

The Hydrated and Hydrolyzed States of Exchangeable Cations in the Montmorillonite and Their Quantitative Assessment

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Abstract: In the paper is submitted opinion according to which, a part of the hydrated exchangeable cations in the montmorillonite is hydrolyzed. A new experimental method has been proposed, which allows to estimate the hydrated/hydrolyzed state of these cations. The method consists in the use of thermal analysis data of mineral, and is particularly effective in the study of homoionic forms of montmorillonite. The mathematical formulas have been proposed for processing the obtained experimental data.

Keywords: Thermal Analysis, Montmorillonite, Exchangeable Cations, Interlayer Water, Hydrolyzed Cations, Mathematical Processing of Data

1. Introduction

The montmorillonite is a widespread aluminosilicate – mineral having large application in various industries [1-4]. As demonstrated by spectroscopic studies, this material might be present on others celestial bodies, such as Mars, comets and asteroids [5-10]. Due to the chemical composition and its layered structure, the montmorillonite has a good adsorption, ion-exchange and catalytic properties. Some researches consider that this mineral could be a “matrix” on whose surface was realized the chemical synthesis of complex of substances which have become the basis of proto-life on the Earth [11-14]. The montmorillonite is an interesting object of study for specialists in various fields of science – geologists, chemists, physicists, ecologists etc. In the study, the scientists use sophisticated equipment and methods such as Raman and IR spectroscopy, X-Ray and thermal analysis and others [15-17]. The current level of development of techniques and informational technologies allows the automating processes to study the minerals. But it also requires developing the mathematical methods for processing these experimental data. The thermal analysis shows that upon heating of cation-exchanged montmorillonite they lose water, and this process occurs in few stages. First dehydration of samples occurs at 80-250°C, followed by their dehydroxilation at 450-800°C. Further

heating is accompanied by processes of recrystallisation, amorphing and formation of new phases (interval 850-950°C) [17-19].

It was observed that dehydration process of varies homoiones samples of montmorillonite is marked by appearance on a DTA curve of a simple or double endothermal effect, the form of which depends of the nature of the exchanged cation and of its state [19]. The remove of these two types of water with minima on DTA, 180 and 200-210°C, is accompanied by mass losses, easily identified by the steps on TG curve. The respective changes are marked likewise on DTG curve at the temperature, on which appear the endothermal effects on DTA curve.

2. Experimental Methods and Instruments

Sometimes, for scientific or practical purpose (in production) it is necessary to know the nature and hydration degree of interlayer cations of montmorillonite. In their scientific work [20] the authors proposed the following interesting method to determining this parameter. Let's consider adsorption of water vapors on modified samples of montmorillonite with exchanged cation. It is know that the adsorption isotherms plotted in standard variables of BET equation are linear for the small value of $P/P_s = 0.05 - 0.35$.

Under such conditions the “monolayer capacity” A_m obtained from BET equation is essentially a measure of the number of water molecules in the interlayer space of the adsorbent. The authors suggested using this conclusion in order to calculate the number of water molecules per interlayer cation:

$$N_{H_2O/cat} = \frac{A_m z}{E} \quad (1)$$

where A_m is the monolayer capacity (from BET) in $mMoles/g$, E is the exchange capacity of the mineral in meq/g and z is the electric charge (conventional unites) of the cation.

However the measurement of adsorption isotherms using vacuum chamber is a difficult and time consuming procedure. Therefore it was necessary to find a simple and convenient method for determining the hydration number of interlayer cations of montmorillonite. The most promising in this respect is the thermal analysis. In the experiments [19] with montmorillonite from Republic of Georgia (*Na*, *Ca*, *Al*, *Fe* modifications of Ascangel, Derivatograph of MOM, Hungary) it was demonstrated that the amount of adsorption water eliminated from cation-exchanged samples upon programmed heating, depends of the nature of interlayer cation, and the two kinds of water registered on DTA curves (as well as on DTG), are in a certain quantitative relationship clearly observed from TG curves (Fig.1). Also, this relationship depends on the pH of the solution in which these samples were prepared. Georgian montmorillonite (Ascangel) is characterized by the thermal effects that are well distinguished on derivatogram during thermal analysis. Due to these properties it has been used as object of study in our research.

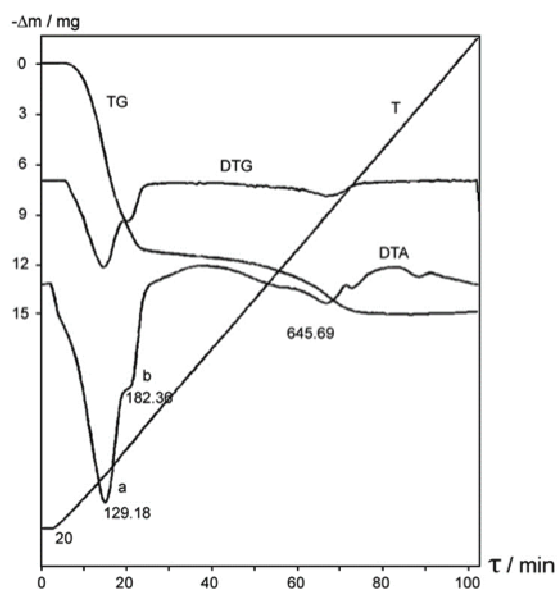


Fig. 1. Derivatogram of Ca-montmorillonite.

The purpose of this paper was to elaborate a rapid and simple method for estimate the hydrated/hydrolyzed state of the interlayer cations in the montmorillonite using data from derivatogram and proposed for this, mathematical formulas. The mass losses corresponding of thermal effects a and b on DTA curve (Fig. 1), are different for each of the exchangeable cation species in the montmorillonite and serve as

characteristics of these homoionic modified samples.

3. Results and Discussions

Let's assume that, using thermal analysis, the contents of adsorption water of the first and second kind in a sample of montmorillonite are found to be C_a and C_b percents, respectively (Fig.1). Thus 100 g of the mineral contains the following number of Moles of both kinds of water:

$$C_a + C_b = \frac{a}{\mu_{H_2O}} + \frac{b}{\mu_{H_2O}} \quad (2)$$

In the sample with arbitrary mass m are (Moles):

$$C_a + C_b = \frac{am}{100\mu_{H_2O}} + \frac{bm}{100\mu_{H_2O}} \quad (3)$$

Since a *Mole* of any substance contains $A = 6.02 \cdot 10^{23}$ molecules (Law of Avogadro), we obtain that the number of water molecules in a mineral sample of mass m is:

$$N_a + N_b = \frac{amA}{100\mu_{H_2O}} + \frac{bmA}{100\mu_{H_2O}} \quad (4)$$

Adsorbing quality of montmorillonite is characterized by cation-exchange capacity E , i.e. the amount of adsorbed ion expressed in milliequivalents (meq) which is contained in 1g of adsorbent. If 1g of adsorbent contains E (meq) amount of cation, then the sample of m grams contains Em (meq) of cation. Multiplying by chemical equivalent ε and dividing by 1000, we obtain the mass of the cation in the sample expressed in grams:

$$m_c = \frac{Em\varepsilon}{1000} \quad (5)$$

Multiplying (5) by A (number of Avogadro) and dividing by molecular mass μ_c of the cation, we obtain the number of exchangeable (interlayer) cations in the sample of the adsorbent:

$$n_c = \frac{Em\varepsilon A}{1000\mu_c} \quad (6)$$

Dividing (4) by (6) produces the formula for calculating the number of water molecules per exchangeable cation in the sample of montmorillonite:

$$N_{H_2O/cat} = \frac{(N_a + N_b)}{n_c} = \frac{(a+b)mA}{100\mu_{H_2O}} \cdot \frac{\mu_c}{Em\varepsilon A} = \frac{10(a+b)\mu_c}{E\varepsilon\mu_{H_2O}} \quad (7)$$

Observation: In the formula (6) the chemical equivalent can be replaced with its value:

$$\varepsilon = \frac{\mu_c}{z} \quad (8)$$

We obtain the following:

$$n_c = \frac{EmA}{1000\mu_c} \cdot \frac{\mu_c}{z} = \frac{EAm}{1000z} \quad (9)$$

The formulas (6) and (9) shows that the number of cations in the interlayer space of montmorillonite depends on the nature and the electric charge of the cation, and that the finding of the exchangeable cations in the mineral is an

electrically compensatory phenomenon. Taking into account the formulas (3) and (5), we can receive from (6) a new (modified) formula:

$$N_{H_2O/cat} = \frac{10(a+b)z}{E\mu_{H_2O}} \quad (10)$$

The number of the water molecules surrounding a cation of the chemical species is called the hydration degree of this cation. Comparing formulas (1) and (10) we see that:

$$A_m = \frac{10(a+b)}{\mu_{H_2O}} = \frac{10}{16} (a+b) = 0.56 (a+b) \quad (11)$$

This formula (11) allows formal to calculate the maximum monolayer adsorption of water vapors according to BET

$$N_{H_2O/Al^{3+}} = \frac{10(8+7)3}{1 \cdot 18} = 25, \text{ and, } N_{H_2O/Al(OH)^{2+}} = \frac{10(8+7)2}{1 \cdot 18} = 16.7 \quad (12)$$

As can be seen from these results, the calculated hydration degree of cations are close to each other [20], however they do not correlate with the X-ray analysis data (Table 1).

Table 1. The processed data from literature and the results of the thermal analysis.

Cation	N coordin.	N _{H₂O / Mⁿ⁺}	N _{H₂O (M-OH)⁽ⁿ⁻¹⁾⁺}	R _{Mⁿ⁺} , nm	Δd ₀₀₁ , nm	pH susp. (1%)	Ratio H ₂ O C _a /C _b	A _m , mMoles/g	H
Na ⁺	3, 4, 6	3.9	-	0.101	0.35	-	-	3.9	-
		6.1	-		0.30	9.8	11/0	6.16	-
Ca ²⁺	6, 8	15.4	-	0.105	0.62	-	-	7.7	-
		13.3	1.8		0.50	8.2	12/3	8.40	0.20
Al ³⁺	6	17.1	-	0.055	0.62	-	-	5.7	-
		13.3	8.2		0.54	3.7	8/7	8.40	0.47
Fe ³⁺	6	16.8	-	0.067	0.49	-	-	5.6	-
		8.3	10.6		0.49	2.8	5/9	7.84	0.64

Note relating to Table 1:

1. The values in odd lines are taken principally from [20]. The data were obtained on Montmorillonite Pyzhevskiy (Ukraine) using vacuum installation.
2. The values of H from the table means that 20; 47 and 64 percents of the interlayer (Ca²⁺, Al³⁺ and Fe³⁺) cations contains one hydroxyl group in their hydration sphere.

So large number of water molecules (20-25) per cation is unrealistically high simply because it cannot represent a simple two layer of water molecules in the hydration sphere of this cation.

We are forced to assume that a part of di- and trivalent exchangeable cations is hydrolyzed, hence the calculation of the amount of water is erroneous because it doesn't take into consideration the new state of the cations having reduced electric charge. Therefore, we have made calculations for each mass loss corresponding to endothermal effect (a and b – Fig.1), separately, considering that the first effect belongs of water molecules of non-hydrolyzed cations and the second one – of the water of complex ion $(M-OH)^{(n-1)+}$. The results are in the Table 1. Knowing total water content ($a+b$) and the percentage of each water types in the montmorillonite sample, we calculate the share of hydrolyzed cations, or the degree of hydrolysis of the interlayer cations:

$$H = \frac{b}{(a+b)} \quad (13)$$

It is well known that liquid water contains molecular complexes linked by hydrogen bonds in the shape of dimers and other geometrical structures – linear as well as cyclic (clusters) [21-26]. The polar water molecules are oriented

theory. Adsorption amount ($mmol/g$) in this case is approximately equal to half the sum of content (%) of the two kinds of water in montmorillonite detected using thermal analysis.

4. Argumentation of the Hydrolyzed State of the Interlayer Cations

From the data on Fig.1 can be calculated the amount (percentage or number) of the hydrated cations as well as the part of their hydrolyzed form into the interlayer space of the mineral. As an example, we calculate the hydration degree of the cations Al^{3+} and $Al(OH)^{2+}$ using the formula (10):

along the electric field lines of the ion and their electronic shells are strongly distorted (especially when hydrogen bonds are present) which leads to breaking of other bonds – the chemical ones. This can be illustrated by the following scheme of the process:

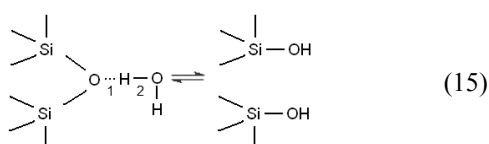


where M^{n+} is the interlayer exchangeable cation, 1 – the shortening, 2 – the lengthening of bindings. The nearest from cation water molecule is one of those molecules that are in its first coordination sphere, while the second one is respectively one of the molecules from external coordination sphere. So process is a cationic hydrolysis and it is typical for transition metal cations with an incomplete $3d$, $4d$ or $5d$ electronic layer, and for amphoteric cations having vacant p -orbitals. The presence of water molecules in the first coordination sphere of cations is evidenced in the IR spectrum of montmorillonite as a band of valence $O-H$ oscillations in the interval of $3440-3100\text{ cm}^{-1}$ depending on the nature of cations. The molecules from the external sphere are in the spectrum an $O-H$ band in the interval $3370-3500\text{ cm}^{-1}$ [27].

The difference in energy states of the $O-H$ groups in the

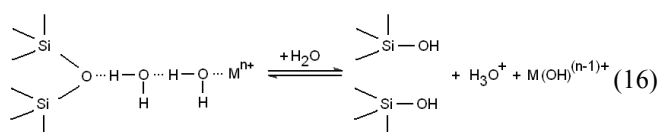
water molecules with or without hydrogen bonds was evidenced by the analysis of montmorillonite IR spectrum. The first of these are highlighted by a broad absorption band in the interval $3400-3440\text{ cm}^{-1}$ and the others (without H-bonds) – by narrow band with maximum of IR absorption at 3630 cm^{-1} [28].

It is known that the water molecules from the second (extern) sphere of cations are under the influence of the surface electric field of the mineral layers. These molecules also can form the hydrogen bonds with oxygen on these layers [29]. The SiO_4 tetrahedra of the montmorillonite are associated into ditrigonal lattice with the cavities-hexagons. The configuration of electron orbitals of the oxygen atoms of these hexagons (on the tetrahedral sheet) gives the cavities a character of Lewis bases [30]. These properties are more pronounced in the case of isomorphic substitutions in the montmorillonite structure, especially in the octahedral layer. Due to this fact it is possible to complex dipolar water molecules and their transformation:



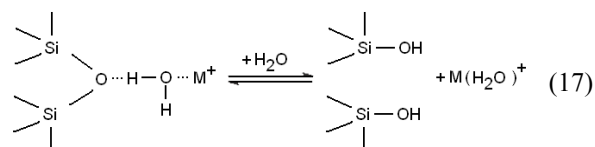
where 1 - is the shortening and 2 – the lengthening (up to breaking) of the bindings.

The suspensions of the better part of cationexchanged samples of montmorillonite have low pH values, but not the suspensions of samples with alkali metal ions. The hydrolysis process in these types of mineral has the anionic origin, and can be explained by the following. The Na^+ cation (for example) have a small potential (z/r), a spheric symmetry of the extern electrons, no property to polarize and to accept electrons, so it does not hydrolyze as shown in the scheme (14). Its state is only hydrated. The interlayer complex of montmorillonite can be compared with the concentrated salt solution, which volume is equal of the basis of a structural unit of the mineral multiplied by the interlayer spacing Δd_{001} . More precisely, we have a solution in a bowl (a cell) whose walls serve as anion. Therefore, the effect of hydrolysis is the result of the competition of the exchangeable cations and the basal face of the tetrahedral sheet of the montmorillonite (and maybe of the edges of the particles) in the polarization of water molecules, and this process is accompanied by another one – the donation-acceptance of protons of the associated molecules. Taking into account the above mentioned the state (and the role) of the interlayer cations can be more correctly rendered as follows:



Note: Explications regarding the number of water molecules involved in the processes, here and below, see the scheme (14).

In particular, for alkali metal cations can be used another chemical scheme of process:



The hydration of the siloxane groups and appearance of free from mineral matrix a cations has the effect of the shifting the equilibrium of the electric charges in the system, here is why the suspension responds by changing the pH . It is necessary to note, that the siloxane groups on basal face of the mineral layer are considered inactive in the protonation processes, and in this case the emphasis is on the functional groups from the edges of montmorillonite particles. From the other hand, it is known that the reactivity of the siloxane surface depends on the nature of the local charge distribution [31] in the clay layer. In [32,33] authors point out that in case if isomorphic substitutions occur in the octahedral sheet, the resulting excess negative charge makes it possible for the surface to form reasonably strong adsorption complexes with cations and water molecules.

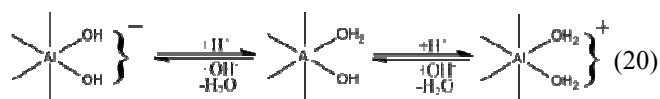
The hydrolysis of the cation depends upon its nature: charge, radius and electronegativity [34], and is considered as a process in equilibrium characterized by the constant K_a or its logarithm:

$$pK_a = 15.14 - 0.8816 (z^2 / r) \quad (18)$$

$$pK_a = 15.14 - 0.8816 [(z^2 / r) + 9.60 (\chi - 1.50)] \quad (19)$$

where z , r and χ are the charge, radius and Pauling electronegativity. In conditions that $pH = pK_a$, about the half of the cations can be hydrolyzed. Comparing the pH of the suspensions (Table 1) and pK_a values of the exchangeable cations we can observe that these values decreases according to the same natural law and this suggest the hydrolyzed state of the part of the cations (for example, respective pK_a of cations Na^+ , Ca^{2+} , Al^{3+} and Fe^{3+} are: 14.2; 12.8; 5.0; 2.2 [34]). However, it should be noted that due to the specific conditions in the interlayer space of the dry mineral, the value of hydrolysis constant of cations can be different than in aqueous solutions.

The formed in hydrolysis process H_3O^+ - ion can interact with basic groups from lateral faces of the montmorillonite particles according to the following scheme, thereby influencing the cationic exchange capacity:



The possibility of such processes (14-17, 20) on the surface of montmorillonite is confirmed by the pH of the suspension (Table 1) as well as adsorption and ion exchange phenomena, dependent on the value of pH [28, 35]. As shown in the Table 1, the calculation of the hydration degree of the hydrolyzed interlayer cations using thermal analysis is closer to value

obtained from the adsorption isotherm using formula (1). This also confirms the hydrolyzed state of the fraction of these cations, although the authors [20] have not taken into account in this case the possibility of the hydrolysis.

5. Conclusions

1. The interlayer exchangeable cations in the montmorillonite are hydrated and a part of them can be hydrolyzed. This state is characteristic for polyvalent cations and the degree of hydrolysis depends of the species of the cation.

2. The use of thermal analysis data allows calculating the number of water molecules surrounding an exchangeable cation of the montmorillonite and indicates the state of them in the interlayer space.

3. Thermal analysis allows finding rapidly the maximum value of monolayer adsorption of water vapors onto surface of the montmorillonite; that is important in the scientific study.

4. The proposed method for determining the degree of hydration and the hydrolyzed state of the interlayer cations is much easier, and having the special calculation program it is possible to automate the process.

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