

MECHANISM OF SYNTHESIS OF 10-Å HYDRATED KAOLINITE

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Abstract—The synthesis of 10-Å hydrated kaolinite was accomplished by: (1) direct reaction of HF with a dimethyl sulfoxide (DMSO)-kaolinite intercalate and water washing; (2) methanol washing of a DMSO-kaolinite intercalate followed by reaction with any alkali fluoride salt and water washing; and (3) room-temperature (RT) water-washing of a methanol-washed DMSO-kaolinite intercalate. In all syntheses the optimum yield required a kaolinite in which DMSO was bound strongly to the interlayer surface. In the first synthesis, water inclusion between clay layers appeared to be facilitated by the reduction of cohesive interlayer forces brought about by replacement of surface and edge OH⁻ by F⁻. The fluorination reaction was accomplished either by direct reaction of HF or by HF produced through the hydrolysis of NH₄F at 60°C. In the second synthesis, intercalated DMSO was replaced by methanol. F⁻ solvated readily in methanol but not in DMSO. Consequently, F⁻ produced through hydrolysis of the alkali fluoride salt entered the interlayer space and contributed to the fluorination reaction. Furthermore, the diffusion of methanol out of the interlayer space during the RT-washing step was slowed by F⁻ solvation which aided the exchange of methanol for water. High yields of 10-Å kaolinite hydrate were obtained irrespective of choice of alkali fluoride salt. The third synthesis was dependent on matching the diffusion of methanol out of the interlayer space with diffusion of water into this space. At room temperature the diffusion rates were close enough to maintain the clay in the expanded state throughout the hydration process, and high yields of 10-Å kaolinite hydrate were obtained. At 60°C the diffusion rates were too dissimilar, and very low yields of hydrate were obtained.

Key Words—Dimethyl sulfoxide, Fluoride salt, Hydrate, Kaolinite, Methanol, Synthesis, X-ray powder diffraction.

INTRODUCTION

In 1980, Costanzo *et al.* reported the laboratory synthesis of a 10-Å hydrate of a well-crystallized kaolinite. In their synthesis, prior to water intercalation, the kaolinite layers were expanded with an organic solvent, dimethyl sulfoxide (DMSO), followed by treatment with ammonium fluoride salt at a temperature above ambient. The room-temperature water washing of this final product resulted in a 10-Å hydrate. In a later investigation (Costanzo *et al.*, 1982), the DMSO-kaolinite complex was washed with methanol prior to treatment with ammonium fluoride solution, and a quasi-stable kaolinite dihydrate free of interparticle water (pore water) was obtained. The dihydrate was stable for an indefinite period of time at a temperature below about 10°C, but at ambient temperature the material underwent spontaneous dehydration unless it was left in contact with water. The dehydration product resulting from air drying at room temperature was a stable 8.6-Å monohydrate.

In reporting their synthesis technique Costanzo *et al.* (1980, 1982, 1984a) noted that: (1) ammonia gas was given off during the reaction; (2) treatment with fluoride salts other than NH₄F yielded very little, or

no hydrated kaolinite; (3) indirect evidence existed that the reaction led to replacement of some kaolinite inner-surface and edge hydroxyls by fluoride ions; (4) the yield of hydrated kaolinite depended on the nature of the kaolinite starting material; and (5) the yield of hydrated kaolinite increased when the DMSO-kaolinite complex was washed with methanol prior to the ammonium fluoride treatment.

The observations listed above are consistent with the following fluorination reaction based on the hydrolysis of ammonium fluoride and loss of ammonia gas:



The evolution of ammonia gas drives the reaction towards the production of HF. The HF species penetrates the interlayer and reacts with interlayer surface hydroxyls, resulting in surface exchange of F⁻ for OH⁻.

These considerations raised a number of questions which are the subject of the present investigation: (1) why was the synthesis yield dependent on choice of starting kaolinite material? (2) what was the role of methanol washing in the synthesis? (3) is it possible to achieve fluorination by a direct reaction with HF or a buffered NaF-HCl solution? (4) why was fluorination not effective with fluoride salts other than the ammonium salt, and do experimental conditions exist

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Table 1. Yield of 10-Å kaolinite hydrate for different starting materials.¹

Kaolinite in kaolinite-DMSO complex ²	Amount of NH ₄ F salt (g)	Reaction time (hr)	Yield of 10-Å hydrate (%)
RLO2125	1.3	5	34
		20	43
	2.3	8	55
		20	59
		36	54
KGa-1	1.3	10	75
KGa-2	1.3	8	<10

¹ 3 g of clay in 60 ml H₂O was used in each synthesis.

² RLO2125 = kaolinite, Cornwall china clay; KGa-1, KGa-2, well-crystallized and poorly crystallized kaolinite, Georgia, respectively.

which permit fluorination with other fluoride salts? The result of experiments designed to answer these questions led to a synthesis procedure which eliminated the fluorination step entirely.

EXPERIMENTAL

The dependence of the yield of hydrated kaolinite on starting material was studied using three different materials: (1) Cornwall china clay (RLO2125) from English China Clays, St. Austell; (2) a well-crystallized Georgia kaolinite (KGa-1); and (3) a poorly crystallized Georgia kaolinite (KGa-2), both from the Source Clays Repository of The Clay Minerals Society. All other experiments were carried out on sample KGa-1, the

Table 2. Yield of kaolinite hydrate from methanol-washed DMSO-KGa-1 and DMSO-RLO2125 complexes.¹

Number of methanol-wash treatments	Reaction time (hr)	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
DMSO-KGa-1 complex			
1	14	89	80
	24	84	80
	36	83	78
3	10	95	88
	26	93	88
	40	89	85
9	10	95	90
	22	95	90
15	10	—	—
DMSO-RLO2125 complex			
1	8	<10	<10
3	8	<10	<10

¹ In each methanol wash the 3-g sample of the DMSO-kaolinite complex was treated with 30 ml of methanol. In the fluorination reaction, 1.3 g of NH₄F was reacted with the 3-g sample at 60°C. The 8.6-Å hydrate was the product resulting from room temperature air drying of the 10-Å hydrate.

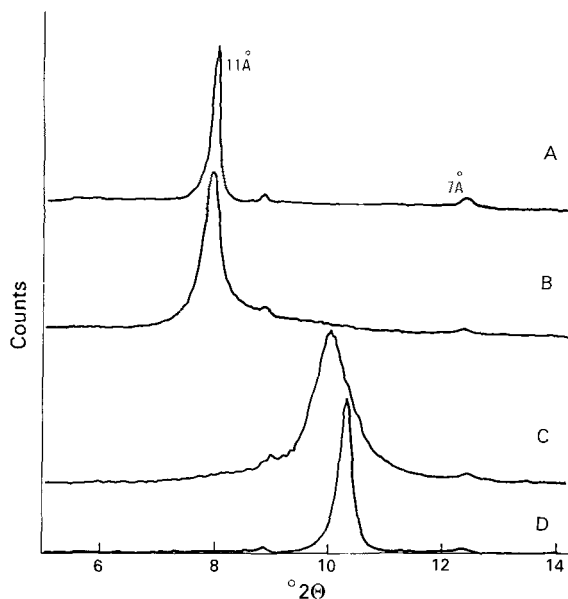


Figure 1. X-ray powder diffractograms of the DMSO-RLO2125 kaolinite complex showing interstratification and eventual layer collapse caused by methanol washing. (A) DMSO-RLO2125 complex; (B), (C), and (D) DMSO-RLO2125 complexes after 3, 6, and 9 methanol washings, respectively.

starting material which gave the highest yield of hydrate. Kaolinite particles <2 μm in size were collected from 1% suspensions in water. They were washed repeatedly with deionized water to remove any soluble impurities and finally freeze dried. All subsequent experiments were performed with these purified kaolinites. X-ray diffraction (XRD) measurements were carried out using a Philips 3100 automated X-ray diffractometer, with CuKα radiation. Wet samples, prepared by smearing a water-wet thick clay slurry on a glass plate, were scanned from 5° to 20° at 0.02°/2θ step/sec. Hydrate yields were estimated by comparing the integrated intensities of the 7-Å and 10-Å d(001) peaks (or the 7-Å and 8.6-Å d(001) peaks for the yield of room-temperature, air-dried hydrate product). Infrared (IR) spectra of hydrate samples prepared as Fluorolube mulls or as sedimented thin films were obtained with a Pye-Unican 3-300 ratio-recording spectrometer. A 1-mm thick disc of optically polished polycrystalline silicon was used as a substrate.

All kaolinites used in the synthesis of kaolinite hydrate were first intercalated with DMSO. The intercalated kaolinite product will be referred to here as the DMSO-kaolinite complex. Typically, a suspension of 12 g of kaolinite in 400 ml of DMSO (containing 9% water by volume to accelerate intercalation) (Olejnik *et al.*, 1968) was stirred at room temperature (RT). Periodic measurements of the 001 reflection showed that at room temperature a minimum of 200 hr was

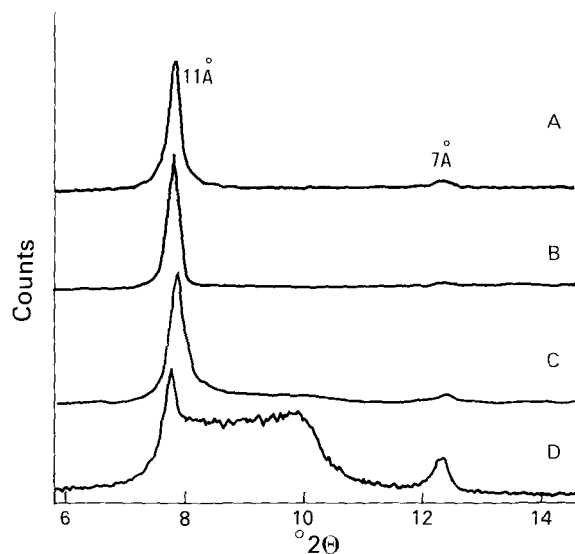


Figure 2. X-ray powder diffractograms of the DMSO-KGa-1 kaolinite complex showing interstratification caused by methanol washing. (A) DMSO-KGa-1 complex; (B), (C), and (D) DMSO-KGa-1 complexes after 3, 6, and 9 methanol washings, respectively.

required for a nearly complete (>95%) intercalation of DMSO into the layers of kaolinite. The rate of DMSO intercalation was increased when the reaction temperature was raised to 60°C; however, all work was carried out at room temperature to avoid the possibility of the oxidative degradation of DMSO. The DMSO-intercalated kaolinites were collected by centrifugation (11,000 rpm), and excess DMSO was discarded. XRD showed a strong, sharp 001 reflection at 11.14 Å.

RESULTS AND DISCUSSION

Table 1 summarizes the dependence of the yield of kaolinite hydrate product on the choice of starting material and the time duration of the reaction of NH_4F with the DMSO-kaolinite complex. All reactions were carried out at 60°C without methanol washing of the DMSO-kaolinite complex. In Table 2 the yields for syntheses carried out at 60°C on methanol-washed DMSO-kaolinite complex are compared for the KGa-1 and RLO2125 starting materials. Three grams of DMSO-kaolinite complex in 60 ml of H_2O was used in each synthesis.

From the data in Tables 1 and 2 the synthesis yield appears to be dependent on the choice of kaolinite starting material. The key factor which distinguishes the three starting materials is crystallinity. Optimum yield was achieved for sample KGa-1, a well-crystallized kaolinite (Hinckley index = 1.0) which is not, however, as well crystallized as sample RLO2125 (Hinckley index = 1.45). Differences in synthesis yield were found to correlate with strengths of bonding of

Table 3. Yield of kaolinite hydrate from the methanol-washed DMSO-KGa-1 complex reacted with different salts.¹

Salt	Temperature (°C)	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
NH_4F	60	95	88
NaF	60	98	95
KF	60	90	85
RbF	60	95	86
CsF	60	92	81
NH_4Cl	60	0	0
NaF	25	98	95
NH_4Cl	25	92	82

¹ 9 methanol wash treatments. The 8.6-Å hydrate was the product resulting from room temperature air drying of the 10-Å hydrate.

DMSO to the clay interlayer surface. DMSO was less strongly bound to samples RLO2125 and KGa-2 than to sample KGa-1. XRD observations indicated that after three washings with methanol, significant interstratification could be noted in the DMSO-RLO2125 complex (Figure 1), whereas the interlayer spacing of the DMSO-KGa-1 complex remained at 11.14 Å after the same treatment (Figure 2). Continued washing with methanol gave rise to the total loss of the 11.14-Å phase in the DMSO-RLO2125 complex, but only produced interstratification in the DMSO-KGa-1 complex (Figures 1 and 2). The connection between the bonding strength of DMSO to the clay surface and the hydrate product yield is clarified below.

The data of Table 1 indicate that the hydrate yield was a function of NH_4F concentration and reaction time. The optimum combination provided a controlled concentration of HF over time which avoided clay dissolution by HF attack of the clay surface. Other authors have argued that the exchange of hydroxyl by fluoride at the edges and on the interlayer surface of the kaolinite reduces the cohesive interlayer-surface force (Wolfe and Giese, 1978; Costanzo *et al.*, 1980, 1984b) and thus facilitates water inclusion between the layers.

The synthesis yields shown in Table 2 confirm the observation of Costanzo *et al.* (1982) that methanol washing of the DMSO-KGa-1 complex prior to the ammonium fluoride reaction markedly increased the yield of hydrate; however, a comparison of Tables 1 and 2 also shows that the yield of hydrate from the DMSO-RLO2125 complex was greatly reduced by the methanol washing. In Table 3 the yields of kaolinite hydrate are given for the methanol-washed DMSO-KGa-1 complex reacted with a number of different fluoride salts. These high yields contrast with the observation (in the absence of methanol washing) of Costanzo *et al.* (1984a) that only NH_4F was effective in the synthesis of kaolinite hydrate from the DMSO-KGa-1 complex.

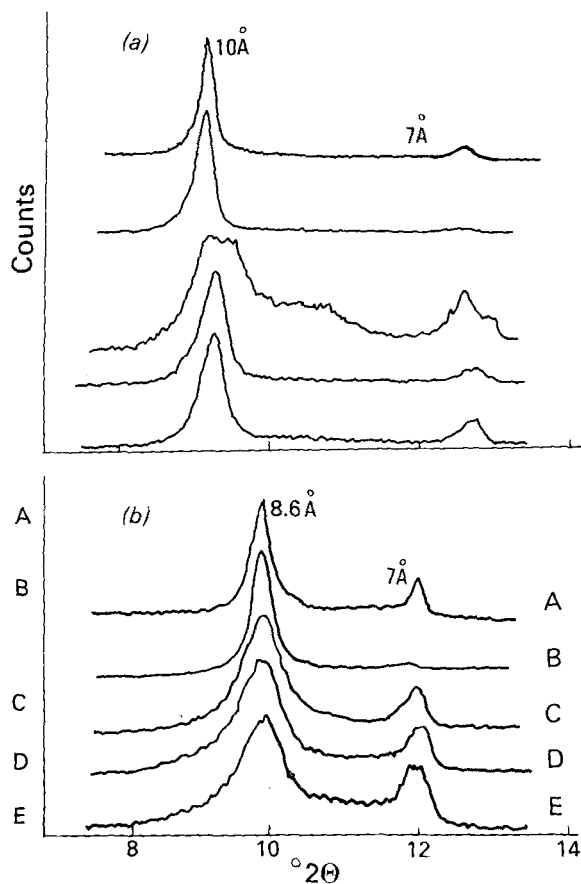


Figure 3. X-ray powder diffractograms of 10-Å and 8.6-Å hydrates produced from syntheses using fluoride salts. (a) 10-Å hydrate; (b) product of 10-Å hydrate after air drying at room temperature. (A) NH_4F ; (B) NaF ; (C) KF ; (D) RbF ; (E) CsF .

The data presented in Tables 1 and 2 suggest that the dominant factors controlling the yield of kaolinite hydrate were the strength of bonding of the DMSO to the interlayer surface and the extent to which the expanded interlayer spacing was preserved when methanol replaced DMSO in the interlayer space and water replaced methanol at room temperature.

Hydrogen bonding of DMSO to the clay interlayer surface, which was strongest in the DMSO-KGa-1 complex, led to considerable stacking disorder which was predominantly due to $b/3$ shifts of the layers (see Barrios *et al.*, 1977). This disorder apparently exposed additional edge hydroxyls to fluoride ion replacement (Costanzo *et al.*, 1984a). Thus, the most effective reduction of the interlayer cohesive force due to hydroxyl-fluoride ion replacement (Wolfe and Giese, 1978) was expected to occur in this intercalate. This, in turn, should have facilitated water intercalation and an increased yield of hydrate, relative to that obtained with the DMSO-RLO2125 and DMSO-KGa-2 com-

Table 4. Yield of 10-Å and 8.6-Å kaolinite hydrates by direct reaction of 3 g of the DMSO-KGa-1 complex with HF (0.16 g of 49% HF) or 0.1 g NaF and 0.112 g HCl.

Reactants	Reaction temperature (°C)	Reaction time (hr)	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
HF	60	6	92	0
HF	25	6	92	0
NaF + HCl	60	6	76	0

plexes. Furthermore, strong attachment of DMSO to the interface surface led to a slower rate of diffusion of DMSO out of the interlayer space during water washing at room temperature, which reduced the probability of layer collapse and favored a high yield of hydrate.

Methanol washing removed most of the intercalated DMSO as indicated by the XRD and IR observations. Provided the clay remained expanded after the methanol washings, high yields of hydrate were obtained as shown in Table 2 for the DMSO-KGa-1 complex. The extent to which the clay remained expanded depended on the ease with which DMSO was replaced in the interlayer space by methanol through a diffusive process. In the DMSO-RLO2125 complex, the DMSO was largely mobile inasmuch as it was not strongly bound to the clay surface, and some layer collapse occurred during the diffusive replacement of DMSO by methanol. This factor contributed to the low yield of hydrate for the DMSO-RLO2125 complex shown in Table 2.

The removal of intercalated DMSO by methanol washing of the DMSO-KGa-1 complex resulted in an increased concentration of F^- in the interlayer space, a consequence of the fact that small "hard" ions, such as F^- , do not solvate well in dipolar aprotic solvents such as DMSO (Martin, 1975). The increased F^- concentration could have led to increased hydrate yield in two ways: (1) the F^- could have participated in the

Table 5. Yield of kaolinite hydrate by direct reaction of 3 g of methanol-washed DMSO-KGa-1 complex with HF (0.16 g of 49% HF) or with 0.1 g NaF and 0.112 g HCl.

Reaction time (min)	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
Reaction temperature = 25°C		
5	95	80
10	95	80
15	95	74
30	95	73
60	70	21
360 ¹	84	0
Reaction temperature = 60°C		
180	49	0
360 ¹	15	0

¹ Reaction with 0.1 g NaF + 0.112 g HCl.

Table 6. Yield of kaolinite hydrate from room-temperature (RT) water washing of the methanol-washed DMSO-KGa-1 complex.

Number of methanol-wash treatments	Number of RT-water-wash treatments	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
3	1	93	85
	2	94	88
	3	92	86
6	1	96	90
	2	95	91
	3	95	90
9	1	96	90
	2	95	91
	3	95	88

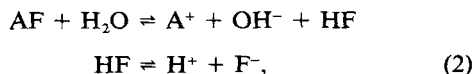
Table 7. Yield of kaolinite hydrate from 60°C-water washing of the methanol-washed DMSO-KGa-1 complex.¹

Number of methanol-wash treatments	Number of 60°C water-wash treatments	Yield of 10-Å hydrate (%)	Yield of 8.6-Å hydrate (%)
3	1	39	27
	2	21	28
	3	10	20
6	1	66	85
	2	32	81
	3	25	78
9	1	55	82
	2	39	81
	3	23	81

¹ Yield of 8.6-Å hydrate expressed as a percentage of 10-Å hydrate yield.

surface OH⁻ exchange reaction, or (2) the diffusion of methanol out of the interlayer space during water washing could have been retarded by the presence of F⁻, thereby favoring less layer collapse and an optimum yield of hydrate. (The diffusion coefficient of a fluid in which ions are solvated is generally lower than that of the solvent fluid itself.)

The yield of HF from the hydrolysis of alkali fluoride salts:



was much lower than from the NH₄F hydrolysis reaction, Eq. (1). Furthermore, the presence of DMSO in the interlayer of the DMSO-kaolinite complex did not allow fluoride ions to penetrate this space in any quantity. Alkali fluoride salts were thus not effective in fluorinating the interlayer surface of DMSO-kaolinite complexes as, indeed, found by Costanzo *et al.* (1984a). Methanol washing, however, allowed fluoride ions access to the interlayer space leading to the high yields of kaolinite hydrate shown in Table 3. XRD patterns of the 10-Å and 8.6-Å hydrates obtained with different alkali fluoride solutions are shown in Figure 3.

The data in Table 4 suggest that the direct reaction of HF with the DMSO-KGa-1 complex provided an effective fluorination step in the synthesis of 10-Å kaolinite hydrate. Careful control of the reaction time was necessary, however, because prolonging the reaction with too high a concentration of HF resulted in clay dissolution. The hydrate produced in these reactions collapsed directly to 7 Å when air dried. The 8.6-Å hydrate did not form, apparently because of an excessive reaction of HF with the silica surface. Because most of the water in the 8.6-Å hydrate consisted of molecules keyed into the ditrigonal holes of the silica surface (Costanzo *et al.*, 1984b), retention of this water was very dependent on the condition of the surface.

Clay dissolution due to excessive HF reaction at 60°C also reduced the yield of 10-Å hydrate. This effect was more evident for the methanol washed DMSO-KGa-1 complex (Table 5) indicating that, indeed, HF is more reactive in methanol solvent than in DMSO.

The data of Table 5 show that by working at room temperature and completing the HF reaction in a short time it was possible to obtain a high yield of 10-Å kaolinite hydrate which collapsed to an 8.6-Å hydrate on air drying. The high yields of the 10-Å and 8.6-Å hydrates obtained from the RT-reaction of NaF, HF, and even of NH₄Cl with the methanol-washed DMSO-KGa-1 complex (Table 3) suggest that the water intercalation reaction at room temperature did not require the prior substitution of interlayer hydroxyls by fluoride ions. This observation prompted a synthesis based on direct washing of methanol washed DMSO-KGa-1 samples with RT-water. The excellent yield obtained from these RT-water reactions are shown in Table 6. By contrast, the poor yields obtained with identical syntheses based on warm water (60°C) are shown in Table 7. The large contrast in yields between RT- and warm-water washing suggests that, at room temperature, the rates of diffusion of water and methanol in the interlayer space were sufficiently close that exchange of water for methanol was possible, with the layer remaining expanded; whereas, at 60°C, the dynamic balance between water diffusing into the interlayer space and methanol diffusing out was not maintained and significant collapse of the expanded layers took place. XRD patterns (Figure 4) illustrate the reduction of interstratification in the product after repeated methanol and RT-water washings. The direct replacement of intercalated DMSO by water, either at room temperature or at 60°C, was not possible (see Figure 5).

No investigation was made of the molecular motions and desorption kinetics of any of the 10-Å hydrates discussed in this paper to determine whether the prop-

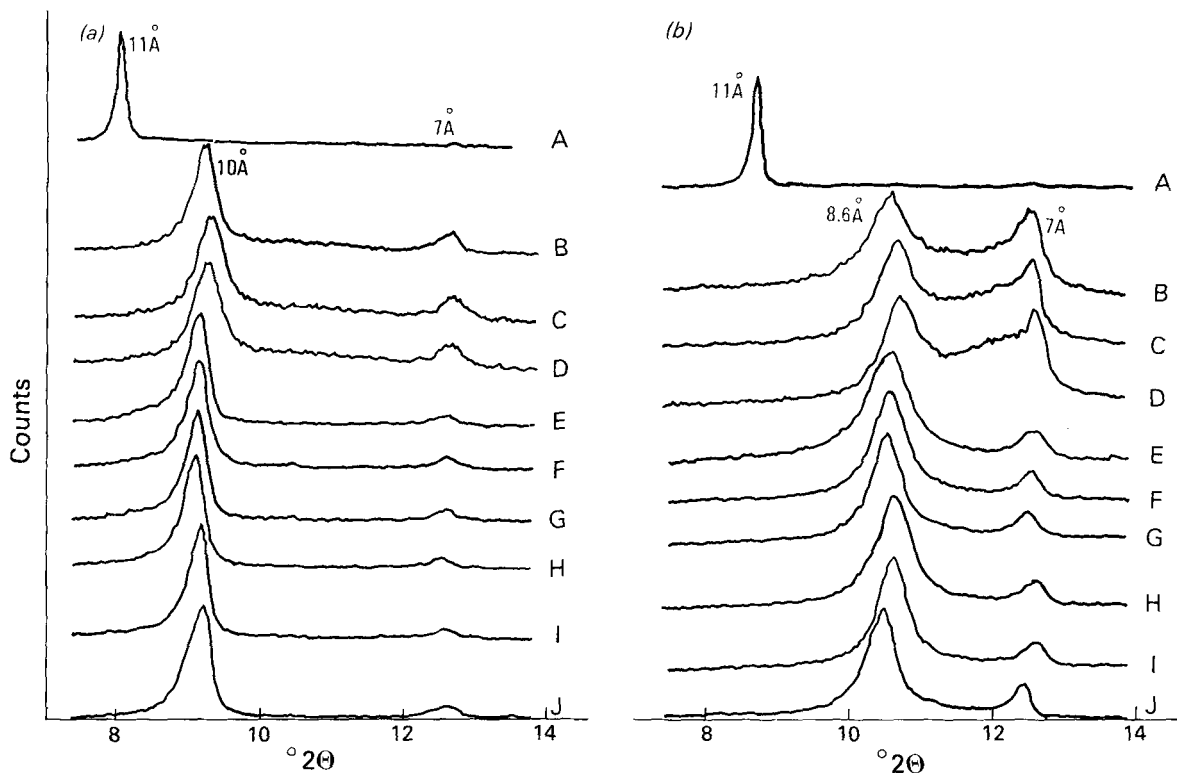


Figure 4. X-ray powder diffractograms of hydrates produced from the methanol-washed DMSO-KGa-1 kaolinite complex and room-temperature (RT) water washing. Reduction in interstratification following repeated methanol and RT-water washings is apparent. (a) before exposure to room temperature air drying; (b) after exposure to room temperature air drying. The number of methanol and RT-water washings, respectively, are (A) 0:0; (B) 3:1; (C) 3:2; (D) 3:3; (E) 6:1; (F) 6:2; (G) 6:3; (H) 9:1; (I) 9:2; (J) 9:3.

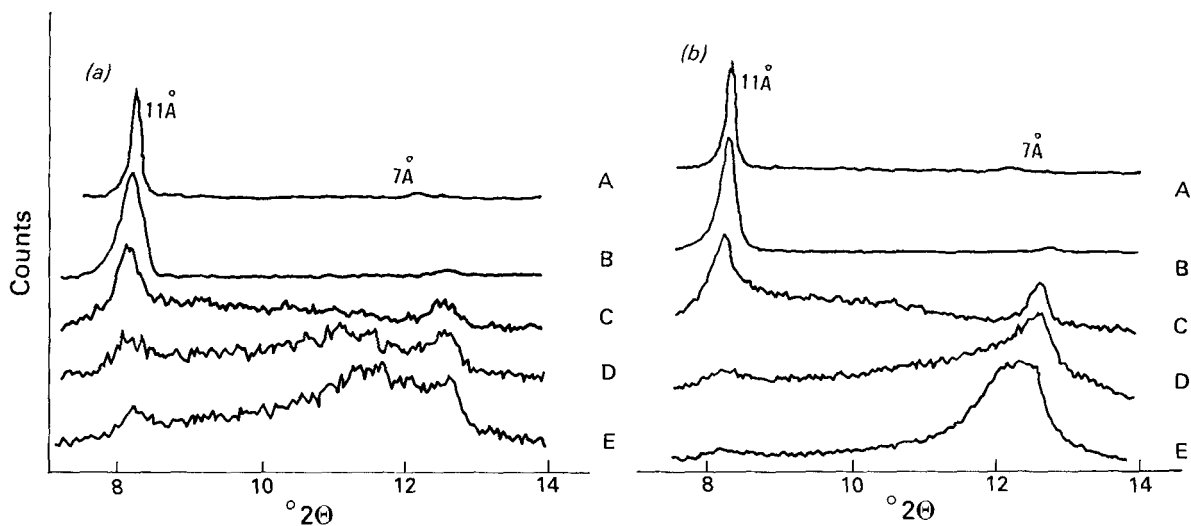


Figure 5. X-ray powder diffractograms of the DMSO-KGa-1 kaolinite complex after repeated washings with (a) room temperature and (b) warm water. No yield of hydrate was obtained in either experiment. The number of water washings respectively, are: (A) 0; (B) 1; (C) 2; (D) 3; (E) 5.

erties of the intercalated water were identical to those of the 10-Å hydrate of Costanzo *et al.* (1982). Thus, it is not known whether there was any difference in the binding of the water to the interlayer surface or whether the hydrates were free of pore water. Similarly, it is not known whether differences exist between the 8.6-Å products of RT-air drying of the 10-Å hydrates in the present investigation; however, the IR spectra of the 10-Å and 8.6-Å hydrates reported here appear to be identical with the spectra of the corresponding hydrates reported by Costanzo *et al.* (1982, 1984b).

CONCLUSIONS

The synthesis of 10-Å kaolinite hydrate from DMSO-kaolinite intercalates by means of a fluorination reaction using ammonium fluoride (Costanzo *et al.*, 1980, 1982, 1984) was based on the idea that the interlayer bonding is weakened by exchange of interlayer hydroxyls with fluoride ions (Wolfe and Giese, 1978); in particular, that fluorination at crystallite edges reduced the possibility of collapse being initiated at the edges. A second, equally important consideration for a successful synthesis is that water be able to diffuse into the expanded interlayer space at a rate which is roughly comparable with diffusion of the reactants out of this space.

The effectiveness of the fluorination process, as judged by the yield of hydrate, was very dependent on the strength of bonding of DMSO to the clay interlayer surface. It appears that strong binding of DMSO to the surface caused stacking disorder, which increased the number of edge hydroxyls exposed to fluoride ion replacement. Layer collapse during replacement of DMSO by water was also reduced as a result of slower diffusion of DMSO out of the interlayer. In the absence of methanol washing of DMSO-kaolinite, only the ammonium fluoride hydrolysis reaction was effective. Methanol washing allowed the alkali fluoride hydrolysis reaction to be effective because it permitted higher F^- concentrations in the interlayer. Methanol washing was only effective, however, when DMSO was strongly bound to the clay interlayer surface; otherwise, the washing led to appreciable layer collapse.

The fluorination reaction was also carried out by direct treatment with HF. In this treatment, however, reaction conditions had to be very carefully controlled to prevent excessive reaction of HF with the silica surface.

The synthesis of 10-Å kaolinite hydrate from a DMSO-kaolinite complex was achieved by direct RT-water washing of methanol-washed intercalate. Yields were comparable to those obtained by a fluorination reaction and the 10-Å product air-dried at room temperature to an 8.6-Å product. Hot-water washing (60°C) of methanol-washed intercalate gave low yields of the 10-Å hydrate. The difference in yields is most readily explained in terms of relative rates of diffusion. At room temperature, the rates of diffusion of water and methanol in the interlayer space were, presumably, sufficiently well matched that water replaced methanol without collapse of expanded layers. At 60°C, the mismatch in rates of diffusion led to layer collapse and a much reduced yield of hydrate.

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REFERENCES

- Barrios, J., Plancon, A., Cruz, M. I., and Tchoubar, C. (1977) Qualitative and quantitative study of stacking faults in a hydrazine treated kaolinite-relationship with the infrared spectra: *Clays & Clay Minerals* **25**, 422-429.
- Costanzo, P. M., Clemency, C. V., and Giese, R. F., Jr. (1980) Low temperature synthesis of a 10-Å hydrate of kaolinite using dimethyl sulfoxide and ammonium fluoride: *Clays & Clay Minerals* **28**, 155-156.
- Costanzo, P. M., Giese, R. F., Jr., Lipsicas, M., and Straley, C. (1982) Synthesis of a quasi-stable kaolinite and heat capacity of interlayer water: *Nature* **296**, 549-551.
- Costanzo, P. M., Giese, R. F., Jr., and Clemency, C. V. (1984a) Synthesis of a 10-Å hydrated kaolinite: *Clays & Clay Minerals* **32**, 29-35.
- Costanzo, P. M., Giese, R. F., Jr., and Lipsicas, M. (1984b) Static and dynamic structure of water in hydrated kaolinites: I. The static structure: *Clays & Clay Minerals* **32**, 419-428.
- Martin, D. (1975) Solvation and association in DMSO: in *Dimethyl Sulfoxide*, D. Martin, H. G. Hauthal, and E. S. Halberstadt, eds., Van Nostrand-Reinhold, Wokingham, United Kingdom, 500 pp.
- Olejnik, S., Aylmore, L. A. G., Posner, A. M., and Quirk, J. P. (1968) Infrared spectra of kaolin mineral-dimethyl sulphoxide complexes: *J. Phys. Chem.* **72**, 241-249.
- Wolfe, R. and Giese, R. F., Jr. (1978) The stability of fluorine analogs of kaolinite: *Clays & Clay Minerals* **26**, 76-78.

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