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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 constituting two series of mono- and di-valent cations were studied together with TG and DTA. 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. The results support a diffusion controlled mechanism for the dehydration with an energy and entropy of activations23 kJ mol^{-1} and -220 JK^{-1}, respectively.

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 became of interest in the past decade. Birch Holt et al investigated the rate of thermal dehydration of muscovite (1). Mikhail et al studied the dehydration of some clay minerals in various atmospheres (2-4).

The present study deals with the effect of exchangeable cations on the TG, DTA and the kinetics of isothermal dehydration of Jelsovy-Potok montmorillonite.

EXPERIMENTAL

The Jolsovy-Potok montmorillonite derivatives were prepared by replacement of different exchangeable cations by soaking 5g. of the original sample (usually Ca-Mg montmorillonite) in 100cc. of 0.1 N chloride solution of the various cations, namely, Li^+, Na^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} for a period of 12 hours. The prepared derivative was washed five times with the specific chloride solution and then with alcohol until the solution was free from chloride ions and were kept under a relative humidity of 51.5-55% in the temperature range 18-20^{o}C.

Differential thermal analysis was carried out in a locally made apparatus according to the technique adopted by Mackenzie (5) and McAdie (6).

Thermogravimetric analysis and kinetic experiments were carried out using an automatic thermobalance provided by Gebruder Netzsch, West Germany.

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RESULTS AND DISCUSSION

Thermogravimetric and Differential Thermal Analysis

TG and DTA indicate that dehydration takes place almost to completion at ca 150°C before dehydroxylation starts and achieved at ca 800°C.

DTA of the seven montmorillonite derivatives, show that they differ mainly in the dehydration region (50-150°C), whereas their dehydroxylation peaks are more or less similar attributed to the use of the same clay mineral origin in the preparation of all the derivatives studied (7-9). The variation in the dehydration peaks is related to the amount of water molecules liberated and the bonding energy holding them inbetween the clay flakes. The tendency of some derivatives to display more than one peak above 100°C, is attributed to the tendency of hydrated water molecules to form more than one shell surrounding the cation (8).

The effect of the charge density of the cation surface on the highest DTA peak as a measure of the potential energy binding the inner water shell to the surface of the cation is shown in Fig. 1, where a satisfactory linear relationship was obtained and the presence of two linear plots is related to the difference in the cation character.

Kinetics of the Isothermal Dehydration

DTA and TG results, indicate that the suitable temperature range for the study of the isothermal dehydration is between 50° and 150°C. The dehydration isotherms obeyed first order kinetics and the values of the first order rate constant, k, are given in Table 1. First order kinetics were also reported by Mikhail et al (2-4).

Table 1 shows that the k values, are higher for the monovalent than those for the divalent cations of the same cationic radius, due to the tendency of multivalent cations to tie clay mineral flakes together and thus hindering the dehydration process (10). It also shows that k increases as the cationic radius increases for the same series attributed to the tendency of large cations to increase the distance of separation betweeen the layers of montmorillonite and thus facilitating the dehydration reaction. This was proved by Walker who reported an increase in the c dimension from 14.4 to 15 A° when Sr was replaced by Mg in vermiculite (10).

The Ba derivative is the only exception 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.

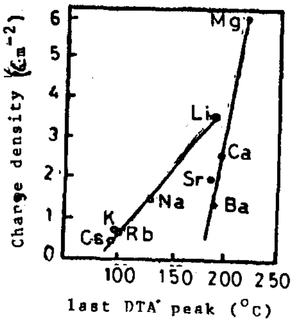

Fig.1 Variation of the last DTA peak with the charge density.

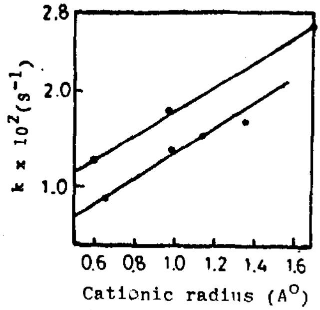

Fig.2 Variation of k with the cationic radius.

TABLE 1. Values of the cationic radius, charge density and the first order rate constant, for the various montmorillonite derivatives.

Cationic derivative	k x 10^{2} (s^{-1})					Cationic radius x 10^{10} (m)	Cationic* charge density (Cm^{-2})
	70°C	85°C	100°C	120°C	140°C		
Li	0.32	0.38	0.53	0.89	1.27	0.60	3.540
Na	0.41	0.64	0.91	0.65	1.80	0.95	1.410
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	2.600
Sr	0.34	0.70	0.96	1.22	1.53	1.13	1.990
Ba	0.33	0.42	1.02	-	1.67	1.35	1.400

A plot of k (s^{-1}) at 140°C against the cationic radius, gave a straight line for each group of derivatives, Fig. 2. The two straight lines are of about the same gradient suggesting one and the same mechanism to be operative. They differ in the value of the intercept due to the inhibition of the reaction upon increasing the cationic charge.

The variation of the dehydration rate constant with the charge density on the cation, Table 1, is attributed to either or both of the following factors, the variation in the electrostatic attraction forces between the clay mineral flakes which affects their distance of separation and hence the flow of water during dehydration, and/or the change in the partially covalent bonds between the water molecules adjacent to the clay mineral surface and those of the second and third layers which in turn affects the fluidity of mobile water molecules.

The previous conclusions are confirmed by considering the mechanism of dehydration which is governed by the rate of desorption from the surface followed by the rate of diffusion of water molecules through the lattice interface. If

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*Cationic charge density = cationic charge/$4\pi r^2$.

the desorption is rate determining, it is difficult to visualize how the exchangeable cations could affect the dehydration rate and a value of the order of or probably higher than the heat of evaporation of water (2-4) would have been obtained. Thus the diffusion reaction is the rate determining, since as mentioned earlier, the exchangeable cations affect 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 (12). A relatively high value of the energy of activation, Ea, ca 23 kJ mol^{-1}, was obtained for all the derivatives studied attributed to a phenomenon known as "activated diffusion" (2-4) or to what is known as "two dimensional diffusion", both lead to an apparent increase in the value of Ea. Two dimensional flow was reported to yield two to three times higher values of the free energy of activation than that of the three dimensional due to the lateral interactions (13), and is expected to be due to a restricted translational motion at right angles to the flakes. This is supported by a large negative value for the entropy of activation ca 220 JK^{-1}.

REFERENCES

1. J. Birch Holt, I.B. Culter and M.E. Wadsworth, J. Am. Ceram. Soc., 41, (1958), 842.
2. R.Sh. Mikhail, N.M. Guindy, and S. Hanafi, J. Appl. Chem., 20, (1970), 346.
3. R.Sh. Mikhail and N.M. Guindy, J. Appl. Chem. Biotechnol. 21, (1971), 113.
4. R.Sh. Mikhail, N.M. Guindy and S. Hanafi, Thermochimica Acta, 29, (1978), 289.
5. R.C. Mackenzie, Differential Thermal Investigation of Clays, Mineralogical Section, London, 1957, reprinted 1966.
6. H.G. McAdie, Anal. Chem., 39 (1967), 543.
7. C.F. Walker and W.C. Cole, in "The Differential Investigation of Clays", Edited by R.C. Mackenzie, Mineralogical Society, London, 1957, 191 pp.
8. G.T. Faust, Am. Miner, 36, (1951), 795.
9. C.A. Alexinals, and M.I. Jackson 14th Nat. Conf. Clays and Clay Minerals, Berkeley, C.A., Pergamon Press, London 1966, 35 pp.
10. G.F. Walker, Proc. Intern. Clay Conf., Stockholm, 1963, 177 pp.
11. P.F. Low, in Clay Mineralogy, Edited by Grim, R.E. McGraw-Hill, 1968, 256 pp.
12. R.C. Mackenzie and B.M. Bishui, Clay Minerals Bulletin, 3, (1957), 276.
13. W.J. Moore and Eyring in "The Theory of Rate Processes", Edited by S. Glasstone, K.J. Laidler and H. Eyring, McGraw-Hill 1941, 512 pp.