmorillonite using various physico-chemical methods, the focus being on the thermal analysis.

Experimental

Materials

Montmorillonite monoionic samples (Na, Ca, Al, Fe) have been used in the experiment. The montmorillonite has been extracted from Georgian bentonite(ascangel) by washing and decantation. The selection of this bentonite as object of research is due to its thermal effects that are well manifested during thermal analysis. The homoionic forms have been obtained from Na-montmorillonite by consecutive treatments with chloride solutions of corresponding cations up to saturation. After several washings (until the absence of Cl^- ion), the samples have been dried up at room temperature (23°C) till they reached a constant mass and then kept in closed vessels.

Methods

For thermal analysis research, montmorillonite samples in the form of sifted dust with particles dimensions of 0.10–0.16 mm, have been used. The investigations have been done using the OD-102 derivatograph (made by MOM, Hungary). Determination of water quantities released at heating has been done by processing the information of curves TG, DTG and DTA applying well known methods [14].

While researching with X-rays, preparates orientated by the montmorillonite in the form of thin stratum and obtained from suspension at drying on glass plates (2×2 cm^2) at room temperature, have been utilized. Difractograf 'Dron-3' with CoK_α emanation as well as Fe filter have been used.

For obtaining additional information about the interlaminary water of montmorillonite cationexchangeable forms, some of the samples have been treated with aqueous solutions with various pH values. These solutions have been prepared by adding small quantities (milliliters) of acid (HCl) or basic (NaOH or KOH) solutions to the distilled water so as to obtain a series with consecutive values after every 0.5 pH units. The measuring of the latter has been done by a pH-meter, the measurements error being ±0.01 pH. After a 15 h contact of the montmorillonite with these solutions (0.5 g solid/100 mL liquid), the solid phase was separated by centrifugation, dried up at room temperature, then subjected to thermal analysis. In the liquid phase (after centrifugation), the equilibrium pH was measured along with the concentrations of exchangeable cations and of Al^{3+}, Fe^{3+} cations outgoing from the composition of the mineral.

Also orientated preparates to be studied by means of X-rays were prepared from the pre-centrifugation suspension of samples treated with solutions (acid or basic).

Results and discussions

DTA curves, obtained for various homoionic forms of montmorillonite, are given in Fig. 1. DTA curves show that in the case of Na-montmorillonite the endothermic ef-

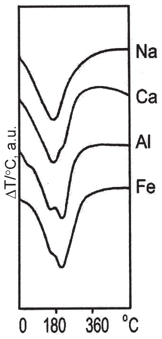


Fig. 1 DTA curves for various cationic forms of montmorillonite

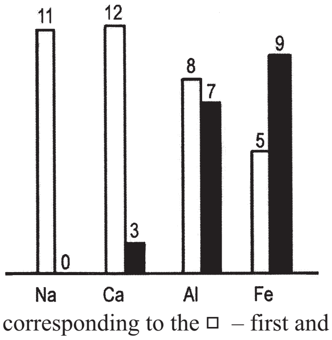


Fig. 2 Water quantity (%) corresponding to the □ – first and the ■ – second endothermal effect for various monoionic forms of montmorillonite

fect is simple while with the others double. These effects correspond to the elimination of two types of water that are energetically different, called by us as type I and type II, following the sequence of their elimination.

Figure 2 shows the quantities of water that correspond to these types of water for various montmorillonite monoionic forms calculated on the basis of TG curves. From these data one can see a clear dependence of water quantities (I and II) on the nature of the exchangeable cation. However, the reason for this phenomenon is not clear. For clarification, additional investigations have been conducted by treating the montmorillonite samples with acid and basic solutions with various pH, analyzing both the solid and the liquid phases. Measurements of equilibrium pH, obtained after treatment, demonstrate the titration of basic (M–OH) and acid (Si–OH) groups of the mineral.

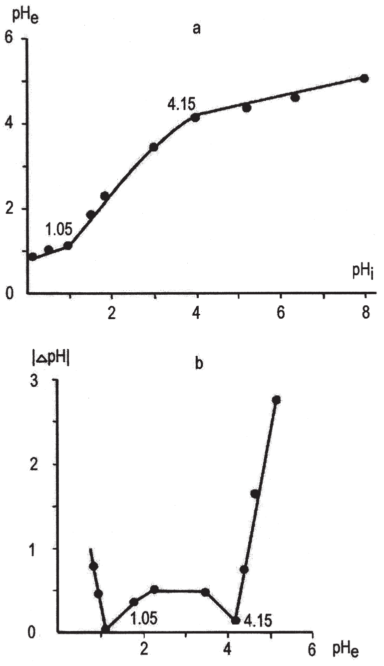


Fig. 3 Dependencies $pH_e=f(pH_i)$ and $|\Delta pH|=f(pH_e)$ a – and b – respectively, of obtained solutions after contacting Al-montmorillonite samples (pH_i-initial and pH_e-equilibrium values, $\Delta pH=pH_i-pH_e$)

Figure 3 confirms the above-mentioned statement – on the curves one can see two critical points: at pH_e 1.05 and at pH 4.15, corresponding to values pH_i Si–OH and pK_1 Al^{3+}. This means that at $pH<1$ in the sorbent we have non-dissociated groups Si–OH, in the pH 1–2 interval there is equilibrium, while at $pH>2$ practically all silanol groups are dissociated [15]:

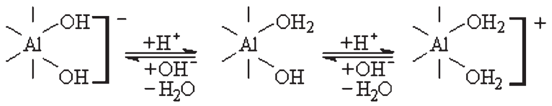
$$Si\text{–}OH=SiO^{-}+H^{+} \tag{1}$$

As for interlaminary exchangeable cations – compensators of the negative charge which have appeared as a result of isomorphous substitutions in the structure, the following can be said: they are likely to be hydrolyzed like cations from the solution of a soluble salt. By arbitrarily admitting that in both cases (solution and sorbent) the cations have a similar behavior depending on pH and having as model the equilibrium of various forms of the aluminium cation in the solution (Table 1), one can also presuppose the existence of various forms of sorbents exchangeable cations.

Table 1 Distribution (%) of Al hydroxocomplexes depending on the solution's pH (according to [16])

Complex	pH										
	0	3	4	5	6	7	8	9	10	11	12
Al^{3+}	100	98	90	40	2	0	0	0	0	0	0
$Al(OH)^{2+}$	0	2	10	40	48	0	0	0	0	0	0
$Al(OH)_2^+$	0	0	0	18	25	10	0	0	0	0	0
$Al(OH)_3$	0	0	0	2	25	90	98	22	18	4	0
$Al(OH)_4^-$	0	0	0	0	0	0	2	78	82	96	100

Depending on pH, the basic groups from the lateral faces of montmorillonite particles are also subjected to some changes that can be illustrated by the following scheme [15]:



(2)

The above-said denote a complex behavior of montmorillonite's active centers depending on the conditions the mineral sorbent is in, which often makes it difficult to interpret the experimental results.

Figure 4 shows the aspects of endo effects on DTA curves for samples of Al-montmorillonite that have been in contact with solutions of various pH, while Fig. 5 shows the data of information processed from TG curves.

From Fig. 5, one can observe that a certain correlation of the quantities of those two types of water is preserved within the pH 0.9–2.3 interval. Later on, this correlation sharply turns into another one (pH 3.5–4.4) which, in its turn, is substituted for by the third one (pH 4.6–5.1). The beginning of each new interval coincides or is close to the critical points on the titration curve (Fig. 3). If we compare the type I water content at pH 0.9 and 4.15, we observe a difference of 10.5–7.5=3%, this making up approximately the sixth part of the total content (types I and II) of sample's adsorption water. Taking into account the state of active centers and the complexity of their behavior at various pH values, and also confronting the obtained figure (3%) with the data from literature on the content of Si–OH groups (0.24 mmol g^{-1} [15] or about 4% of the sample's mass, recalculated according to the mass of OH groups), we can presuppose that this reflects the quantity of water lost by the silanol group.

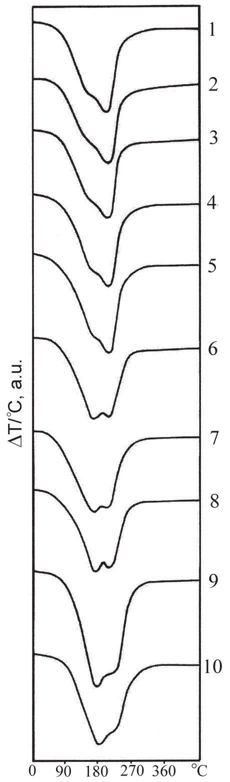


Fig. 4 DTA curves for samples of Al-montmorillonite, treated with solutions of various pH$_e$ values (0.90–5.10)

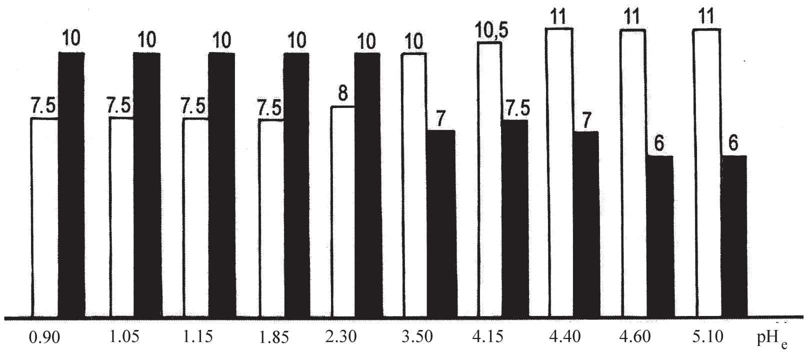


Fig. 5 Quantity (%) of released water corresponding to the □ – first and the ■ – second endothermal effects of Al-montmorillonite treated with solutions of various pH values

In the pH 3.5–4.4 interval, almost all adsorption water belongs to interlaminary exchangeable cations because in this pH interval the Si–OH groups are dissociated and the contribution of Al–OH groups is small (0.1 mmol g^{-1} [15], or 1.7% of sample's mass recalculated according to the mass of OH group). The existence of two types of water (I and II) in conditions when almost all water belongs to exchangeable cations is, in our opinion, explained by the influence of cation's electric charge on H_2O molecules and by some phenomena generated by this influence (orientation of H_2O dipoles, two covers of interaction water molecules, hydrolysis). They create conditions for the differentiation of the interaction energy of some or other H_2O molecules with the corresponding cation. The above mentioned can be illustrated through the following scheme:

$$M^{n+}\underset{1}{\cdots}\underset{H}{\overset{}{O}}\underset{2}{-}H\underset{1}{\cdots}\underset{H}{O}-H \rightleftharpoons (M-OH)^{(n-1)+} + H_3O^{+} \qquad (3)$$

where M^{n+} – is the interlaminary exchangeable cation, 1 – the shortening, 2 – the lengthening of bindings. The first water molecule is one of those six molecules that are in the first coordination sphere, while the second one is respectively one of the other (six or less) molecules from the second coordination sphere.

Analyzing the correlation of types I and II water content within the pH 4.4–5.1 interval, we observe that in respect to the sample from pH 2.3 the type II water has decreased by 10–6=4%. This loss of mass is probably due to the changes occurring in the sphere of exchangeable cations hydration and by a new state of Al–OH groups, both being imposed by the new conditions (another pH).

Table 2 Basal spacing d_{001} (nm) for Al-montmorillonite samples treated with solutions that have various values of pH equilibrium

pH	0.90	1.00	1.05	1.85	2.30	3.50	4.15	4.40	4.60	5.10
d_{001}	1.32	1.32	1.33	1.49	1.53	1.53	1.53	1.53	1.53	1.31

The data of X-ray analysis do not seem to cast doubt on our judgement . As it can be seen from Table 2, the Basal spacing d_{001} is constant in the pH 0.9–1.05 interval. Then it rises passing through an intermediate value at pH 1.85, and again preserves its constant value in the pH 2.3–4.6 interval, decreasing only at pH 5.1. It is to by noticed that parameter d_{001} changes its value in the proximity of the same critical points on the titration curve (Fig. 3), a fact that does not seem chancy at all.

There are no dissociated silanolic groups at pH<1 values [15], the summary ionic exchange capacity *E* being determined by the cations from the interlaminary space. The latter are not hydrolyzed, having only H_2O molecules situated only in one stratum. When pH is increased (interval 1.85–4.60) the Si-OH groups dissociate and negative charges appear ($Si–O^-$) which interact electrostatically with the opposite basic face thus leading to the increase of d_{001} parameter. On the other hand, the interlaminary cations get hydrolyzed and their summary charge decreases being partially neutralized by the OH group (Table 1). To re-establish the ionic equilibrium, hydrated cations (which may be partially hydrolyzed) come into the interlaminary space from the solution. This is something that also contributes to the increase of d_{001}. Thus the water molecules from the interlaminary space are already arranged in two strata.

Table 3 Dependence of methanol vapour adsorption and structural parameters of Al-montmorillonite samples on the pH of solutions (equilibrium value)

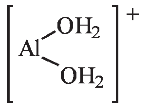
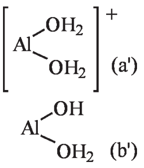
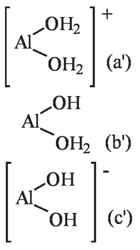
Sample No.	pH_e	A_m/mmol g^{-1}	S/m^2	V/cm^3 g^{-1}	r/nm
1	0.90	10.3	538	0.416	2.4
2	1.05	12.0	490	0.450	2.7
3	1.15	11.7	453	0.440	3.0
4	1.85	11.5	447	0.421	2.8
5	2.30	10.7	442	0.400	2.6
6	3.50	9.4	410	0.360	2.6
7	4.15	10.5	406	0.390	2.8
8	4.40	10.8	432	0.400	2.8
9	4.60	10.0	450	0.401	2.6
10	5.10	11.3	432	0.420	2.7

The following increase of pH (pH>4.6) leads to a more advanced hydrolysis of interlaminary cations and, thus, to a restructuring of their hydration sphere due to the existence and interaction of already two groups OH at the same cation. The interaction between the OH groups, as well as their interaction with basic faces imposes to the coordinating group and molecules an orientation that runs parallel with the basic plane in a single stratum. The value of parameter d_{001} decreases.

As seen from Table 3, the restructuring of active centers in the interlaminary space, both from the face and lateral sides of sorbents particles under the influence of pH, leads to the modification of structural parameters of investigated samples. Essential changes occur in the same pH critical points of which we already know from Fig. 3.

As it has been mentioned in [17], when pH increases (interval 1–3) there also rises the humidity and the specific volume of samples treated with solutions that have a corresponding pH. At pH 3–10 (the interval but not the equilibrium value), these values remain constant, then, after pH>10, they decrease sharply. The texture of the material changes, the value of ionic exchange capacity changes, too. This is also true for some electrokinetic parameters, both in a strong basic medium and in the acid one.

Table 4 Probable state of active centers of Al-montmorillonite treated with solutions of various pH values

pH interval	Si–OH groups	Interlaminary exchangeable cation	Al–OH groups
0.90–1.05	Si–OH	$\{[Al(H_2O)_6]\cdot mH_2O\}^{3+}$	
1.05–2.30	Si–OH SiO^-, H^+	idem	idem
2.30–4.15	SiO^-, Me^+	$\{[Al(H_2O)_6]\cdot mH_2O\}^{3+}$ (a) $\{[Al(OH)(H_2O)_5]\cdot nH_2O\}^{2+}$ (b) $C_a>C_b$	 $C_{a'}>C_{b'}$
4.15–4.40	idem	$\{[Al(H_2O)_6]\cdot mH_2O\}^{3+}$ (a) $\{[Al(OH)(H_2O)_5]\cdot nH_2O\}^{2+}$ (b) $\{[Al(OH)_2(H_2O)_4]\cdot kH_2O\}^{+}$ (c) $C_a>C_b>C_c$	 $C_{a'}>C_{b'}>C_{c'}$
4.40–4.60	idem	idem	idem
4.60–5.10	idem	idem, $C_a \geq C_b > C_c$	idem, $C_{a'} \geq C_{b'} > C_{c'}$

Note:
1. We do not rule out the coordination of exchangeable cations with oxygen atoms on the basic surface, but we believe that at advanced hydration they leave the coordination sphere being replaced by H_2O molecules
2. a, b, c and a', b', c' denote the forms of corresponding complexes.
3. C_a, C_b, C_c and $C_{a'}$, $C_{b'}$, $C_{c'}$ denote the contents of complexes in samples.
4. In a general case, $m \neq n \neq k$ and m, n, $k \leq 6$

Taking into consideration the behavior of the aluminium ion [16] and of Si–OH, Al–OH groups depending on pH [15] , (Table 1), as well as the results of X-ray analysis (Table 2), one can draw the conclusion that the active sites of montmorillonite are, depending on the medium, in various states, probably as it is schematically indicated in Table 4.

Our analysis of cation from the liquid phase has shown that when pH is decreased (pH<3), there is an increase of the concentration of cations emanated both from the exchangeable positions and from the montmorillonite structure. This confirms that a dynamic equilibrium of ions, very sensitive to environmental conditions, is available with the montmorillonite. Everything that has been said so far is the result of analysis of data obtained while studying the Al-montmorillonite . However, the conclusions are also valid for other forms (Na, Ca, Fe) of this mineral. The distinction is only in a more reduced clarity of the observed appropriateness because in the same conditions the interlaminary exchangeable cations are easily replaced by Al^{3+} cations emanated from the structure, a fact that somehow complicates the investigations and the analysis of obtained data.

References

1 R. E. Grim, Clay mineralogy, McGraw-Hill series in geology, New York 1953, p. 55 (in Russian).
2 V. Balek, Z. Malek, S. Yariv and G. Matuschek, J. Therm. Anal. Cal., 56 (1999) 67.
3 Z. Malek, V. Balek, D. Gorfinkel-Shweky and S. Yariv, J. Thermal Anal., 48 (1997) 83.
4 E. Mendelovici, J. Thermal Anal., 49 (1997) 1385.
5 I. W. M. Brown , K. I. D. Mackenzie and R. H. Meinhold, J. Mater. Sci., 22 (1987) 3265.
6 B. Cicel and G. Kranz, Clay Minerals, 16 (1981) 151.
7 R. C. Mackenzie, Min. Soc. Gr. Britain Clay Min. Bull., 4 (1950) 115.
8 R. I. Zlochevskaya, S. I. Zlochevskiy and G. A. Kuprina, In: Bound water in the dispersion systems, Moskow, 1972, p. 195 (in Russian).
9 S. Yariv, Thermochim. Acta, 274 (1996) 1.
10 A. Maftuleac, I. Dranca and T. Lupascu, Bull. Mold. Acad. Sci., Biol. Chem. Sci., 6 (1993) 43.
11 A. Maftuleac, V. Motoc and T. Lupascu, Russ. J. Appl. Chem., 12 (1997) 2063.
12 A. Maftuleac, T. Lupascu and V. Motoc, Bull. Mold. Acad. Sci., Biol. Chem. Sci., 2 (1996) 54.
13 Iu. I. Tarasevich and F. D. Ovcharenko, Adsorption onto clay minerals, Kiev 1975, p. 213.
14 F. Paulik, Special trends in thermal analysis, Wiley, Chichester 1995, p. 39, 127.
15 Iu. I. Tarasevich, Surface's structure and chemistry of layer silikates, Kiev 1988, p. 159, 173.
16 V. A. Nazarenko, V. P. Antonovich and E. M. Nevskaya, Hydrolisis of metal's ions in the diluted solutions, Moscow 1979, p. 57 (in Russian).
17 R. I. Zlochevskaya, V. I. Divisilova, G. A. Kuprina and E. M. Sergeev, In: Bound water in the dispersion systems, Moscow 1974, p. 4.