

# Thermogravimetric analysis of different molar mass ammonium cations intercalated different cationic forms of montmorillonite

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**Abstract** Different cationic forms of montmorillonite, mainly K-, Na-, Ca- and Mg-montmorillonites were intercalated in this study via ion exchange process with mono-, di-, and triethanolammonium cations. The developed samples were characterized by TG, XRD, and CHNS techniques. Thermogravimetric study of ammonium-montmorillonites shows three thermal transition steps, which are attributable to the volatilization of the physically adsorbed water and dehydration, followed by the decomposition of the intercalated ammonium cations and dehydroxylation of the structural water of the modified clay, respectively, while untreated and cationic forms of montmorillonite showed only two decomposition steps. The type of ammonium cation has affected both desorption temperature (Position) and the amount of the adsorbed water (intensity). XRD results show a stepwise change in the crystallographic spacings of montmorillonite with the molar mass of ammonium cation, reflecting a change in the structure of the clay. CHNS data confirm the intercalation of ammonium cations into the interlayer space of montmorillonite and corroborate the effect of the molar mass of ammonium cation on the amount adsorbed by the clay.

**Keywords** Thermogravimetric analysis · Montmorillonite · Organoclay · XRD · TG

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## Introduction

Bentonite clay is a naturally occurring material that contains montmorillonite clay mineral as a major constituent with traces of organic matters, quartz, and calcite as impurities. Montmorillonite clay mineral is a 2:1 phyllosilicate clay mineral, which consists of two tetrahedral silicon oxide sheets with octahedral aluminum oxide sheet sandwiched between them. Montmorillonite has a high surface area, and the presence of the negative charge on its sheets contributes to accumulation of inorganic and organic cations. Both reasons are considered as key factors which have made montmorillonite clay mineral a very suitable mineral, which can be further modified and used in different industrial and environmental applications [1–3]. The positive charge deficiency originates from the isomorphic substitution in the clay sheets. Such substitution includes the displacement of  $\text{Al}^{3+}$  by divalent cations, such as  $\text{Mg}^{2+}$  in octahedral sheet or the  $\text{Si}^{4+}$  replaced by  $\text{Al}^{3+}$  in tetrahedral sheet, resulting in a permanent negative charge appearing on the sheets. Inorganic exchangeable cations initially located in the interlayer space of montmorillonite compensate the positive charge deficiency. Montmorillonite clay mineral is a hydrophilic material due to the hydrated nature of exchangeable cations present in the interlayer space. Organic compounds intercalated into montmorillonite clay mineral can change the surface chemistry from hydrophilic to organophilic and alter the structure of the clay [4–6]. Intercalation of organic compounds in the clay can be defined as the topotactic incorporation of mobile guest molecules (may be neutral, anhydrous, or solvated ions) into the accessible interlayer space of the layered host structure. Previous studies [7, 8] have revealed that the thermal analysis of the desorption of the bases, such as amines, can be utilized to evaluate

rapidly the amount and type of the acid sites in clays. Thermogravimetric studies on alkyl ammonium and phosphonium intercalated montmorillonite have been extensively reported [9–18]. These previous studies did not investigate the influence of the molar mass of short chain ammonium cations on the thermal stability of the intercalated montmorillonite. Hence, in this context, it is worthwhile to evaluate the effect of the size of different short chain ammonium cations on the thermal decomposition of ammonium-montmorillonites. The crystallographic spacings and elemental composition of the examined samples were also studied by XRD and CHNS techniques.

## Experimental

### Materials

Bentonite clay with a cation exchange capacity (CEC) of 0.928 meq/g, monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were purchased from R&M Chemicals, Marketing, Essex, U.K. Inorganic metal chlorides of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , were supplied from Merck, Malaysia. Cationic forms of montmorillonite were developed via ion exchange reaction mechanism. The clay was separately dispersed in the above mentioned metal chloride solutions with the concentration of (1 M for monovalent cations and 0.07 M for divalent cations). The mixture was stirred for 24 h at 80 °C, to contribute ion exchange reaction. The resulting clay was separated by centrifugation, and the supernatant was discarded. The procedure was repeated several times, and the excess salt was removed by washing with distilled water until the washing solution was free from chloride. The clay thus obtained was dried overnight at 80 °C and mechanically ground into powder.

Protonated amines were obtained by neutralization of the respective amount of each amine (taken as 5 times CEC) with HCl (1 N). The corresponding ammonium solutions were separately mixed with the suspension of the cationic forms of montmorillonite. The product was well stirred at 80 °C for 2 h; then the mixture was separated by centrifugation and the supernatant liquid was removed. The procedure was repeated, and then the clay was washed by same process by aqueous solution of acetone (acetone: distilled water, 9:1) till a negative  $\text{AgNO}_3$  test. The clay was then dried at 80 °C overnight and ground into powder.

### Characterization techniques

The present synthesized amine–montmorillonite complexes were characterized using TG, X-ray diffraction, and CHNS methods to establish their thermal decomposition characteristics, physical, and chemical properties.

### Thermogravimetric analysis

Thermogravimetric analysis (Perkin Elmer, Pyris 1 TGA, USA) were made at a heating rate of 10 °C  $\text{min}^{-1}$  from room temperature to 850 °C in the presence of high purity nitrogen/20  $\text{cm}^3 \text{min}^{-1}$ .

### X-ray diffraction

X-ray diffraction study was performed in a diffractometer (Bruker, axs, D8 ADVANCE) with monochromatic  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 40 mA in a range of 2°–40°.

### Elemental analysis using CHNS

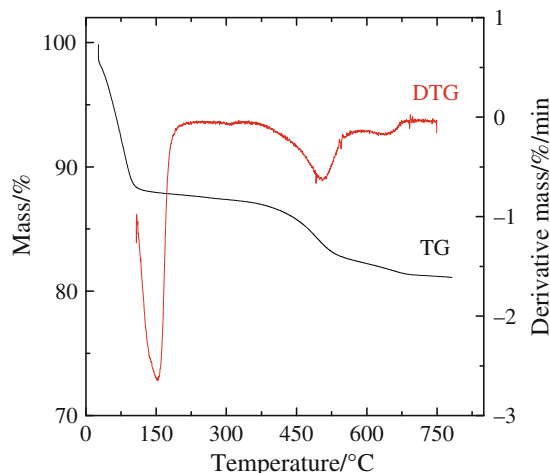
It is worthy of note that the chemical composition of ammonium-montmorillonites is of prime importance. Elemental analysis was performed using a Perkin Elmer 2400 series II CHNS elemental analyzer, where a sample of less than 2 mg of each ammonium-montmorillonite was burned at 1000 °C under oxygen flow. The sulfamethazine was used as a standard.

## Results and discussion

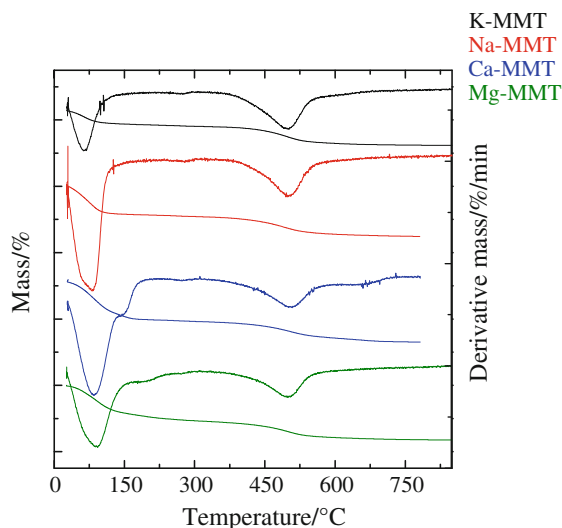
### Thermogravimetric analysis

Thermogravimetric (TG) and derivative thermogravimetry (DTG) curves of montmorillonite clay mineral and modified montmorillonites are shown in Figs. 1, 2, 3, 4, 5 and 6, respectively.

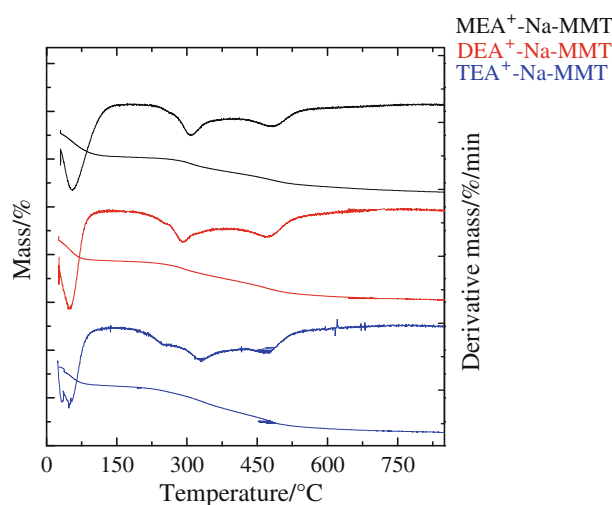
The thermal transition steps of the examined samples are demonstrated in Tables 1 and 2, respectively. Two thermal



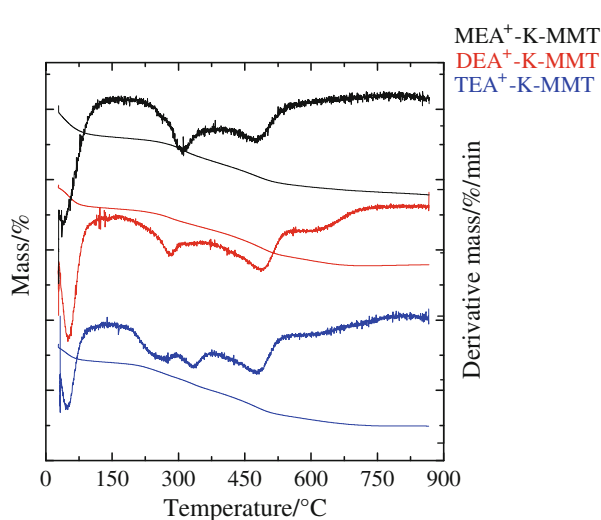
**Fig. 1** Representative TG and DTG profiles of montmorillonite clay mineral



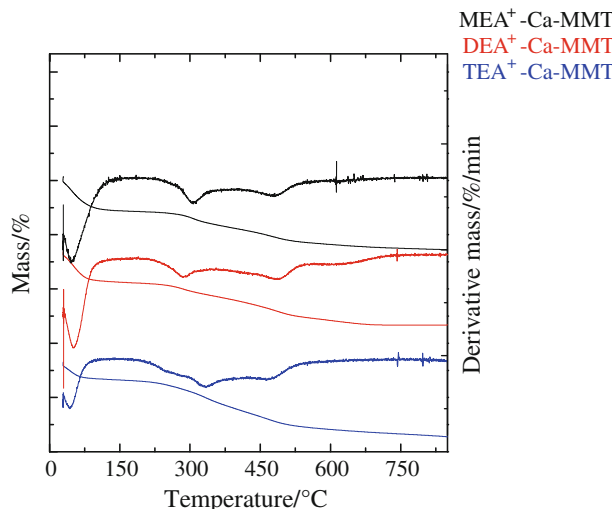
**Fig. 2** Representative TG and DTG profiles of different alkaline metal cation-saturated montmorillonite



**Fig. 4** Representative TG and DTG profiles of mono-, di-, and triethanolammonium intercalated Na-montmorillonite



**Fig. 3** Representative TG and DTG profiles of mono-, di-, and triethanolammonium intercalated K-montmorillonite



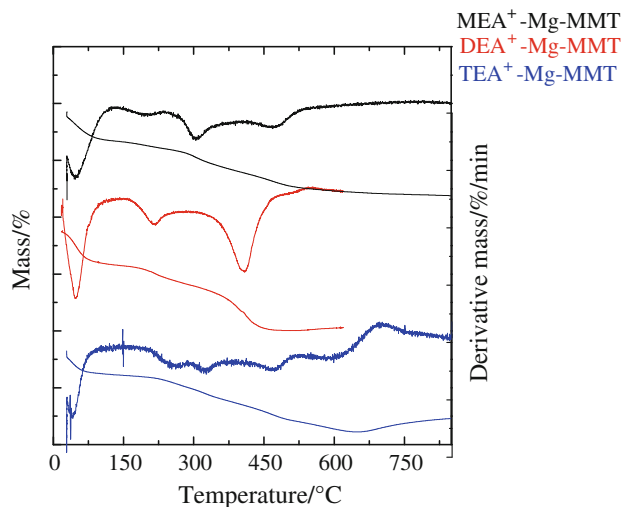
**Fig. 5** Representative TG and DTG profiles of mono-, di-, and triethanolammonium intercalated Ca-montmorillonite

decomposition steps were observed for untreated and homocationic forms of montmorillonite. The first low-temperature decomposition step was observed in the range from ambient temperature to about 150 °C, being attributed to the volatilization of both physically adsorbed water and water molecules bounded to the exchangeable cations in the interlayer space, which form hydration spheres around these cations. An increase in the dehydration temperature was observed, being attributed to stronger hydrogen bonding between water molecules and exchangeable cations having higher polarizing power following the order:  $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ . The second decomposition step was observed between 400 and

600 °C, because of the dehydroxylation of the structural water of the clay [19, 20].

From the figures and the corresponding tables, the quantity of the free and the interlayer water has reduced in ammonium-montmorillonites compared to untreated and homocationic forms of montmorillonites, indicating the weaker hydration of ammonium cations [21]. The type of ammonium cation has affected both desorption temperature (position) and the amount of the adsorbed water (intensity). Triethanolammonium-montmorillonite showed smaller desorption temperature values and water content than those for diethanolammonium and monoethanolammonium-montmorillonites, which is consistent

with less hydrophilic nature of triethanolammonium-montmorillonites [22, 23]. As expected, ammonium-montmorillonites show a decrease in the dehydroxylation temperature compared to untreated montmorillonites



**Fig. 6** Representative TG and DTG profiles of mono-, di-, and triethanolammonium intercalated Mg-montmorillonite

**Table 1** Results of the TG of montmorillonite and homocationic forms of montmorillonite

Sample	Step 1		Step 2	
	Mass loss/%	Temp/°C	Mass loss/%	Temp/°C
MMT clay	11.89	27–150	2.70	400–600
K-MMT	4.37	30–150	2.33	400–600
Na-MMT	8.36	30–150	2.39	400–600
Ca-MMT	10.80	30–150	3.13	400–600
Mg-MMT	11.14	27–150	3.34	400–600

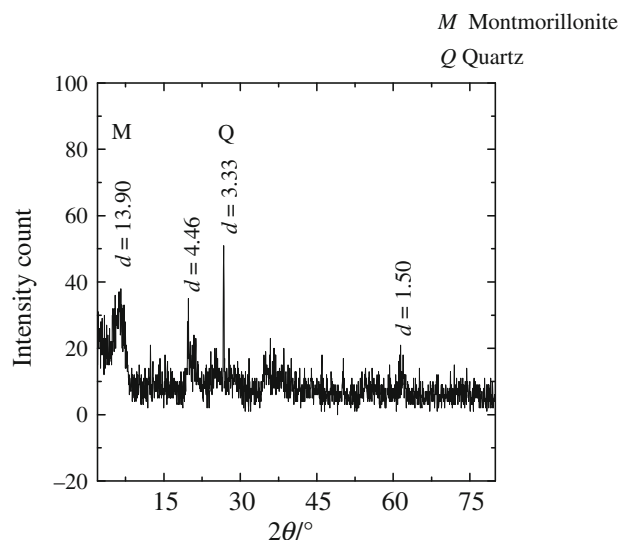
**Table 2** Thermal transition steps of different molar mass ammoniums intercalated different cationic forms of montmorillonites

Sample	Step1		Step2		Step3	
	Mass/%	Temp/°C	Mass/%	Temp/°C	Mass/%	Temp/°C
MEA <sup>+</sup> -K-MMT	6.69	28–150	4.86	250–400	4.85	400–600
DEA <sup>+</sup> -K-MMT	5.04	30–150	5.23	150–400	5.88	500–700
TEA <sup>+</sup> -K-MMT	3.95	28–150	6.68	150–400	6.99	350–600
MEA <sup>+</sup> -Na-MMT	8.25	30–150	4.77	200–400	4.43	400–600
DEA <sup>+</sup> -Na-MMT	7.73	26–150	5.83	200–400	4.93	400–600
TEA <sup>+</sup> -Na-MMT	6.02	25–150	7.43	200–400	5.47	400–600
MEA <sup>+</sup> -Ca-MMT	9.52	29–150	4.70	200–400	4.34	400–600
DEA <sup>+</sup> -Ca-MMT	8.76	30–150	4.79	200–400	5.47	400–600
TEA <sup>+</sup> -Ca-MMT	5.00	29–150	7.67	200–400	5.59	400–600
MEA <sup>+</sup> Mg-MMT	8.92	29–200	6.96	200–400	4.98	400–600
DEA <sup>+</sup> -Mg-MMT	8.49	20–100	7.43	150–350	5.24	400–500
TEA <sup>+</sup> -Mg-MMT	8.24	27–150	7.87	150–400	5.87	400–600

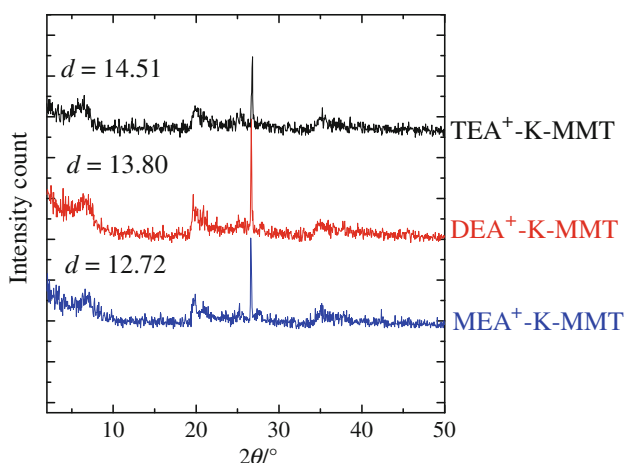
because of a decrease in the relative amount of inorganic material in ammonium-montmorillonites.

#### X-ray diffraction study

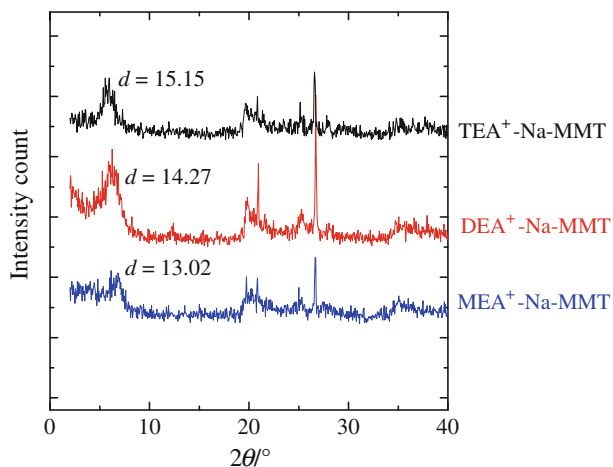
From the diffractogram of montmorillonite (Fig. 7), the characteristic peaks at  $d_{001} = 13.90 \text{ \AA}$ ,  $d_{020-110} = 4.46 \text{ \AA}$ , and  $d_{060-033} = 1.50 \text{ \AA}$  were assigned for montmorillonite clay mineral, and at  $d_{101} = 3.33 \text{ \AA}$  for quartz as impurity, suggesting that bentonite clay might be in the calcium form [24]. The changes in the basal spacing of ammonium-montmorillonites were due to intercalation of different-sized ammonium cations in the interlayer space of montmorillonite (Figs. 8, 9, 10, 11). These changes in the crystallographic spacings were reflecting structural changes of montmorillonite after modification with organic compounds.



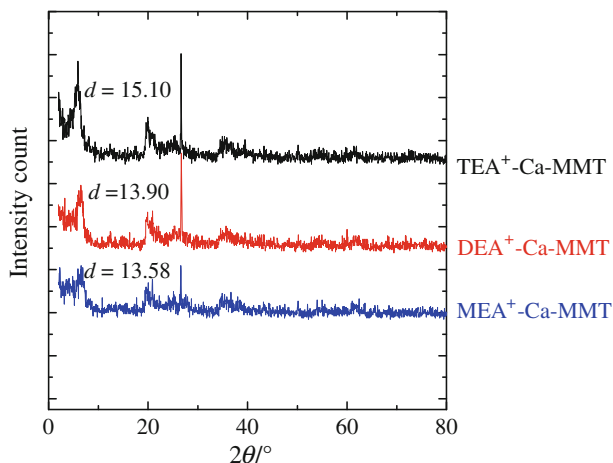
**Fig. 7** XRD patterns of montmorillonite clay mineral



**Fig. 8** XRD patterns of mono-, di-, and tri-ethanolammonium cations intercalated K-MMT



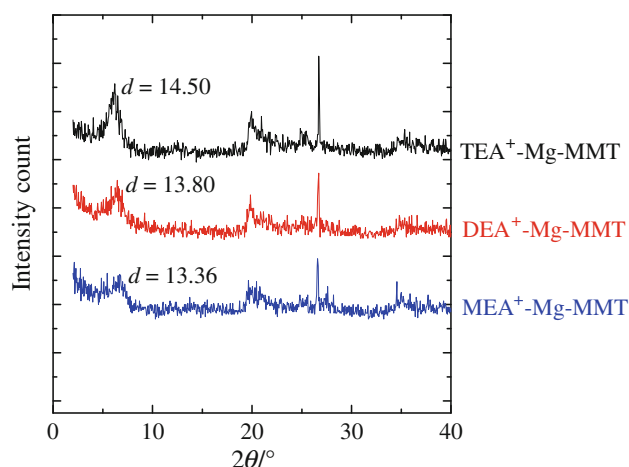
**Fig. 9** XRD patterns of mono-, di-, and tri-ethanolammonium cations intercalated Na-MMT



**Fig. 10** XRD patterns of mono-, di-, and tri-ethanolammonium cations intercalated Ca-MMT

The size of ammonium cation (molar mass) used has influenced the structure of the clay. Table 3 demonstrates a linear relationship between an increase in the basal spacing of ammonium-montmorillonites and the size of the ammonium cations used.

From Table 3, it is observed that the basal spacings of monoethanolammonium-montmorillonites have lower values compared to diethanolammonium- and triethanolammonium-montmorillonites due to their low molar mass compared to di- and triethanolammonium cations. Based on the basal spacing values, a monolayer configuration of alkyl ammonium cations in the interlamellar space of montmorillonite is observed which is attributed to low molecular mass of amines used.



**Fig. 11** XRD patterns of mono-, di-, and tri-ethanolammonium cations intercalated Mg-MMT

**Table 3** Basal spacings of ammonium-montmorillonites in relation to molar mass of amines used

Sample <sup>a</sup>	M. mass <sup>b</sup> of amines/g/mol	d-value <sup>c</sup> /Å
MEA <sup>+</sup> -K-MMT	61.08	12.72
MEA <sup>+</sup> -Na-MMT	61.08	13.02
MEA <sup>+</sup> -Ca-MMT	61.08	13.58
MEA <sup>+</sup> -Mg-MMT	61.08	13.36
DEA <sup>+</sup> -K-MMT	105.14	13.80
DEA <sup>+</sup> -Na-MMT	105.14	14.27
DEA <sup>+</sup> -Ca-MMT	105.14	13.90
DEA <sup>+</sup> -Mg-MMT	105.14	13.80
TEA <sup>+</sup> -K-MMT	149.19	14.51
TEA <sup>+</sup> -Na-MMT	149.19	15.15
TEA <sup>+</sup> -Ca-MMT	149.19	15.10
TEA <sup>+</sup> -Mg-MMT	149.19	14.50

<sup>a</sup> Ammonium–montmorillonite complexes

<sup>b</sup> Molar mass of amine used

<sup>c</sup> Basal spacing of the respective sample

**Table 4** Elemental chemical analysis of different ammonium-montmorillonites

Sample	Carbon/%	Hydrogen/%	Nitrogen/%
MEA <sup>+</sup> -K-MMT	1.676	2.261	0.886
MEA <sup>+</sup> -Na-MMT	1.690	1.993	0.876
MEA <sup>+</sup> -Ca-MMT	1.650	2.041	0.811
MEA <sup>+</sup> -Mg-MMT	1.637	1.902	0.857
DEA <sup>+</sup> -K-MMT	2.706	1.960	0.750
DEA <sup>+</sup> -Na-MMT	3.044	2.133	0.829
DEA <sup>+</sup> -Ca-MMT	2.771	2.009	0.715
DEA <sup>+</sup> -Mg-MMT	2.741	1.967	0.725
TEA <sup>+</sup> -K-MMT	3.575	1.970	0.634
TEA <sup>+</sup> -Na-MMT	4.329	2.221	0.761
TEA <sup>+</sup> -Ca-MM	4.727	2.193	0.837
TEA <sup>+</sup> -Mg-MMT	4.273	2.385	0.734

### Elemental analysis of ammonium-montmorillonites

Table 4 summarizes the average chemical composition of each element (C, H, and N) of different ammonium-montmorillonite samples. The presence of these elements confirms the intercalation of ammonium cations into the interlayer space of montmorillonite and reflects the effect of the cation size on the amount of ammonium cations adsorbed by the clay.

### Conclusions

It is worthy of note that the development and characterization of ammonium-montmorillonite materials are of great importance, as these materials may be used as effective adsorbents for gaseous and liquid contaminants. In this study, a combination of thermogravimetric, XRD, and CHNS analyses were used. The thermal behavior of ammonium-montmorillonites investigated was affected by the nature and size of ammonium cation used, where the type of ammonium cation has affected both desorption temperature and the amount of the adsorbed water. Ammonium-montmorillonites show a decrease in the dehydroxylation temperature compared with untreated montmorillonites. This is due to a decrease in the relative amount of inorganic material in ammonium-montmorillonites. XRD data showed that the crystallographic spacings ( $d_{001}$ ) of ammonium-montmorillonites increased with the increase of molar mass of ammonium cation used, and indicated a monolayer arrangement of the alkyl chains of ammonium cation in the interlayer spacing of montmorillonite. CHNS results confirm the intercalation of ammonium cation in the interlayer space of montmorillonite.

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