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THERMAL ANALYSES OF MONO- AND DIVALENT MONTMORILLONITE CATIONIC DERIVATIVES

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ABSTRACT

DTA and TG analyses were carried out for mono- and divalent cationic derivatives of Jelsovy–Potok montmorillonite. A certain relation between the charge density and the highest dehydration DTA peak was established for both series, since the two variables are a function of the magnitude of binding the hydrated water molecules. According to the charge density levels the cationic derivatives can be classified into three categories: (i) the single peak group falls in the range of charge density lower than 1 C m^{-2}; (ii) the double peak group falls between 1 and about 2 C m^{-2}; and (iii) for the higher charge densities three peaks are observed. The Ba derivative presents the only exception in this series. As the charge density increases, not only the number of dehydration peaks increases, but also the isolation between them becomes better, i.e., the overlapping of these peaks decreases in the order Ca>Li>Mg.

The slopes of the TG curves in the temperature range 200–500°C increase with increase in charge density on the cationic derivative. This indicates that the rate of dehydration differs by changing the exchangeable cation of the surface, whereas the rate of dehydroxylation for all derivatives is the same since they all have the same origin.

INTRODUCTION

In recent decades, a few extensive works dealing with the thermal investigation of clay minerals, specifically dehydration, dehydroxylation and high temperature transformation, have been carried out. Montmorillonite, which is the most famous member, received special priority in such studies in view of its wide application and industrial uses.

Observations show that the dehydration of various montmorillonites is only affected to a major degree with the type of exchangeable cations rather than with the clay lattice composition [1–3]. On the other hand, the dehydroxylation behaviour of a clay mineral is largely affected by the structure and composition of the unit cell, whereas the type of exchangeable cation has almost no effect. It is worth mentioning that the thermal character of the transformations taking place beyond the dehydroxylation region between 800 and 1200°C is not only affected by the lattice composition, but also by the type of exchangeable cations.

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The present work deals with the relation between the charge densities, calculated for each cationic montmorillonite derivative, and the rate of dehydration and dehydroxylation as detected from DTA and TG analyses.

EXPERIMENTAL

Material

The Jelsovy–Potok montmorillonite derivative was prepared by different replacements of exchangeable cations. This was achieved by soaking 5 g of the original sample (usually Ca–Mg montmorillonite) in 100 cm^3 of 1 N chloride solution of different cations for a period of 12 h. The prepared derivative was washed with 0.1 N of the specified chloride solution five times and then with alcohol several times until the solution was free from Cl^- ions. The derivatives thus prepared in the present study involved the following exchangeable cations: Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}. Before carrying out any experiment, the samples were kept for 7 days in a vacuum desiccator containing a saturated solution of $Mg(NO_3)_2$, whereby a relative humidity of 51.5–55% in the temperature range 18–20°C could be developed. Under such conditions the weight loss during the dehydration of the montmorillonite derivatives is mainly dependent on the water characteristics of each sample and not the weathering conditions.

Apparatus

Differential thermal analysis

This was performed on the tested samples of montmorillonite derivatives using a locally made accurate apparatus with a d.c. amplifier (Leeds and Northrup type) and a two-channel recorder (H and B polycomposite type). The technique adopted in this test was according to the recommendations of Mackenzie [4] and McAdie [5].

Thermogravimetric analysis (TG)

Thermogravimetric analysis of the tested montmorillonite samples was carried out using an automatic thermobalance provided by Gebrüder Netzsch, W. Germany, the thermograms being obtained at a constant heating rate.

RESULTS AND DISCUSSION

The differential thermograms of the derivatives of Jelsovy–Potok montmorillonite (Li, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} montmorillonite) are shown in Fig. 1. It can be seen that these derivatives

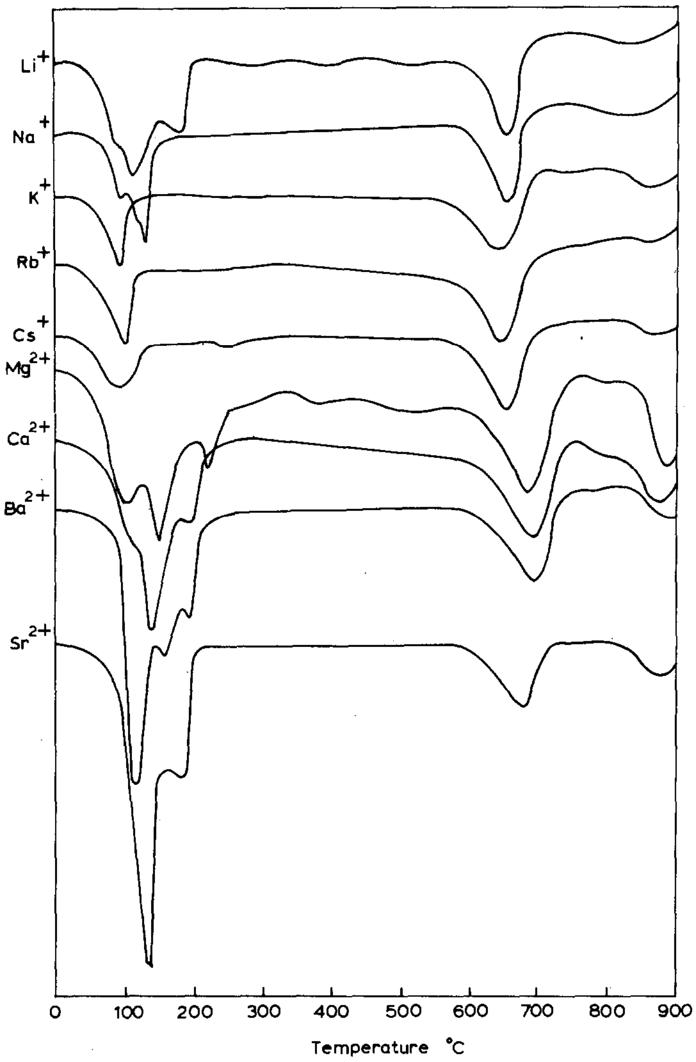

Fig. 1. DTA curves of mono- and divalent cationic derivatives of Jelsovy–Potok montmorillonite.

differ mainly in the dehydration region 50–250°C, whereas their dehydroxylation peaks appear at more or less the same temperature. The similarity in the dehydroxylation behaviour may be related to the use of the same clay origin (Jelsovy–Potok montmorillonite) throughout the preparation of these derivatives [1–3].

In the dehydration region, the observed peaks are all endothermic. Derivatives such as K^+, Rb^+ and Cs^+ exhibited a single peak, while others exhibited well-defined double peaks, e.g., Na^+ and Sr^{2+}; the remainder are characterized by three peaks, either well defined, e.g., Mg^{2+} and Ba^{2+}, or overlapped e.g., Li^+ and Ca^{2+}.

The peaks are also variable in width, sharpness and intensity. These variations can be related to the amount of liberated water molecules and the binding energy holding them in between the clay flakes, or on the clay cation surface. According to Boenisch [6], these water molecules can be classified into three types: (1) the "free water" which is mainly found in the case of suspensions or pastes and easily dehydrates at exactly 100°C. It acts as a carrier for exchangeable cations during the exchanging process; (2) the "surface water" which is physically bound to the clay surfaces and requires relatively higher energy to be liberated; and (3) the "hydrated water molecules" which, due to their polarity are attracted to the positively charged cations and are electrostatically bound to them, hence requiring the highest energy to overcome such attractive forces.

Since in some derivatives the peaks displayed above 100°C number more than one, this may be correlated with the tendency of the hydrated water molecules to form more than one shell surrounding the cation. This is in agreement with the assumption of Mackenzie [4] regarding the possibility of the formation of multi-shells of hydrated water molecules covering the cation surface. Accordingly, the number of peaks in the DTA curve related to that type of hydrated water should agree with the number of water shells about the cation surfaces. The inner water shell which is directly held to the cation is the shell most strongly bound to it, and consequently requires the highest energy to be liberated, an effect that corresponds to the highest temperature peaks on dehydration. As the water shell is far from the cation surface, its binding energy and its dehydration temperature both decrease since the interaction energy between polar water molecules and the charge density on the cation surface are effectively reduced in view of the masking effect of the first shell of water molecules. Thus, the interaction force becomes progressively less the further the shell is from the cation surface.

Relation between the charge density on the cation surface and highest temperature DTA peak

The afore-mentioned achievement can be confirmed experimentally on comparing the calculated charge density on the cation surface (based on available data concerning cation radius and electron charge) and the highest temperature peak which is probably a function of the potential energy electrostatically binding the inner water shell to the cation surface. Throughout these calculations, the shielding effect of the outer electron shell of these cations (saturated, in the case of alkali and alkaline earths, by eight electrons) was neglected. Table 1 summarizes the values of charge density on each cation surface and the corresponding temperature of the highest temperature dehydration peak. The relation between them is illustrated in Fig. 2. The observations can be summarized as follows.

(1) There is a satisfactory linear relation between the charge density and

TABLE 1

Values of charge density on each cation surface and the corresponding temperature of the highest temperature DTA peak

	Cation radius (Å)	Cation surface area $4\pi r^2$ ($m^2 \times 10^{20}$)	Charge density [a] on cationic surface ($C\ m^{-2}$)	Temp. of highest temp. DTA peak (°C)
Li^+	0.6	4.52	3.539	185
Na^+	0.95	11.33	1.411	130
K^+	1.33	22.22	0.721	95
Rb^+	1.48	27.51	0.581	100
Cs^+	1.69	35.87	0.446	95
Mg^{2+}	0.65	5.30	6.038	220
Ca^{2+}	0.99	12.31	2.60	195
Sr^{2+}	1.13	16.04	1.99	185
Ba^{2+}	1.35	22.90	1.399	190

[a] The electric charge on the monovalent and divalent cations is 1.603 and 3.206×10^{-19} C, respectively.

the highest peak temperature for both series of the monovalent and divalent derivatives, individually. This may be true since the charge density and highest peak temperature are functions of the magnitude of binding the hydrated water molecules to the cation surface. The presence of two linear plots is related to the difference in the cation character when one or two valence electrons are separated.

(2) Arbitrary levels of charge densities can be drawn and thus the different clay derivatives can be classified into three categories corresponding to the occurrence in the DTA analysis of one, two and three dehydration peaks. The single peak group falls in the range of charge density lower than 1 C m^{-2}. The second group of double peaks falls in the range 1 to about 2 C m^{-2}. For the higher charge densities, three peaks are noticed in the DTA. Perhaps the Ba derivative presents the only exception to this representation. This can probably be correlated with the possible dehydroxylation of Ba(OH), which could possibly be contaminated with the Ba derivative during its preparation.

(3)As the charge density increases, not only the number of dehydration peaks increases but also the isolation between them becomes better, and well-defined peaks are observed, i.e., the overlapping of three peaks decreases in the order Ca > Li > Mg derivatives.

The heavy alkali cations (K^+, Rb^+, Cs^+) represent the group of derivatives which display a single peak on dehydration at 100°C. This peak is probably related to the dehydration of surface water molecules and not to

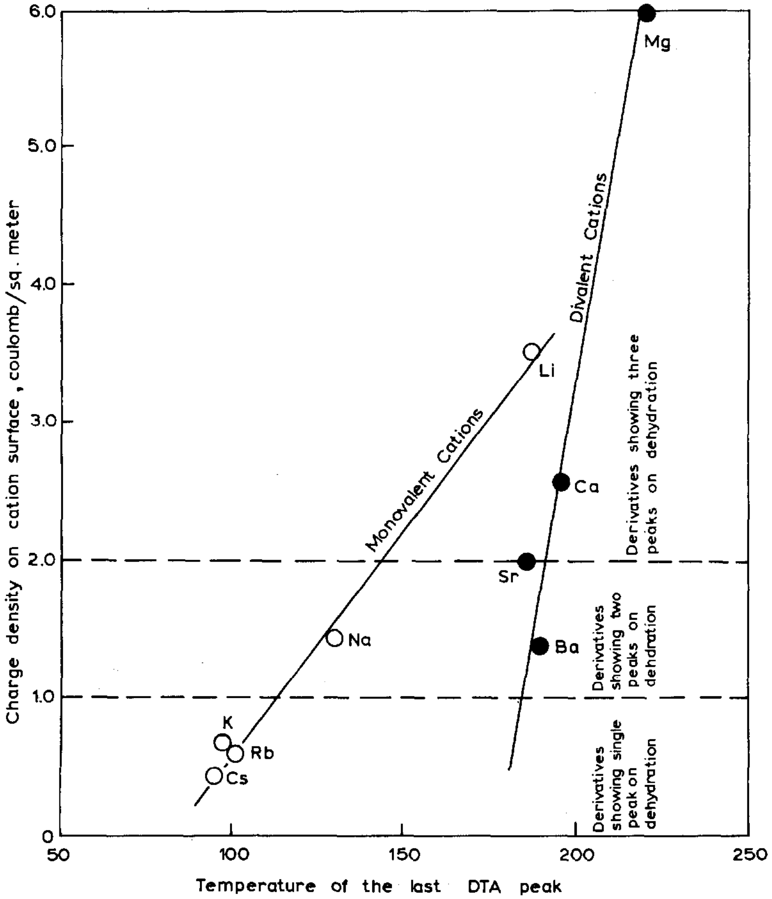

Fig. 2. Relation between charge density on cation surface and the highest temperature DTA peak.

the dehydration of hydrated water. This effect could be confirmed from the TG (cf. Fig. 3) of such derivatives whereby they possess the least but the same value of weight loss on dehydration. This value should be a function of the specific surface area of the clay origin.

The thermogravimetric analysis curves for montmorillonite derivatives under investigation are graphically represented in Figs. 3 and 4 for the monovalent and divalent derivatives, respectively. Before analysis, the samples were kept for 7 days in a vacuum desiccator containing a saturated solution of $Mg(NO_3)_2$, whereby a relative humidity of 51.5–55% can be developed in the temperature range 18–20°C. Accordingly, the water adsorption characteristics of each sample are independent of the natural humidity or weathering conditions. Figures 3 and 4 show that the dehydration is nearly accomplished at a temperature not so far from 150°C. Atomic weight loss values for Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba montmorillonite are in

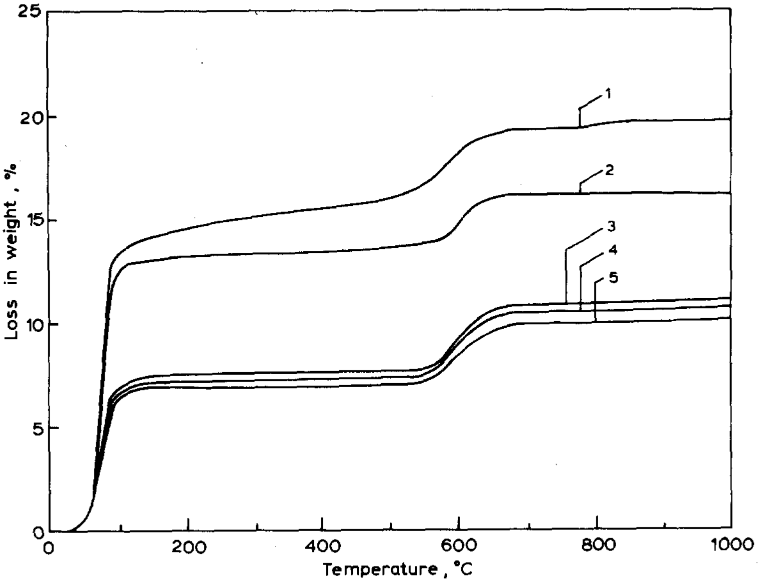

Fig. 3. TG curves of monovalent cationic derivatives of Jelsovy–Potok montmorillonite. 1, Li^+; 2, Na^+; 3, K^+; 4, Rb^+; 5, Cs^+. Heating rate, 5°C min^{-1}.

the order of 14.5%, 13.0%, 7.4%, 7.0%, 6.8%, 16.0%, 18.3%, 18.0% and 15.2%, respectively. It seems that the dehydration value decreases on increasing the ionic radius, the Ba derivative being the exception.

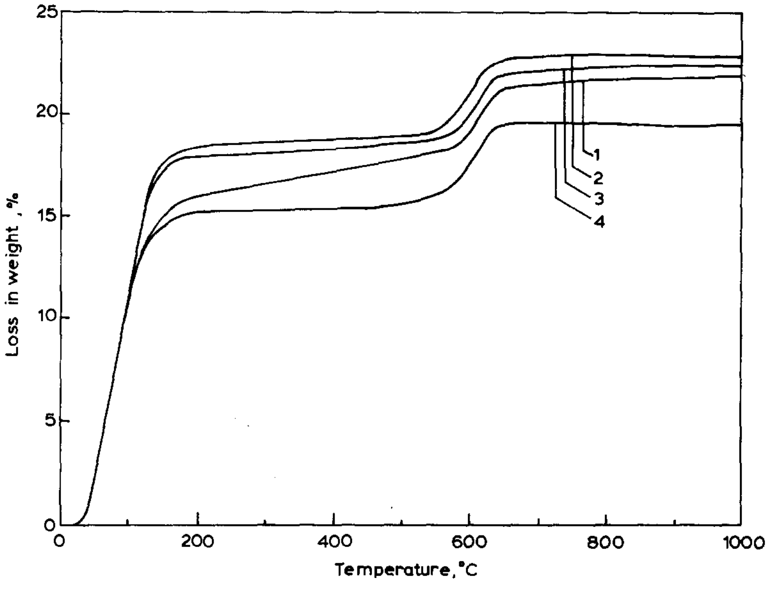

Fig. 4. TG curves of divalent cationic derivatives of Jelsovy–Potok montmorillonite. 1, Mg^{2+}; 2, Ca^{2+}; 3, Sr^{2+}; 4, Ba^{2+}. Heating rate, 5°C min^{-1}.

Heavy alkalis (K^+, Rb^+, Cs^+) have almost the same dehydration pattern. This can be explained on the basis that they only possess the surface water and not the hydrated water molecules. The weight loss decreases in the order $K^+ > Rb^+ > Cs^+$ and is related to their differing atomic radii, noting that the clay unit cell contains the same number of cations in each monovalent derivative.

In the temperature range 200–500°C (just before the dehydroxylation region) there are slight and continuous weight loss slopes which differ from one derivative to another. This may be explained on the basis that not all the water molecules are completely dehydrated in the low temperature range (20–150°C), but some (which are firmly held to the cation surfaces) cannot be recovered quickly if a relatively high rate of heating is applied, and hence it is recovered slowly and continuously from the very narrow channels formed after the collapse of the clay flakes. It is found that there is a direct relation between the slope of the TG curve in that temperature range (which is a function of the residual water molecules held to the cation surface beyond the temperature at which collapsing takes place) and the charge density on these surfaces (which is a function of both the quantity of hydrated water and the force binding them to the cation surface), as shown in Table 2 and Fig. 5.

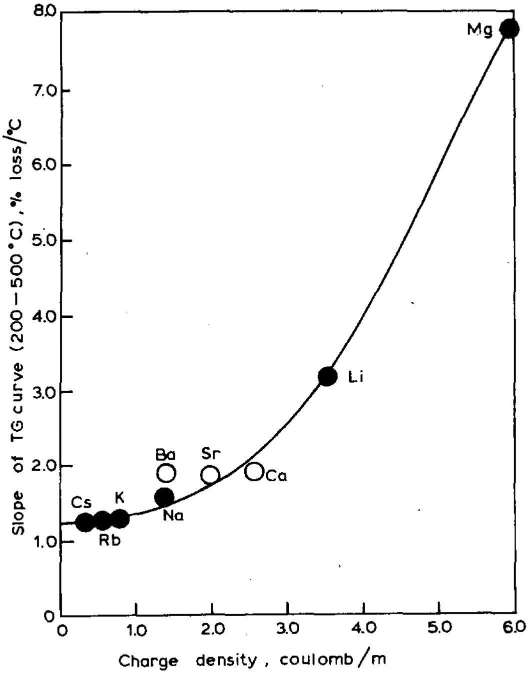

Fig. 5. Relation between slopes of TG curves (200–500°C) and the charge density on montmorillonite.

TABLE 2

Slopes of TG curve versus cation charge density

Exchangeable cation	Charge density on cation surface ($C\ m^{-2}$)	Slope of TG curve over 200–500°C (% wt. loss °C)
Li^+	3.54	3.15
Na^+	1.41	1.6
K^+	0.72	1.3
Rb^+	0.58	1.3
Cs^+	0.45	1.3
Mg^{2+}	6.04	7.7
Ca^{2+}	2.63	1.9
Sr^{2+}	1.99	1.9
Ba^{2+}	1.40	1.9

The dehydroxylation of the derivatives under investigation seems to occur in almost the same temperature range and the same weight loss value is obtained for all of them. This is true since the clay origin (Jelsovy–Potok montmorillonite) was always used during their preparation. Beyond the dehydroxylation region, the TG curve shows marked change since the physical transformations involve no weight change.

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