PREPARATION OF STABLE SUSPENSIONS OF DELAMINATED KAOLINITE BY COMBINED DIMETHYLSULFOXIDE-AMMONIUM FLUORIDE TREATMENT

The separation of kaolinite crystallites into their layer components involves two problems, namely, overcoming the bonding energy which holds these layers together, and imparting the latter with a new surface potential that prevents their reunion, once they are separated. To chemical this author's knowledge, the separation of kaolinite into its lamellae to form a stable suspension has never been reported. It is the purpose of the present note to demonstrate experimentally (1) the dissociation of kaolinite crystallites into their lamellar components, and (2) the formation of stable suspensions by such lamellae.

The key to the successful delamination of a kaolinite crystallite into its isolated layers is the initial use of an intercalating agent, which opens up the crystallite and decreases the cohesion energy. Additional steps are then needed to continue this separation and bring about a complete removal of the lamellae from each other, as is shown below.

Intercalation of molecules by kaolinite has been studied quite intensively during recent decades, and the list of intercalated species includes organic as well as water molecules (for review of early works, see Theng, 1974; more recent works include Constanzo *et al.,* 1984; Sugahara *et al.,* 1988) and ionic species (Yariv, 1986).

Consider the intercalation reaction of dimethylsulfoxide (DMSO), with kaolinite. According to Cruz *et al.* (1973), the hydrogen bonds between the DMSO and the kaolinite internal hydroxyls are stronger than the initial hydrogen bonds. Due to the high dielectric constant of the DMSO (compared to that of the crystal lattice), a chemical driving force causes the intercalation of the DMSO molecules (presumably starting at the crystal edges; see also Giese, 1978), followed by diffusion of the intercalated molecules into the interlayer zones. As the distance between the unit layers increases, the energy needed to bring about a complete separation of two adjacent layers to a distance of zero attraction is now lower than before the intercalation.

To reduce the attraction energy between the unit layers further, some of the hydroxyls can be exchanged by fluoride (Giese, 1973; Constanzo *et al.,* 1984). The presence of DMSO attached to the layer surfaces gives them a new surface potential, which causes them to repel each other; once they are separated, their re-as-

sociation will be prevented or hindered, and a stable suspension will be formed.

EXPERIMENTAL

Fisher colloidal kaolinite (NF) powder was used in all experiments. Three replicates of the air-dried clay, each of 6.0 g, were immersed in DMSO : water (9:1 v/v) solutions for several days at room temperature and then treated with ammonium fluoride at 60°C, following Constanzo *et al.* (1984), for various periods of time. Excess NH_4F was removed by centrifugation, washing four times with DMSO : water solution. The clay was never dried during this procedure; the resulting yellowish-brown suspension became stable as the NH_4F was washed out.

To study the effects of both duration of the NH_4F-DMSO treatment and removal of soluble species from suspension, reaction periods of as much as 50 days and as many as 17 short (1.5 hr) cycles of DMSO-NH_4F treatments were employed. The resulting suspensions were used for particle size analysis and spectrophotometry, the control treatment being kaolinite dispersed in a 2.5% pyrophosphate solution, which brings about a complete dispersion but does not delaminate the kaolinite crystallites.

The <0.12- and >0.12-μm size fractions were collected by sedimentation analysis to evaluate the effect of the treatments on the delamination of the kaolinite crystallites. The particles having equivalent radii of <0.12 μm were removed repeatedly and collected, the desired decantation depth being calculated for each of the solutions by Stokes' law. Viscosity was measured by an Ostwald viscometer. In the control treatment, the removal of this fraction continued until the turbidity of the upper liquid layer, estimated visually, was negligible. In the DMSO-NH_4F treatments, the separation procedure was stopped before the turbidity of the upper liquid layer was neglible, even though it was always rather low at this stage of the decantation. The great majority of the turbidity caused by the <0.12-μm size fraction was probably collected by this procedure. The amounts of both the >0.12- and <0.12-μm size fractions were determined gravimetrically in suspension aliquots, after the removal of the DMSO

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by washing four times with ethanol:water (8:2, v/v) solution and heating to 100°C overnight.

The electric charge of the DMSO-NH₄F-treated kaolinite particles was determined by a U-shaped electrophoretic tube. The pH of the treated suspensions was about 9.5. The measurements were carried out in the presence of ~1 mM NaCl in the suspension.

RESULTS AND DISCUSSION

The measured weight percentages of the <0.12- and >0.12-μm size fractions are given in Table 1. In all the DMSO-NH₄F treatments the weight percentage of the >0.12-μm size fraction was significantly lower than that of the control. It was affected only slightly by the heating time with the ammonium fluoride. Increasing the number of reaction cycles resulted in a decrease in the percentage of the >0.12-μm size fraction. Inasmuch as the separation of the DMSO-NH₄F-treated samples into two size fractions was not complete (see above), the real percentages of the <0.12-μm size fractions were somewhat greater, and those of the >0.12-μm size fractions were somewhat smaller, than those reported in Table 1. DMSO treatment (without ammonium fluoride) resulted in an unstable suspension, which sedimented within several hours.

The measured weight percentage of the <0.12-μm size fraction is not simply related to that of the coarse fraction, nor does it seem to be related to either the heating time or the number of reaction cycles. Moreover, summing the two size fractions shows that part of the kaolinite was removed during the preparation procedure. This missing mass was largest in the 17-cycle treatment; the differences among the other treatments do not seem to indicate any obvious tendency. The missing kaolinite is attributed to the removal of both dissolved clay and the very fine particles during the washing procedure.

Dissolution of kaolinite, i.e., by the formation of soluble complexes of Si and F, could have taken place during the NH₄F treatment; the washings with DMSO: water which followed the NH₄F treatment may have removed these dissolution products. The observation that increasing reaction time from 1.5 hr to 50 days did not bring about an increase in the missing mass indicates that the dissolution reaction was of limited importance in the disappearance of matter from the reaction vessel. Presumably a saturation point was reached in the solution.

The pH of the DMSO:water solutions under study was generally >9. The pH effects on the dissolution reactions should be further studied.

Delamination of the kaolinite into very thin lamellae could have also resulted in the removal of these small crystallites during the washings which followed the NH₄F treatment. Moreover, the stability of these suspensions increased as the NH₄F was removed, and

Table 1. Weight percentages of the >0.12- and <0.12-μm size fractions, and missing mass.

Treatment			Measured wt. % of size fraction		Calculated missing mass (wt. %)
			>0.12 μm	<0.12 μm	
(1)[2]	2.5% pyrophosphate solution (control)		87.5 ± 1.0	ND	ND
(2)	DMSO-NH₄F				
	Number of NH₄F cycles	Heating time of each cycle			
(2a)[2]	1	1.5 hr	67.4 ± 2.4	18.7 ± 1.4	13.9
(2b)[2]	6	1.5 hr	61.3 ± 1.6	23.9 ± 2.1	14.8
(2c)[3]	17	1.5 hr	39.1 ± 1.4	24.4 ± 6.9	36.5
(2d)[2]	1	20 day	72.2 ± 3.8	14.0 ± 0.9	13.8
(2e)[3]	1	50 day	71.5 ± 8.2	23.0 ± 12.1	5.5

[1] Presumably removed as dissolved matter and very thin lamellae during washings.
[2] Size fraction separation at room temperature (~25°C).
[3] Size fraction separation at a constant temperature of 25°C.
ND = not determined.

became very high after the fourth washing by DMSO: water. Very thin layers of kaolinite crystallites are rather transparent in the visible light; presumably they were not detected as turbidity in the supernatant during these washings, and were probably decanted and discarded.

Repeated removal of the supernatant could have caused a considerable mass loss, as seen in the 17-cycle treatment; however, the relative importance of the above-discussed dissolution and delamination reactions for the disappearance of kaolinite is not known at present. In principle, the kaolinite dissolution products, i.e., Si and Al, can be determined in the supernatant solution by an established method, such as atomic absorption spectroscopy. Here, however, both dissolved species and dispersed fine particles must be measured. In preliminary measurements of the supernatant of a DMSO-NH₄F-treated kaolinite, both Al and Si were detected; filtering was found to decrease the solution concentration of Al to zero, whereas Si was not totally removed from the solution. Both dissolved species and very fine lamellae may have been affected by the filter; this problem is currently under study.

Electrophoretic measurements of the DMSO-NH₄F-treated kaolinite suspensions have shown that the electric charge of the particles was positive. Presumably, the new surface potential of the DMSO-NH₄F treatments was high enough to prevent association between kaolinite particles; the treated suspensions were more stable than those of the control (pyrophosphate) suspensions and the fine particles remained suspended for months. Gradually, however, the stability decreased, and, after a few months at room temperature, the par-

Table 2. Slopes d log A/d logλ of kaolinite suspensions of several treatments.

Treatment (see Table 1)	$\frac{d \log A}{d \log \lambda}$
(1)	-2.249 ± 0.081
(2a)	-2.114 ± 0.029
(2b)	-1.916 ± 0.055
(2d)	-1.644 ± 0.090

ticles sedimented in what seemed to be a slow flocculation process.

In the visible light range, the relationships between the absorbance, A, of a kaolinite suspension, and λ, the wavelength of light, is given (see Bartoli and Philippy, 1987) by:

$$A = K\lambda^{-m}, \tag{1}$$

where K is a constant, m = $-d \log A/d \log \lambda$ = 4 − b, b is a function of the major dimension of the particle and λ. Eq. (1) was used (Kahn, 1959; Lahav and Banin, 1970) to estimate the clay particle size. In a suspension of very fine bentonite particles, b is close to zero and m is about −4 (Lahav and Banin, 1970). In the suspension having the small size fraction of the kaolinite used by Bartoli and Philippy (1987), m was −2.

Eq. (1) may be used for both kaolinite and montmorillonite because their particle shapes can be approximated by a disc geometry. As long as the delamination process under study brings about the dissociation of the kaolinite crystallites into lamellae with the same basic geometry, this equation adequately relates the spectrophotometric data with the major and minor dimensions of the particles. If, however, the delamination proceeds to its limit, i.e., the formation of unit layers having a thickness of 7 Å, these unit layers should not behave like the symmetric montmorillonite unit layers. Due to the asymmetry of the kaolinite unit layer, with tetrahedra and octahedra surfaces, these unit layers, and perhaps even thicker lamellae, dissociated by the above treatments, should form rolls similar to those characterizing halloysite. The formation of a uniform external surface on such a particle may have interesting implications regarding the stability and electrophoretic mobility of these rolls. Preliminary work on this possibility is being carried out in this laboratory. Here, the spectroscopic characteristics of the suspension will be affected by the extent of delamination and the geometry of the particles; the use of Eq. (1) for the estimation of particles' geometrical parameters will be valid for comparative purposes, but problematic otherwise.

A comparative spectroscopical study was made of treatments 1, 2a, 2b, and 2d (Table 1) as follows: small samples were taken from a predetermined depth of the suspension containing the <0.12-μm size fraction, and

their optical density in the visible light range was measured. The slope, d log A/d logλ, for each of these suspensions was calculated at wavelengths between 380 and 710 nm (Table 2).

The differences in the magnitude of the slopes between the pyrophosphate and the DMSO-NH₄F treatments for the <0.12-μm size fraction cannot be fully interpreted at present, because the extent of both delamination and loss of very fine particles is not known. The absolute values of the slopes of the three DMSO-NH₄F treatments, however, are significantly smaller than that of the control. Moreover, the slope seems to be related to the reaction time with NH₄F; its absolute value is greatest in treatment 2a (1.5-hr reaction time), and smallest in treatment 2d (20-day reaction time). These data may indicate an increasing effectiveness of the delamination process with increased reaction time.

Dispersed kaolinite lamellae, such as those postulated in the present study, are excellent candidates for various reactions, including the synthesis of cross-linked (pillared) kaolinites, using the approach outlined by Lahav et al. (1978). Many questions are still to be answered by future research. For example, does the delamination process proceed from the outer lamella to delaminate each time a new lamella, or can it take place simultaneously also in inner surfaces? Also, does the delamination proceed preferentially from the side of the oxygens or from the side of the hydroxyls? Can a delamination reaction of a crystallite proceed to completion? Is it a reversible reaction, taking place in both directions? Is it possible to reverse the delamination process by replacing the DMSO by water?

These problems are now under investigation.

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