

## PREPARATION AND CHARACTERIZATION OF AN 8.4 Å HYDRATE OF KAOLINITE

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**Abstract**—A stable 8.4 Å hydrate of kaolinite was prepared by exchanging ethylene glycol for water in the 10.8 Å intercalate of ethylene glycol in kaolinite. The hydrate of kaolinite was characterized by XRD, FTIR and TGA/DSC. From the TGA data, one can estimate that there is 0.60 water molecule per  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  units. The IR data suggest a similarity of the local environment of the intercalated water in this 8.4 Å hydrate of kaolinite and the 8.4 Å hydrate of nacrite previously described by Wada (1965).

**Key Words**—Ethylene glycol, Hydrate of kaolinite, Intercalation, Kaolinite, Organo-clay.

### INTRODUCTION

Interlayer water in the kaolin minerals has attracted considerable attention over the years (Giese, 1988). Halloysite is known to readily intercalate water to yield a 10 Å hydrated phase and an 8.35 Å hydrate of nacrite has been prepared by first intercalating with potassium acetate and then washing with water (Wada, 1965). Kaolinite does not naturally exist in a hydrated form, and hydrates that may be formed by displacing a previously intercalated species by washing with water are not stable and quickly decompose.

Costanzo and coworkers have prepared various synthetic hydrates of kaolinite by first treating the Kao-DMSO intercalate with ammonium fluoride to exchange some of the interlamellar hydroxyl groups with fluoride and then washing with water (Costanzo and Giese, 1985, 1990; Costanzo *et al.*, 1984; Costanzo *et al.*, 1982). They succeeded in forming both 8.4 Å and 8.6 Å monohydrates of kaolinite as well as two types of 10 Å dihydrates. The stable 8.4 Å hydrate could only be formed if 20% or more of the surface hydroxyls could be replaced with fluorine. The water molecule in the 8.4 Å hydrate was found to be keyed into the silicate sheet and was termed “hole water.” Water in the 10 Å hydrate was found in both the “hole” environment and the more weakly bound “associated” environment.

In the course of our work involving the relationship between two ethylene glycol organokaolinite phases (Kao-EG 9.4 Å and Kao-EG 10.8 Å) (Tunney and Detellier, 1994), a stable 8.4 Å hydrate of kaolinite was prepared without first replacing some of the interlamellar hydroxyl groups with fluorine. This was then characterized by XRD, FTIR and TGA/DSC.

### EXPERIMENTAL

#### Instrumentation

KGa-1 well crystallized kaolinite was used for all experiments. XRD measurements were done on a Phil-

ips PW 3710 based diffractometer using  $\text{CuK}\alpha$  radiation. Samples were mounted on glass slides by either applying the dry powder onto a vaseline coated slide, or by dispersing the clay in an appropriate solvent (water or methanol) and allowing the dispersion to dry on the glass slide. IR measurements were done using the KBr pellet technique. The TGA-DSC measurements were done on a Polymer Labs STA 1500H using a nitrogen flow rate of 85 cc/min and a heating rate of 20°C per minute.

#### Preparation of Kao-EG 10.8 Å

1 g of Kao : DMSO (intercalation ratio greater than 95%) was mixed with 1 ml reagent grade ethylene glycol in a 2 ml glass ampoule and then sealed. The ampoule was then placed in an oven and maintained at 140–190°C for three days. This was then opened up, filtered and washed with methanol, followed by air drying for four hours, yielding a white powder. Powder XRD (Figure 1b) and IR (Figure 2b) showed that significant modification had been achieved when compared to the starting KGa-1 kaolinite (Figures 1a and 2a), and a 10.8 Å ethylene glycol intercalated phase had been obtained. The extent of modification as judged by the relative  $d_{001}$  intensities of the modified ( $d = 10.8$  Å) and unmodified ( $d = 7.2$  Å) was 95%. The material was well-ordered since the  $d_{00n}$  ( $n = 1-6$ ) basal reflections could be assigned. The FTIR spectra showed significant modification of the O-H stretching region of kaolinite as well as C-H vibrations due to the intercalated ethylene glycol molecules.

#### Preparation of hydrated kaolinite

100 mg of the Kao-EG 10.8 Å sample was washed with 10 ml water by mixing together and allowing the suspension to stand for three days. The supernatant liquid was then drawn off with a pipette and the remaining sediment was allowed to dry on two glass XRD slides. An XRD pattern ( $2-70^\circ 2\theta$ ) was measured

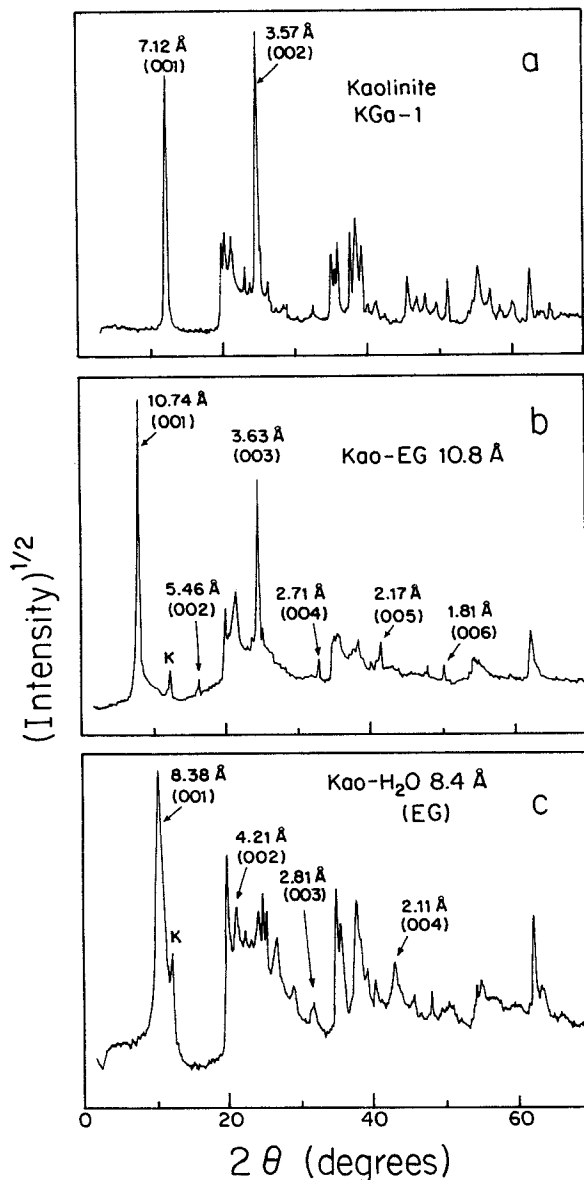


Figure 1. XRD pattern ( $2^\circ$ – $70^\circ 2\theta$ ) of: (a) Kaolinite KGa-1 starting material; (b) Kao-EG 10.8 Å before water washing; (c) Kao- $\text{H}_2\text{O}$  8.4 Å (EG). (K =  $d_{001}$  peak due to residual kaolinite.)

after drying for three hours under ambient conditions (Figure 1c). In addition, the IR spectra ( $2800$ – $3800\text{ cm}^{-1}$ ) of the water washed sample taken two consecutive times are shown in Figures 2c and 2d.

#### RESULTS AND DISCUSSION

Upon water washing of Kao-EG 10.8 Å, the structure collapsed to form an 8.4 Å hydrate of kaolinite [Kao- $\text{H}_2\text{O}$  8.4 Å (EG)]. This can be observed in Figure 1c, where the  $d_{001}$  peak of Kao-EG 10.8 Å (Figure 1b) is

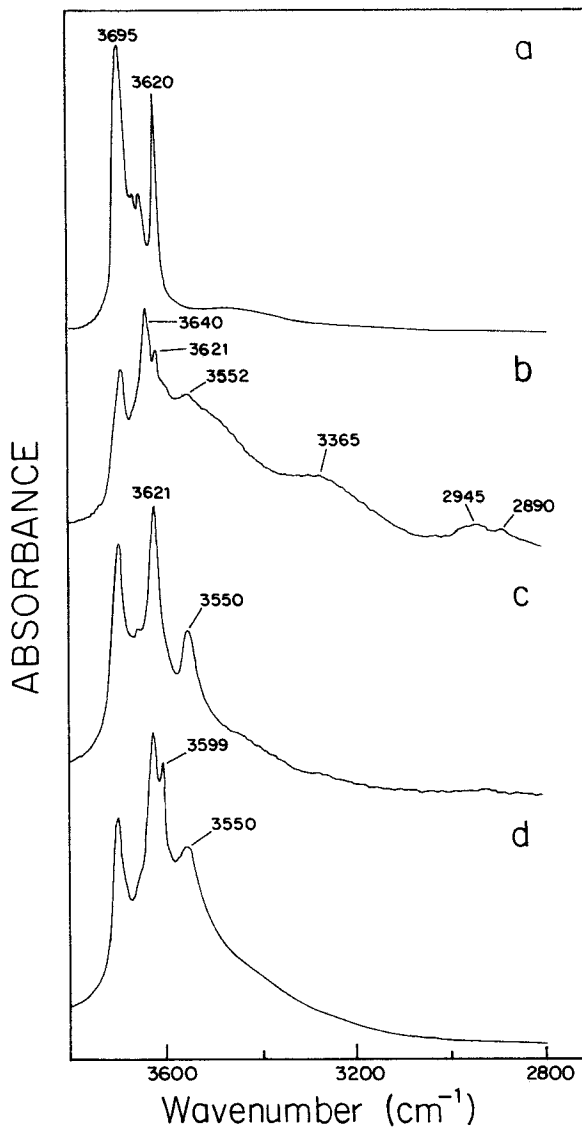


Figure 2. Infrared spectra ( $2800$ – $3800\text{ cm}^{-1}$ ) of: (a) Kaolinite KGa-1; (b) Kao-EG 10.8 Å; (c, d) Kao- $\text{H}_2\text{O}$  8.4 Å (EG) (FTIR spectra of two samples taken from the same bulk product).

replaced by an asymmetric peak at  $d = 8.38\text{ Å}$ . In all cases the peak at  $d = 7.12\text{ Å}$  due to the unexpanded kaolinite remains unchanged. The 8.4 Å hydrated phase was quite stable since even after one day standing in the air, it was found that decomposition of the hydrate had not occurred and the XRD pattern remained unchanged.

The XRD pattern ( $2$ – $70^\circ 2\theta$ ) showed that the 8.4 Å hydrate was the principal phase with an intercalation ratio of 86% based on the relative intensities of the  $d_{001}$  peaks of the hydrated ( $d = 8.38\text{ Å}$ ) and dehydrated ( $d = 7.12\text{ Å}$ ) kaolinite. Reflections corresponding to what

are likely the  $d_{002}$ ,  $d_{003}$  and  $d_{004}$  peaks of 8.4 Å hydrate were also observed. The relative broadness of these peaks suggest that this 8.4 Å hydrate is not as ordered as the 8.4 Å partially fluorinated hydrate of kaolinite [Kao(F)-H<sub>2</sub>O 8.4 Å] (Costanzo and Giese, 1990). In addition, the intensities of the peaks generated by the Kao(F)-H<sub>2</sub>O 8.4 Å appear to be significantly different from those seen for Kao-H<sub>2</sub>O 8.4 Å (EG) hydrate (Figure 1c), suggesting that some structural differences exist between the two types of 8.4 Å hydrate.

TGA/DSC results showed a slow, weakly endothermic 4% weight loss due to the loss of interlayer water and possibly residual ethylene glycol beginning immediately upon heating and finally reaching a plateau near 300°C ( $T_{\text{ons}} = 78^\circ\text{C}$ ,  $T_{\text{peak}} = 150^\circ\text{C}$ ). There was another much more dramatic endothermic weight loss of 13% between 400 and 600°C due to the kaolinite-metakaolinite transition ( $T_{\text{ons}} = 480^\circ\text{C}$ ,  $T_{\text{peak}} = 526^\circ\text{C}$ ). Finally there was an exothermic transition between 980 and 1030°C ( $T_{\text{ons}} = 998^\circ\text{C}$ ,  $T_{\text{peak}} = 1009^\circ\text{C}$ ) which corresponds to a structural reorganization of metakaolinite. There was no associated weight loss for this last thermal event.

If one assumes that only water occupies the interlayer spaces, and that all the interlayer water was lost in the first endothermic transition, one finds that there is 0.60 water molecule per Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> unit. This is slightly less than the 0.78 water molecule per Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> unit that Wada found for the 8.4 Å hydrate of nacrite (Wada, 1965).

The IR spectra of the O-H and C-H stretching region of the Kao-EG 10.8 Å phase both before and after water washing supported the XRD results that an ordered hydrate had been formed. Figure 2a shows the characteristic O-H stretching region of well-crystallized kaolinite KGa-1. Upon formation of Kao-EG 10.8 Å one observes the pattern shown in Figure 2b. The O-H stretching pattern has changed due to intercalation of ethylene glycol, and an ill defined C-H stretching pattern due to the intercalated ethylene glycol units appears. Upon washing with water, one sees the appearance of an O-H stretching band at 3550 cm<sup>-1</sup> (Figures 2c and 2d), as well as the water deformation vibration at 1655 cm<sup>-1</sup> (not shown). In some instances, a sharp peak at 3599 cm<sup>-1</sup> is also observed for Kao-H<sub>2</sub>O 8.4 Å (EG) (Figure 2d). The difference between the spectra in Figures 2c and 2d could plausibly be due to some heterogeneity in the bulk sample. This inhomogeneity could not be detected by XRD analysis, which showed that different samples taken from the bulk material yielded nearly identical XRD patterns, showing as the principal phase Kao-H<sub>2</sub>O 8.4 Å (EG).

The IR spectra of Kao-H<sub>2</sub>O 8.4 Å (EG) (Figures 2c and 2d) appeared very different than the IR spectra shown for Kao(F)-H<sub>2</sub>O 8.4 Å (Costanzo and Giese, 1990). Costanzo and Giese found that the O-H stretching band at 3620 cm<sup>-1</sup> due to the inner O-H of kaolinite

was red-shifted to 3612 cm<sup>-1</sup> for their Kao(F)-H<sub>2</sub>O 8.4 Å. They also observed a moderately intense band at 3655 cm<sup>-1</sup> and a sharp peak due to the deformation vibration of water at 1580 cm<sup>-1</sup>. These bands were not observed for the 8.4 Å hydrate formed from Kao-EG 10.8 Å. This supports the XRD data in showing that there are significant differences between these two types of 8.4 Å hydrates. This appears to relate to differences in their interlayer bonding schemes, as exhibited by their different infrared spectra.

The local environment of the intercalated water in Kao-H<sub>2</sub>O 8.4 Å (EG) may resemble more closely that of the 8.4 Å hydrate of nacrite (Wada, 1965), where in both cases fairly sharp absorptions at 1655 cm<sup>-1</sup> due to the deformation of water molecules could be observed. In contrast, the deformation band of water adsorbed on the external surface of kaolinite is normally at 1630 cm<sup>-1</sup>. Wada noted that for water dissolved in various solvents, "its deformation band shifts progressively upward as the base strength of the solvent increases."

This absorption band appeared much sharper when the O-H stretching band at 3599 cm<sup>-1</sup> could not be observed as was the case in Figure 2c. When the band at 3599 cm<sup>-1</sup> could be observed (Figure 2d), the H-O-H deformation band was much broader and slightly lower in energy (1647 cm<sup>-1</sup>). Also associated with the appearance of this 3599 cm<sup>-1</sup> band was a sharp band at 968 cm<sup>-1</sup> in place of the band at 940 cm<sup>-1</sup> normally attributed to the Al-O-H deformation of the inner surface hydroxyl groups of kaolinite (Farmer, 1974). Wada (1965) noticed also a shift from 935 cm<sup>-1</sup> to 970 cm<sup>-1</sup> upon going from nacrite to the 8.4 Å hydrated nacrite. This would seem to indicate strong interaction between intercalated water and the aluminate surface of kaolinite. In contrast, the Al-O-H deformation due to the inner O-H group of kaolinite (914 cm<sup>-1</sup>) regardless of the presence (Figure 2d) or absence (Figure 2c) of a band at 3599 cm<sup>-1</sup> was perturbed only very slightly to 910 cm<sup>-1</sup>.

## CONCLUSION

An 8.4 Å hydrate of kaolinite was prepared by first preparing a 10.8 Å ethylene glycol intercalated kaolinite from Kao-DMSO and then washing this with water. The product exhibited well defined IR and XRD patterns. This material began decomposition upon heating but the interlayer water was not fully removed until above 200°C.

## ACKNOWLEDGMENTS

The Natural Sciences and Research Council of Canada is gratefully acknowledged for its financial support.

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(Received 12 January 1994; accepted 3 May 1993; Ms. 2453)