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Partially exchanged organophilic bentonites

Part I. characterization by thermal analysis on calcined mass basis

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Abstract Using a sodium bentonite (VCNa) as substrate differently exchanged organophilic clays were obtained by reaction with hexadecyltrimethylammonium (HDTMA) chloride, at increasing reacting ratios (*R*) from 20 to 120 meq/100 g of clay (VC20–VC120). The sodium bentonite was previously synthesized from a Verde Claro policationic bentonite (VC) from Bravo, Paraiba State, Brazil. From the thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of these clays on calcined mass basis and from TG and DTG curves data of VCNa clay, a method was developed to estimate the mass fraction of the exchanged cation present in each organophilic clay (M_{org}), as a function of *R*. When all sodium cations of VCNa are exchanged by HDTMA, the obtained organophilic clay presents a maximum value for M_{org}. From this value and TG and DTG curves data of VC and VCNa clays, the cation exchange capacity of the original VC bentonite can be estimated.

Keywords Organophilic bentonites · Cation exchange capacity · Calcined mass basis · TG

Introduction

Natural clay particles have inorganic metallic cations adsorbed to their interlayer negative charged surfaces. These cations can then be replaced or exchanged by others including organic ones, which can be obtained by reaction with organic quaternary ammonium salts. When this occurs, the original hydrophilic clay is changed to a material with hydrophobic characteristics, turning the original clay into an organophilic one [1]. This change allows the organoclay to be used as organic matter adsorbent to decontaminate effluents polluted with organic substances [2–11] or in nanocomposites applications [12–16], among other uses.

To study the effect of partial cation exchange on their resulting organic adsorptive properties, differently exchanged organophilic clays were obtained (through a sodium clay intermediate—VCNa) from a Verde Claro policationic bentonite (VC) from Bravo, Paraiba State, Brazil, by reaction with hexadecyltrimethylammonium (HDTMA) chloride in different exchange degrees, in order to be checked as adsorbents in the decontamination of phenolic aqueous solutions. This article presents the characterization of these differently exchanged organophilic clays mainly by thermogravimetry (TG) and derivative thermogravimetry (DTG). The study of their use in phenol adsorption is presented in part II.

Usually the organic content of a sample may be quantified by the carbon, hydrogen, and nitrogen elemental analysis [8]. In this article, the mass fraction of organic cation present in the partially exchanged clays was quantified by a new method, which uses TG data on calcined mass basis. The results suggest the existence of an exchange limit characterized by the amount of organic cations present in the organophilic clay prepared using

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excess of quaternary ammonium salt. This new protocol allows an alternative procedure to estimate the cation exchange capacity (CEC) of the clay.

Materials and methods

The original natural clay used in this study is Verde Claro bentonitic clay, from Boa Vista, Paraiba State, Brazil from Mineração Bravo. The HDTMA chloride (HDTMA$^+$ Cl$^-$) was from Clariant SA and the analytical grade sodium carbonate was from Casa Americana Ltda.

After being ground and milled to particles finer than 74 μ, sieved in an ASTM 200 sieve, a 4 mass% of VC dispersion was prepared in demineralized water. To obtain the VCNa sodium bentonite suspension, sodium carbonate (Na_2CO_3) was then added in a proportion of 120 meq/100 g of VC with constant stirring, letting subsequently the mixture at rest for 24 h [8].

The VCX organophilic clays were then obtained in different partial cation exchange degrees, by reacting VCNa suspensions under constant stirring with *X* meq of HDTMA chloride per 100 g of VC (*X* values being 20, 40, 60, 80 100, and 120). After 24 h at rest, the mixtures were vacuum filtered and washed with demineralized water until no chlorides could be found in the filtrate. This was assured by testing with silver nitrate.

A specific VCNa suspension as previously described was prepared, followed by vacuum filtration and washing steps using demineralized water. VCNa and VCX filtration cakes, after having being dried at 60 °C, were manually ground to obtain particle sizes finer than 74 μ, not retained in ASTM 200 sieve before respective thermal analysis. This was performed in Simultaneous TG/DTA/DSC Q600 TA Instruments equipment from room temperature to 1000 °C by using samples with masses from 15 to 20 mg. 100 mL min^{-1} of air was used as the purge gas, with a heating rate of 10 °C min^{-1}.

The XRD patterns of the studied samples were obtained in a Bruker-D4 endeavor equipment, at the following operating conditions: Co Kα radiation (35 kV/40 mA), with 0.02° 2θ steps at 1.0 s/step and 2θ values from 2 to 80°. The basal spacing values were obtained at the peak maxima, by using Bruker Diffrac$^{\text{Plus}}$ software.

Fundamentals

VC, VCNa, and VCX thermal decomposition main steps

When a bentonite (VC in this case) is heated from room temperature to 1000 °C in air atmosphere, its TG curve shows two main mass loss steps within temperature ranges indicated by respective DTG peak limits. During the first step an initial mass loss Δm_1 occurs, due to the release of adsorbed water from pores and from metallic cation coordinated water in the interlayer space [16]. After this step, which usually ends by 200–250 °C, the residual mass at this condition (Md_{VC}) is considered to be totally dried. During the following step, a mass loss Δm_2 occurs, due to water release from clay structural dehydroxylation [16], remaining a residual calcined mass (Mc_{VC}). Md_{VC} and Mc_{VC} are given by Eqs. 1 and 2, respectively, where M_{iVC} is the initial VC sample mass:

$$\mathrm{Md_{VC}} = \mathrm{M_{iVC}} - \Delta m_{1\mathrm{VC}} \quad (1)$$

$$\mathrm{Mc_{VC}} = \mathrm{Md_{VC}} - \Delta m_{2\mathrm{VC}}. \quad (2)$$

The sodium bentonite VCNa, obtained after total VC cation exchange by sodium, also shows similar thermal decomposition steps. To obtain the respective dried and calcined masses (Md_{VCNa} and Mc_{VCNa}) equations 1 and 2 can be used, changing all VC subscripts to VCNa.

When an organophilic bentonite VCX, obtained by partial or total exchange of sodium ions of VCNa by an organic cation (HDTMA in the present case) is analyzed, the first mass loss Δm_{1VCX}, seen in its TG curve (ending by 150–200 °C), is considered to be practically due to the release of residual free water retained in particle pores after being dried (in the present case at 60 °C). The total mass loss during the second main loss step is given by the sum of two mass losses: the first (Δm_{21VCX}) is considered to be the pyrolysis of the organic cation and its combustion process [8, 17] and the second (Δm_{22VCX}) is due to the water released from the clay structural dehydroxylation, which occurs during Δm_{21VCX} mass loss. In this case, the final calcined mass Mc_{VCX} is given by Eq. 3:

$$\mathrm{Mc_{VCX}} = \mathrm{Md_{VCX}} - (\Delta m_{21\mathrm{VCX}} + \Delta m_{22\mathrm{VCX}}). \quad (3)$$

TG and DTG curves data on calcined mass basis

Thermal analysis curves are plotted on initial sample mass by default. As VC, VCNa, and VCX have different initial compositions, the respective TG and DTG data on respective initial mass basis cannot be used directly to correlate respective mass losses. However, since the calcined compositions of VCNa and VCX clays are practically the same their TG and DTG curves and/or data must be recalculated on calcined mass basis to proceed these correlations. On this same composition basis, by considering that the mass loss of water due to dehydroxylation of the clay structure during thermal analysis of VCNa and VCX clays should be the same, the content of exchanged organic cation ($\Delta m_{21VCcb} = OC_{VCXcb}$) may be estimated by Eq. 4 and subsequently, the cation exchange capacity of VCNa as well, in case of total exchange:

$$\mathrm{OC_{VCXcb}} = (\mathrm{Md_{VCXcb}} - \mathrm{Mc_{VCXcb}}) - (\mathrm{Md_{VCNacb}} - \mathrm{Mc_{VCNacb}}). \qquad (4)$$

To transform a mass loss Δm_i or a value of residual mass M_i from a TG curve, measured on initial mass basis of a sample to the respective calcined mass basis (Δm_c or M_c), Eqs. 5 or 6 may be used [18]:

$$\Delta m_\mathrm{c} = \Delta m_i 100 / \mathrm{Mc_i} \qquad (5)$$

$$M_\mathrm{c} = M_i 100 / \mathrm{Mc_i}, \qquad (6)$$

where $\mathrm{Mc_i}$ is the residual calcined mass of a sample obtained from its TG curve, on initial mass basis.

It must also be noted that is very well known experimentally that when a mass M_VCNa of a VCNa sodium bentonite is obtained from a certain M_VC mass of original VC bentonite, the mass loss due to the water released from each clay matrix dehydroxylation of these masses is the same during respective TG analysis.

Results and discussion

Figure 1 shows the XRD patterns of VCX samples, compared to those of VC and VCNa samples. It can be seen that the interlayer space of VCNa (11.76 Å) is smaller than that of VC (14.69 Å) most probably due to the other original VC cations total exchange by sodium. It can also be seen that interlayer spaces of the partially exchanged organophilic clays show a good correlation with the sodium ion exchange degree and cation dimension characteristics suggesting a function between them [19].

Boyd and Jaynes [7, 9] using cation HDTMA, obtained values of 13.7, 17.7, and 21.7 Å for monolayer, bi-layer and pseudo-tri-layer organic cation structures after exchange. When there is an excess beyond the CEC, there are evidences pointing to the formation of a paraffin complex, with the molecules in diagonal direction with the surface, the resulting organoclay interlayer spacing is greater that 22 Å.

From Figure 1, the interlayer distances (*d*) VC20 and VC40 partially exchanged organophilic clays were practically equivalent (14.18 and 14.37 Å). This suggests that up to this degree of cation exchange, only a monolayer (probably not completely coated on the surface) of the organic substitute is formed in the interlayer space of the clay. As long as the available amount of quaternary salt for the exchange with sodium ion is increased from VC60 to VC80, *d* value increases from 17.41 to 21.46 Å, indicating a progressive higher amount of sodium exchange. The interlayer distance stabilizes in the order of 2.3 nm for clays VC100 and VC120 (22.99 and 22.67 Å), suggesting the formation of a "pseudo" molecular organic cation trilayer in interlayer space [7]. On the other hand this fact indicates in the clay used in this study that the maximum cation exchange capacity of the sodium ion by the organic ion, in the conditions used for their synthesis, is practically of 100 meq for 100 g of clay or very close to this value.

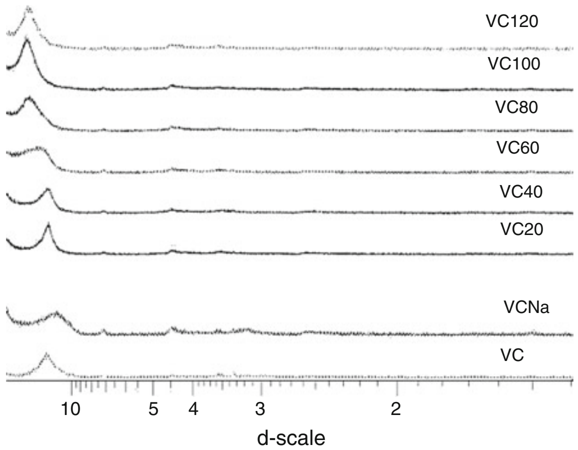

Fig. 1 XRD patterns of VC, VCNa, and VCX organophilic clays

Figure 2 shows the TG and DTG curves of the sodium VCNa clay. After the exit of all the residual water from the pores of the clay and/or from that coordinated with sodium ions of the interlayer space of VCNa, indicated by the end of first DTG peak, the remaining totally dried mass ($\mathrm{Md_{VCNa}}$) represents 91.78% of the initial mass of sodium clay. After this, dehydroxylation of the clay structure occurs, and the final calcined mass at 1000 °C ($\mathrm{Mc_{VCNa}}$), is equal to 86.02% of the initial mass of VCNa (M_iVCNa).

Figure 3 shows typical TG and DTG curves obtained for the organophilic clays (sample VC120). After the exit of the residual water of the initial stage of mass loss, the totally dried mass ($\mathrm{Md_{VC60}}$) is equal to 97.82% of the initial mass. At 150 °C the process of pyrolysis of the organic part of the organophilic clay begins which shows a fist step of combustion between 200 and 350 °C. This pyrolytic process is considered not to happen in VC and VCNa clay thermal

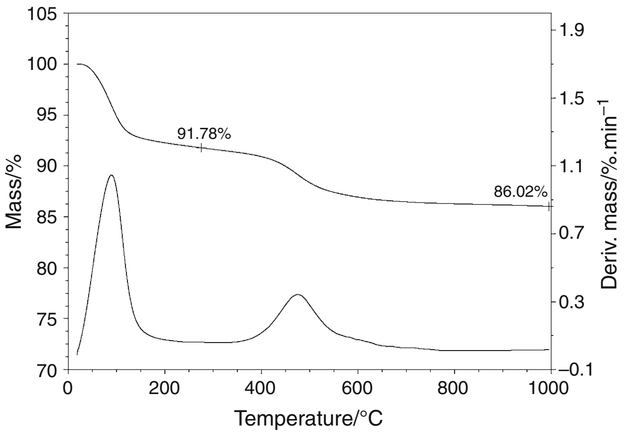

Fig. 2 TG and DTG curves of the sodium Verde Claro clay (VCNa)

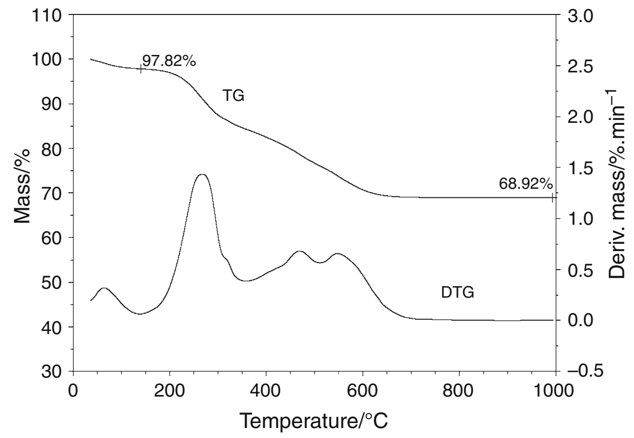

Fig. 3 Typical TG and DTG curves of an organophilic clay (VC120)

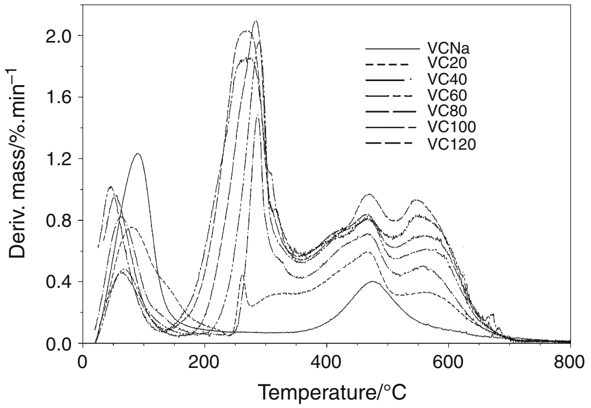

Fig. 4 DTG curves of the differently exchanged organoclays and of VCNa clay

analysis, due to the absence of organic material. From 350 to 800 °C, occurs the so-called burnout of the carbonaceous solid residue which is formed during the first and partial combustion step [8, 20, 21], simultaneously to the clay matrix dehydroxylation identified by the first DTG peak after 350 °C, as occurs in case of VCNa clay in Fig. 2.

Figure 4 shows the DTG curves of all VCX organophilic clays, and that of VCNa clay. It can be seen that the higher is the organic cation exchange degree and respective exchanged amount, the higher is the total area of respective stages of pyrolysis and burnout shown by corresponding DTG peaks and as the basal spacing increases, the lower is the respective onset temperature of the first thermal decomposition stage (pyrolysis) [22], as shown in Table 1. It can also be noted that all organoclays present the dehydroxylation DTG peak, but that happens at little lower temperature ranges than that of VCNa case, because they have a higher basal spacing than VCNa, which promotes an easier condition for the release of water during dehydroxylation, besides the enhancing thermal effect of the burnout of organic matter which is happening simultaneously.

Table 1 Onset temperatures of the pyrolysis of the exchanged organic cation in each case

Organoclay	VC20	VC40	VC60	VC80	VC100	VC120
T/°C	249	247	230	213	177	164

Organic matter estimation

Table 2 shows the dried and calcined residual masses of the several studied clays, which were obtained from their TG curves, on respective initial and calcined mass basis. As the initial compositions of the starting materials are significantly different, they cannot be employed for a comparative study directly. On the other hand, the several sample calcined compositions at 1000 °C are very similar, and they can be assumed practically equal to the VCNa calcined mass at this temperature. To do a comparison on a same basis, the values of dried and calcined masses of Table 2, which were obtained on respective initial mass of each sample (respectively Md_i and Mc_i), were transformed on respective calcined mass basis (Md_c and Mc_c) by using Eqs. 1 and 2. This is equivalent to use the sample calcined masses as the common reference (100%) for all the cases, which allows a more correct data comparison.

Considering the percentage of the VCNa calcined mass as the reference 100%, as the dried mass of VCNa is 106.7% on this basis, we have that 106.7–100 = 6.70% is the percentage of the water released during VCNa dehydroxylation, which occurs from 350 to 800 °C as shown in Fig. 2. For any VCX organoclay the difference between respective dried and calcined masses represents the sum of the loss of water from its dehydroxylation plus the released organic matter.

The VCX organoclays obtained from partial cation exchange, after dried during analysis, have the same mineral matrix than dried VCNa. Thus, on the same calcined mass basis, as the mass of water released during respective dehydroxylation is the same, by Eq. 4, the difference between the value of the ($Md_c - Mc_c$) difference of any VCX organoclay and that of VCNa clay represents the mass of the organics that were released and burned out during analysis of VCX organoclay. For example, for VC60 case, as shown in Fig. 3, this release occurs initially from 180 °C by pyrolysis followed by combustion of the organic matter. The carbonaceous residue formed during the process begins its combustion by 350 °C, and at 1000 °C, in the calcined residual mass there are only the ashes formed during calcination. Table 2, shows the

Table 2 Dried and calcined masses of the sodium and organophilic clays on respective initial and calcined mass basis

Samples	On initial mass basis		On calcined mass basis	
	Dried mass/% $Md_i = Md_i\ 100/M_i$	Calcined mass/% $Mc_i = Mc_i\ 100/M_i$	Dried mass/% $Md_c = Md_i\ 100/M_c$	Calcined mass/% $Mc_c = Mc_i\ 100/M_c$
VCNa	91.78	86.02	106.70	100
VC20	93.74	81.63	114.84	100
VC40	93.63	76.61	122.22	100
VC60	97.35	75.26	129.35	100
VC80	97.43	71.75	135.79	100
VC100	96.09	67.87	141.58	100
VC120	97.82	68.92	141.93	100

resulting differences between the ($Md_c - Mc_c$) values of each VCX organoclay and that of VCNa, which represent the percentage of the organic cation mass present in each organoclay (by Eq. 4), which were initially there from exchange with previous Na^+ ions.

As the effective exchanged HDTMA content is increasing from VC20 to VC120 clay, the respective cation exchange degree is increasing and their calcined masses have not exactly the same composition, because of their decreasing sodium content, according to the number of milliequivalent grams (meq) of exchanged HDTMA cations, which may be estimated from Table 3. Thus, all dried and calcined data of Table 2 on calcined mass of each sample were transformed on VCNa calcined mass basis, as shown in Table 4, to have a same basis of comparison. From the original VCNa clay TG curve, the ratio between calcined and initial masses is 0.8602. Thus, by using Eq. 4 and this ratio, the exchanged masses of HDTMA are also shown in Table 4, on calcined and initial VCNa clay mass basis.

Figure 5 shows the correlation obtained between the HDTMA exchanged masses on VCNa initial mass basis as a function of the number of meq of the quaternary salt used per 100 g of VCNa clay to obtain the organoclays. It can be seen that a same function correlates the experimental data very well up to the VC100 case. After it, there is a discontinuity, suggesting that in VC120 case, an excess of quaternary salt was used indicating that a limit of this exchange has occurred at little higher exchange conditions of VC100 case, which is considered to correspond actually to the CEC condition of VCNa clay. From the effectively exchanged mass on VCNa initial mass basis data for VC120 case (29.35 m%), it can be estimated that VCNa cation exchange capacity is 103.25 meq/100 g of VCNa.

Table 3 Mass percent of exchanged organic cation of each sample on respective calcined mass basis

Samples	Content of exchanged organic Cation on calcined basis/m%
VCNa	0
VC20	8.14
VC40	15.52
VC60	22.66
VC80	29.10
VC100	34.88
VC120	35.24

Table 4 Dried and calcined masses of the organoclays on VCNa calcined mass basis and exchanged HDTMA masses on VCNa calcined and initial mass basis

Samples	Data on VCNa Dried mass Md_{mcVCNa}/%	Calcined mass basis Calcined mass Mc_{mcVCNa}/%	Exchanged HDTMA mass	
			m% of VCNa calcined mass	*m*% of VCNa initial mass
VCNa	106.70	100.00	0.00	0.00
VC20	114.22	99.47	8.06	6.93
VC40	120.91	98.93	15.28	13.15
VC60	127.28	98.40	22.18	19.08
VC80	132.89	97.86	28.33	24.37
VC100	137.79	97.33	33.77	29.05
VC120	138.04	97.26	34.12	29.35

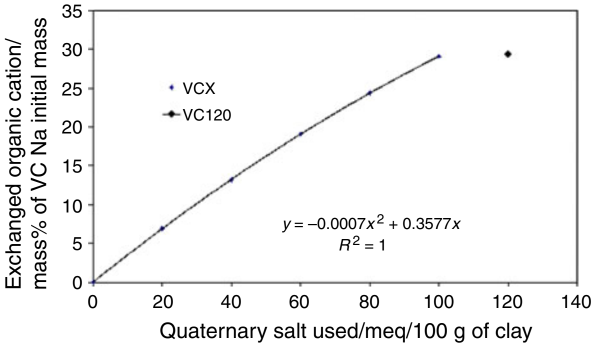

Fig. 5 Correlation between the exchanged organic cation mass and quaternary salt used for cation exchange, on VCNa basis

As seen, from previous data, one can estimate VCNa CEC value. To estimate the original VC bentonite CEC value, this can be done from the “VC and VCNa/TG and DTG” curve data as follows. From Fig. 6, which shows these curves on respective initial mass basis, it can be seen that during their dehydroxylation steps the water mass losses represent, respectively, 5.189 and 5.795% of their initial masses. As these mass losses can be considered to be the same as a mass of VCNa that would be obtained from a certain mass of VC, this means that in the operating

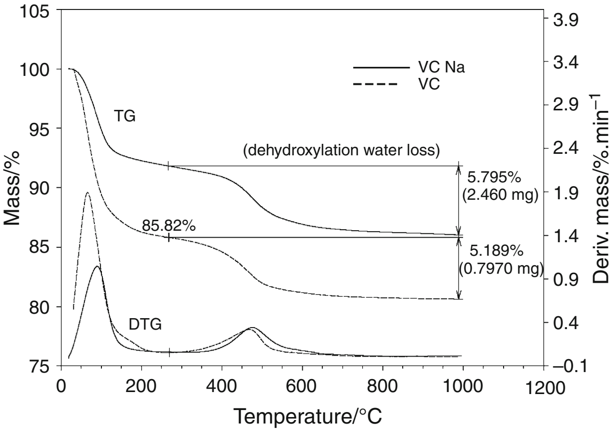

Fig. 6 TG and DTG curves data of VC and VCNa clays on respective initial mass

conditions used in the experiments, the VCNa mass obtained from VC original mass is equal (5.189/5.795) = 89.54% of VC mass. Therefore, the CEC of the original VC clay is 103.25 × 0.8954 = 92.45 meq/100 g of clay.

From Fig. 6 the totally dried VC mass at 268 °C represents 85.82% of the initial VC mass. Thus, on this basis, the CEC of VC clay by the developed method is 107.73 meq/100 g of totally dried VC clay. The CEC obtained by applying the classical methylene blue method, drying VC sample at 105 °C before the essay, was 102.43 meq/100 g of dried VC clay. As at 105 °C, some of the coordinated water with the original Na and Ca exchangeable cations of VC clay has not been totally eliminated, results can be considered compatible between each other.

Conclusions

- As the cation exchange degree is increased, there is a non-linear increase in the basal spacing of the organophilic clay obtained by partial exchange of the Verde Claro sodium bentonite (VCNa), which tends to a limit, when maximum exchange degree occurs. As the several obtained organoclays with different exchange degrees have different initial compositions among each other and from VCNa clay composition from which they were obtained, respective TG and DTG curve data on their initial mass basis cannot be compared directly.
- To have a correct basis of comparison, TG and DTG data must be considered on a same basis. For this purpose, the respective calcined mass basis data have to be converted to VCNa calcined mass basis, from which, exchanged HDTMA cation mass can be calculated on initial sodium VCNa bentonite basis.
- The new method, developed from TG/DTG curve data on calcined mass basis of the organophilic clays and of the sodium bentonite from which they were obtained, allows a quantitative analysis of the exchanged organic contents.
- When all sodium cations are exchanged by the organic cation (HDTMA) of the quaternary ammonium salt, the resulting organophilic clay presents a maximum organic content, from which the CEC of the VCNa clay can be determined.
- From their original TG and DTG curves data, the mass of VCNa clay obtained from a certain mass of VC clay can be determined. This allows to determinate the CEC of the original VC clay, which value was compatible with the value obtained by classical methylene blue method.

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