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THERMAL DEHYDRATION OF MONO- AND DI-VALENT MONTMORILLONITE CATIONIC DERIVATIVES

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ABSTRACT

The kinetics of the isothermal dehydration of seven derivatives of Jelsovy–Potok montmorillonite comprising two series of mono- and di-valent cations were studied together with TG and DTA of these compounds. A certain correlation was established between the charge density and (1) the highest dehydration DTA peak, (2) the first order rate constant for the dehydration reaction.

A diffusion controlled mechanism is suggested for the kinetics of the isothermal dehydration. This is supported by (1) the dependence of the first order rate constant on the cationic radius, (2) the relatively large values of the first order rate constants for the monovalent cations compared with those for the di-valent cations, and (3) the values of the energy of activation (≈ 23 kJ mol^{-1}) for all the derivatives studied.

Values of about 220 J K^{-1} were obtained for the entropy of activation supporting the hypothesis of a two dimensional diffusion reaction.

INTRODUCTION

In view of the wide application of clay minerals in industry, the study of the effects of thermal treatment on its properties, especially its dehydration, dehydroxylation and structure changes, have become of interest in the past decade.

Montmorillonite, which is the most famous member of clay minerals, has received special attention in these studies. Observations show that the dehydration of montmorillonite derivatives is affected to a major extent by the type of exchangeable cations rather than the clay lattice composition, yet the dehydroxylation studies show that the lattice composition plays a prime role [1–3].

Published literature on the kinetics of dehydration of clay minerals is scarce. Birch Holt et al. investigated the rate of thermal dehydration of muscovite [4]. Mikhail et al. studied the dehydration of some clay minerals in various atmospheres [5–7].

The present study deals with the effect of exchangeable cations on the TG,

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DTA and the kinetics of isothermal dehydration of Jelsovy–Potok montmorillonite.

EXPERIMENTAL

Materials

The Jolsovy–Potok montmorillonite derivatives were prepared by replacement of different 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 the various cations for a period of 12 h. The prepared derivative was washed five times with a 0.1 N solution of the specific chloride and then with alcohol until the solution was free of chloride ions. The derivatives thus prepared involved the following exchangeable cations, Li^+, Na^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. Before carrying out any experiment, the samples were kept for several 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 is obtained and hence the loss in weight during the dehydration of each derivative is mainly dependent on its water characteristics and not on the weathering conditions.

Apparatus

Differential thermal analysis was carried out using locally made DTA apparatus with a DC amplifier (Leeds and Northrup) and a two-channel recorder (H and B polycomposite type). The technique adopted was that recommended by Mackenzie [8] and McAdie [9].

Thermogravimetric analysis of the tested samples was carried out using an automatic thermobalance provided by Gebruder Netzsch (West Germany) adjusted to a heating rate of 5°C min^{-1}.

Isothermal experiments were conducted using the automatic thermobalance adjusted to 70, 85, 100, 120 and 140°C.

RESULTS AND DISCUSSION

Thermogravimetric analysis

TG analysis indicates that dehydration takes place almost to completion at ~ 150°C before dehydroxylation starts and is achieved at ~ 800°C. The percentages weight loss are 14.5, 13, 6.8, 16.0, 18.3, 18 and 15.2 for the Li^+, Na^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} derivatives, respectively. It seems that the percentage weight loss decreases on increasing the cationic radius except for the Mg montmorillonite.

Differential thermal analysis

The DTA of the seven montmorillonite derivatives studied are shown in Fig. 1, which shows that they differ mainly in the dehydration region (50–150°C), whereas their dehydroxylation peaks are more or less similar. The similarity in the dehydroxylation behaviour may be related to the use of the same clay mineral origin in the preparation of all the derivatives studied [1–3]. The variation in the dehydration peaks is related to the number of water molecules liberated and the binding energy holding them between the clay flakes or on the clay cation surface. According to Boenisch [10], these water molecules may be classified into three types, (a) the free water which is dehydrated at ~ 100°C and acts as a carrier for exchangeable cations during the exchanging process, (b) the "surface water" which is physically bound to the clay surface and requires relatively higher energy to be liberated and (3) "hydrated water molecules" which, due to their polarity are electrostatically bound to the positively charged cations and hence require the highest energy to overcome such attraction forces.

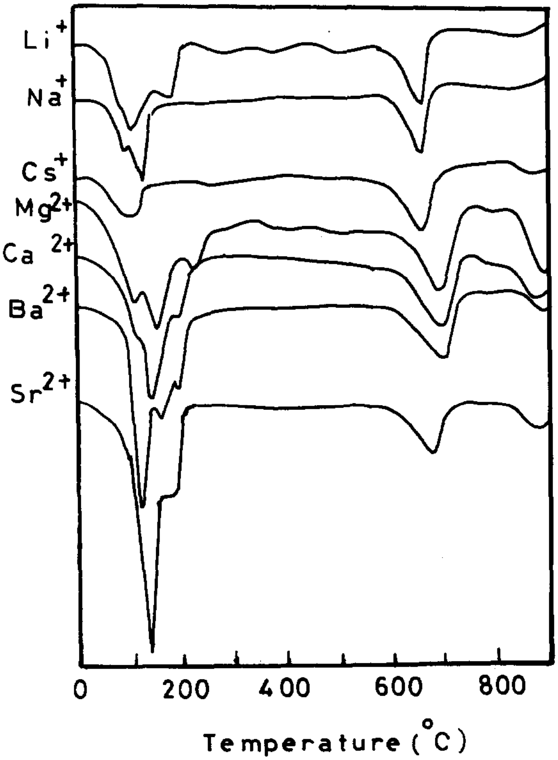

Fig. 1. DTA.

The tendency of some derivatives to display more than one peak above 100°C, Fig. 1, is attributed to the tendency of hydrated water molecules to form more than one shell surrounding the cation. This is in agreement with the assumption of Mackenzie [8] regarding the possibility of formation of a multi-shell of hydrated water molecules covering the cation surface. The inner water shell, which is directly held to the cation, is the one most strongly bound to it and thus requires the highest energy to be liberated, an effect that corresponds to the highest temperature peak on dehydration. As the water shell gets further from the cation surface, its binding energy and hence its dehydration temperature decreases, due to the reduction in the interaction between the water molecules and the charge density on the surface of the cation by the masking effect of the first water shell.

The effect of the charge density on the cation surface (calculated from the radius and charge of the cation) on the highest dehydration peak temperature as a measure of the potential energy binding the inner water shell to the surface of the cation, is given in Table 1 and shown in Fig. 2.

Figure 2 shows that there is a satisfactory linear relationship between the charge density and the highest dehydration peak temperature for each series of derivatives. This may be true since the charge density affects, to a great extent, the binding forces between the water molecules of hydration and the surface of the cation. The presence of two linear plots is related to the difference in the cation character when one or two valence electrons are separated.

Kinetics of the isothermal dehydration

DTA and TG results, indicate that the most suitable temperature range for the study of the isothermal dehydration is between 50° and 150°C.

TABLE 1

Values of the cationic radius, charge density and first order rate constant for the various montmorillonite derivatives

Cationic derivative	$k \times 10^2$ (s^{-1})					Cationic radius (Å)	Cationic charge [a] density ($C\ m^{-2}$)
	70°C	85°C	100°C	120°C	140°C		
Li	0.32	0.38	0.53	0.89	1.27	0.6	3.54
Na	0.41	0.64	0.91	1.65	1.80	0.95	1.41
Cs	0.56	1.15	1.32	1.94	2.66	1.69	0.446
Mg	0.23	0.47	–	0.60	0.86	0.65	6.036
Ca	–	0.42	0.85	1.03	1.38	0.99	2.60
Sr	0.34	0.70	0.96	1.22	1.53	1.13	1.99
Ba	0.33	0.42	1.02	–	1.67	1.35	1.4

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

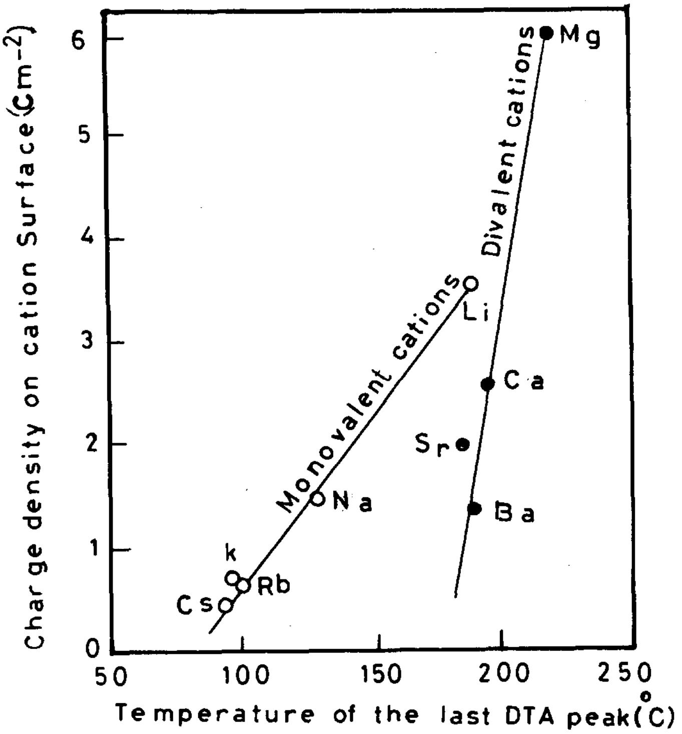

Fig. 2. The variation of the highest dehydration peak temperature with the charge density on the cation.

Typical dehydration isotherms are shown in Fig. 3 for the Na-montmorillonite. Figure 3 represents a plot of w_t/w_l versus time, t, where w_t is the weight lost at time, t, and w_l is that lost at a limiting value, l, reached after heating for 24 hours at the specified temperature. All the dehydration isotherms are sigmoid in shape and obey first order kinetics (Fig. 4). First order kinetics were also reported by Mikhail et al. for the isothermal dehydration of vermiculite, montmorillonite, illite and attapulgite clay minerals [5–7]. A summary of the values of the first order rate constant, k (s^{-1}), obtained from the slopes of the first order plots at various temperatures for all the derivatives studied, is given in Table 1.

The results given in Table 1 show that the values of the first order rate constants, k (s^{-1}), show a certain dependence on the exchangeable cation. The values of k (s^{-1}) obtained for the monovalent cations are higher than those for the divalent derivatives of the same cationic radius, due to the greater tendency of multivalent cations to tie clay mineral flakes together than that of univalent cations [11] thereby hindering the dehydration process.

Table 1 also shows that the value of the first order rate constant, k (s^{-1}),

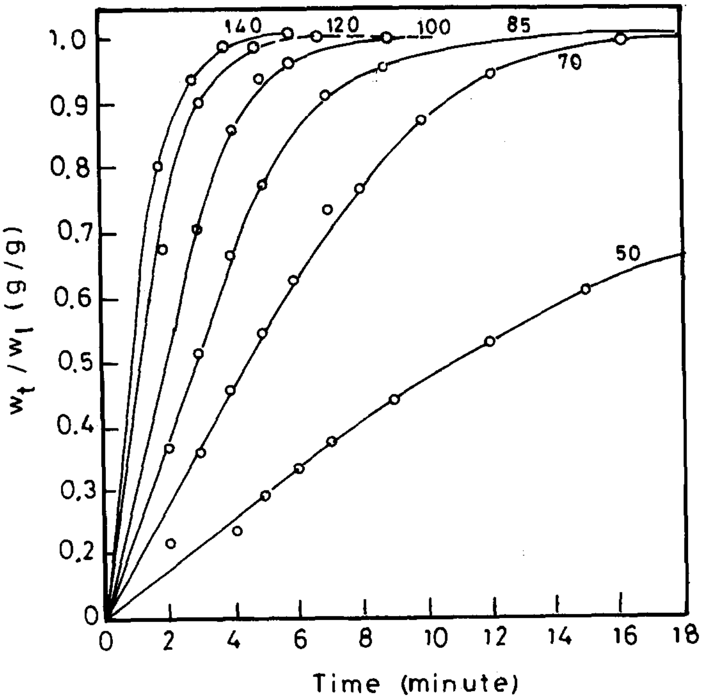

Fig. 3. Dehydration isotherms for Na-montmorillonite. Temperatures on curves in °C.

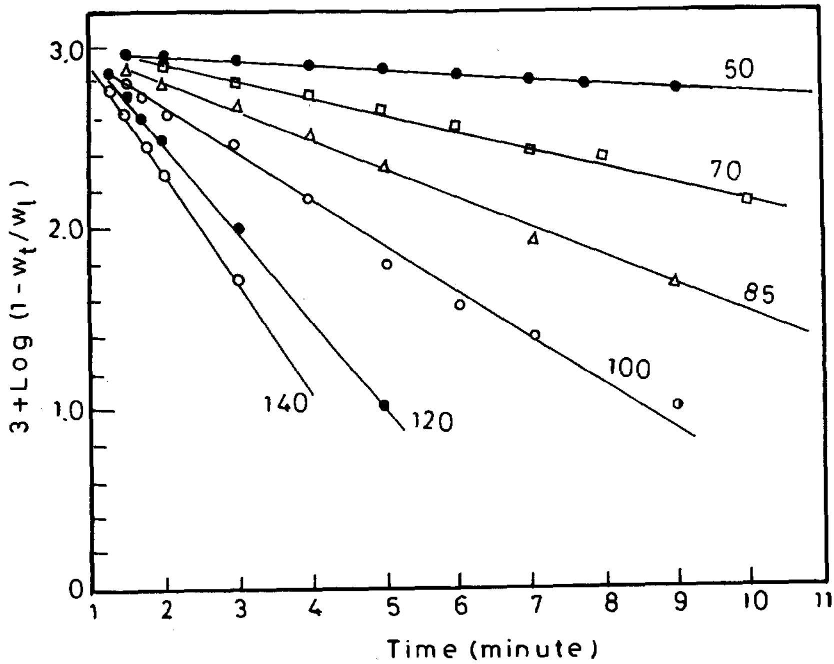

Fig. 4. First order plots for Na-montmorillonite at temperatures indicated on the curves (°C).

increases as the cationic radius increases for the same series of derivatives. This is attributed to the tendency of large cations to increase the distance of separation between the layers of montmorillonite thereby facilitating the dehydration reaction. This was proved by Walker who reported an increase in the C dimension from 14.4 to 15 Å when Sr was replaced by Mg in vermiculite [12].

The Ba derivative is the only exception to these conclusions at low temperatures, probably due to the possibility of low temperature dehydroxylation of $Ba(OH)_2$ which could be contaminating the derivative during its preparation.

A plot of the values of k (s^{-1}) at 140°C against the cationic radius, gave a straight line for each group of derivatives (Fig. 5). The two straight lines are of about the same gradient suggesting that one and the same mechanism is operative for the dehydration of both derivatives. They differ in the value of the intercept due to inhibition of the reaction upon increasing the cationic charge.

The effect of the charge density on the cation, which is a measure of the attractive forces on the clay mineral surface, on the dehydration rate constant at 140°C is shown in Fig. 6. Figure 6 shows that increasing the charge density lowers the dehydration rate. This is attributed to either or both of the following factors.

(a) The increase in the electrostatic attraction forces between the clay

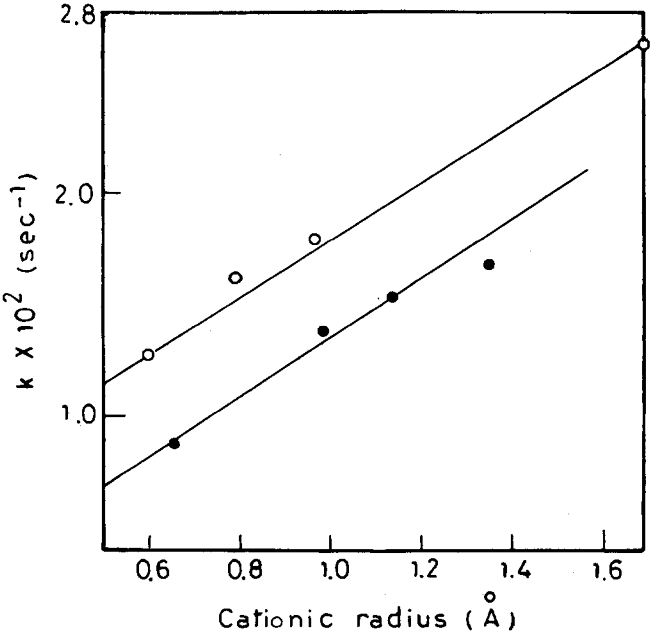

Fig. 5. The variation of the first order rate constant with the cationic radius.

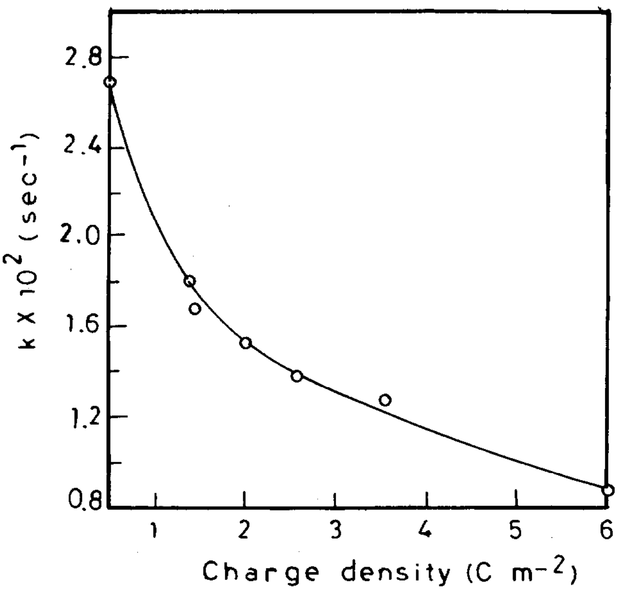

Fig. 6. The variation of the first order rate constant with the charge density on the cation.

mineral flakes which decreases their distance of separation and thus hinders the flow of water during dehydration.

(b) The increase in the partially covalent bonds between the water molecules adjacent to the clay mineral surface and those of the second and third layers [13] which in turn affects the fluidity of mobile water molecules by the rigid (immobile) ones adjacent to the clay mineral surface.

In order to assess the significance of the effect of cationic radius and charge or the charge density on the rate of dehydration of montmorillonite, the mechanism of the reaction must be considered. The dehydration reaction mechanism is governed by (a) the rate of loss of water molecules from the clay mineral lattice and (b) the rate of diffusion of water molecules through the lattice interface.

If reaction (a) is rate determining, it is difficult to vizualize how the exchangeable cations could affect the dehydration rate. Reaction (b) is the only process which seems to be influenced by exchangeable cations since it affects the interlayer spaces through which water molecules diffuse from the hexagonal holes in the sheet surface into the micelle edge. Such a process would involve an absorption of energy to push the layers apart [14]. A diffusion mechanism was also favoured by Mikhail et al. for the dehydration of some clay minerals [5–7].

A value of ~ 25 kJ mol^{-1} was obtained for the energy of activation, E_a, for all the derivatives studied by the application of Arrhenius equation (Fig. 7). Such a value confirms the previous conclusions since reaction (a) requires an energy of activation of the order of, or probably higher than, the heat of

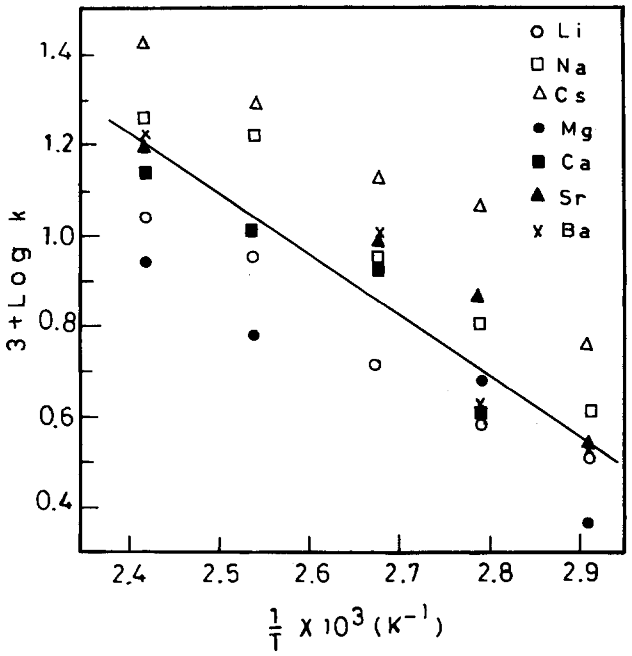

Fig. 7. Arrhenius plots.

evaporation of water molecules [5–7], whereas, reaction (b) needs very low values of E_a. The relatively high value of E_a obtained may be attributed to a phenomenon known as "activated diffusion" [5–7] or to what is known as "two dimensional diffusion". Both lead to an apparent increase in the value of the energy of activation. Two dimensional flow was reported to yield 2–3 times higher values of the free energy of activation than that of the three dimensional due to the lateral interactions [15].

Two dimensional diffusion is expected to be due to a restricted translational motion in the layered structure clay minerals attributed to the forces of interaction between the water molecules and the surface of the clay mineral. Such forces would restrict its motion at right angles to the flakes giving only two degrees of freedom of translational motion.

The previous conclusions were supported by a large negative value of the entropy of activation ~ 200 J K^{-1} due to the restricted, translational and may be rotational, degrees of freedom in the activated complex.

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