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Thermal treatment of the kaolinite/CsCl/H_2O intercalation complex[1]

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Abstract

Four kaolinite/CsCl intercalation complexes were prepared by different methods and characterized using X-ray diffraction, photoacoustic and diffuse reflectance infrared spectroscopy, and simultaneous DTA–TG. Sample A was obtained by wet grinding a mixture consisting of equal amounts of CsCl and kaolinite: in this complex the kaolin-like layers were not arranged in any preferred orientation. This sample contained a great amount of intercalated water which could be eliminated below 250°C. Sample B was derived from sample A by heating it at 250°C. In sample B, the kaolin-like layers were parallel with a *c*-spacing of 1.065 nm. Samples C and D were obtained by ageing sample A or untreated kaolinite, respectively, in a concentrated CsCl solution. Both of the latter samples were similar to sample B.

INTRODUCTION

The grinding of kaolinite with caesium chloride or caesium bromide has previously been shown to bring about substantial changes to the IR spectrum [1–4] and the DTA curve [5, 6] of this important layer silicate. These results were attributed to the formation of complexes in which the alkali halides and water intercalate kaolinite. The kaolinite/CsCl/H_2O complex was obtained when kaolinite and CsCl were either mixed, ground in air, or ground in the presence of water. The degree of intercalation was least with mixing, intermediate with air grinding, and greatest with wet grinding. In contrast, the kaolinite/CsBr/H_2O complex was produced only

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when the mixture of the two solids was kept moist during grinding; moreover, the extent of intercalation in this sample was small.

The changes observed in the IR spectrum of kaolinite due to intercalation include the diminution of bands due to the stretching vibrations of "inner surface" hydroxyl groups, and the concomitant appearance of new bands which can be assigned to perturbed inner surface hydroxyls or to intercalated water. These observations prove that the inner surface hydroxyls form hydrogen bonds with intercalated water molecules and halide ions. Furthermore, the bands due to Si–O stretching are shifted to lower frequencies, which also indicates that the inner surface oxygens form hydrogen bonds with intercalated water molecules.

Most authors who have studied kaolinite intercalation employed X-ray diffraction measurements for the identification of the complexes [7]. The salts or organic compounds penetrate the interlayer space of the kaolin-like layers, and thus expand the crystal from an original basal spacing of about 0.72 nm to about 1.00–1.44 nm. For example, the kaolinite/CsCl complex obtained indirectly from the ammonium acetate intercalation complex by Weiss et al. [8] had an interlayer spacing of 1.03 nm. In contrast, the X-ray diffraction curve of the CsCl complex obtained by mechanochemical synthesis [3, 4, 6] did not show any feature that indicated intercalation; although the 0.72 nm peak disappeared after the kaolinite had been ground with the caesium salt, no other peak appeared in the diffractogram. It was therefore assumed that the layers do not arrange themselves in any particular orientation in this complex [1].

The objective of the present study was to gain better insight into the phenomenon of CsCl intercalation in kaolinite. To accomplish this, four kaolinite/CsCl complexes were prepared using different methods; the samples were then characterized by X-ray diffraction, photoacoustic and diffuse reflectance infrared spectroscopy, and thermal analysis.

EXPERIMENTAL

Materials

The well crystallized Georgia kaolinite used in the present study was supplied by Ward's. Suprapur grade caesium chloride was obtained from Merck. Both materials were used without further purification.

Methods

Preparation of samples A, B, C and D

The kaolinite/CsCl/H_2O complex (sample A) was obtained by wet grinding a mixture consisting of equal amounts of kaolinite and CsCl, using the technique described previously [3]. Sample B was derived from sample A by heating it for 2 h at 250°C, in order to eliminate the intercalated water. Sample C was prepared by suspending 10 mg of sample A in 5 ml of an aqueous 8 M CsCl solution in a sealed glass ampoule, and ageing the suspension for 3 weeks at 60°C. Finally, sample D was prepared in a manner similar to sample C, except that untreated kaolinite was used as the starting material. In the two latter cases, the solid phase was separated from the suspension by centrifugation after ageing.

X-ray diffraction, infrared spectroscopy and thermal analysis

Samples C and D for X-ray diffraction were gently washed with a few drops of water in order to remove excess salt. Oriented samples were prepared by allowing aqueous suspensions to dry in air on glass slides. Samples A and B were examined as powders immediately after their preparation by grinding and heating, respectively. X-ray diffraction patterns were recorded on a Philips automatic powder diffractometer (Diffraction Control Unit PW 1710/00).

Photoacoustic IR spectra were measured with a Bruker IFS 113v spectrometer and a Princeton Applied Research Corporation model 6003 cell and preamplifier, or alternatively with a Bruker IFS 88 spectrometer and an MTEC model 200 cell. Diffuse reflectance spectra were recorded with the IFs 113v and a Harrick sample cell. The use of this equipment for the study of clay complexes was described previously [3]. No further sample preparation was performed before the IR measurements, i.e. no other alkali halides were introduced as diluents for the powdered samples.

Simultaneous DTA–TG curves were recorded in flowing nitrogen using a Stanton-Redcroft model STA 780 apparatus. Calcined alumina was used as the reference. Alumina crucibles were used for the specimen and as the reference material. The quantity of kaolinite/salt mixture for each run was between 10 and 20 mg. The samples were heated from room temperature to 1170°C at a rate of 20°C min^{-1} [6].

RESULTS

X-ray diffraction

No peak was observed in the X-ray diffraction curve of sample A. The lack of occurrence of the 0.72 nm peak, which is characteristic of non-intercalated kaolinite, indicates that the sample was delaminated as a result of the mechanochemical treatment.

The diffractograms of samples B and C contain a very intense peak at 1.065 nm. As discussed in the Introduction, this result characterizes the kaolinite/CsCl intercalation complex. Moreover, the diffraction curve for sample D also shows a peak at 1.06 nm, although it is accompanied by a small and very broad peak at 0.81 nm, with an intensity 13% of that of the main feature. According to Constanzo and co-workers [9–12] a spacing of 0.84–0.86 nm is characteristic for hydrated kaolinite, in which isolated water molecules are keyed into the ditrigonal holes of the silica tetrahedra (this water is defined as "hole water"). The results for sample D therefore indicate that in addition to the kaolinite/CsCl intercalation complex, a small amount of hydrated kaolinite was present.

Thermal analysis

Figures 1 and 2 show DTA and TG curves of the four samples. TG data for samples C and D are similar and are represented by one curve. The peak temperatures and the weight loss (in per cent) recorded at each stage are summarized in Table 1. Samples A and B show an endothermic peak at 525°C, attributed to dehydroxylation of the clay. They do not show any peak that could be attributed to a phase transition of CsCl, or to the melting and evaporation of this salt. This indicates that these samples did not contain excess CsCl: all of the salt that was used for the preparation of these samples was intercalated by the kaolinite.

Table 1 shows that weight loss at this stage is slightly higher than that obtained in the TG of untreated kaolinite. Previously we related this difference to the evolution of HCl whiich can be obtained from the thermal hydrolysis of CsCl [3, 5]. It is also possible that both these samples contain a

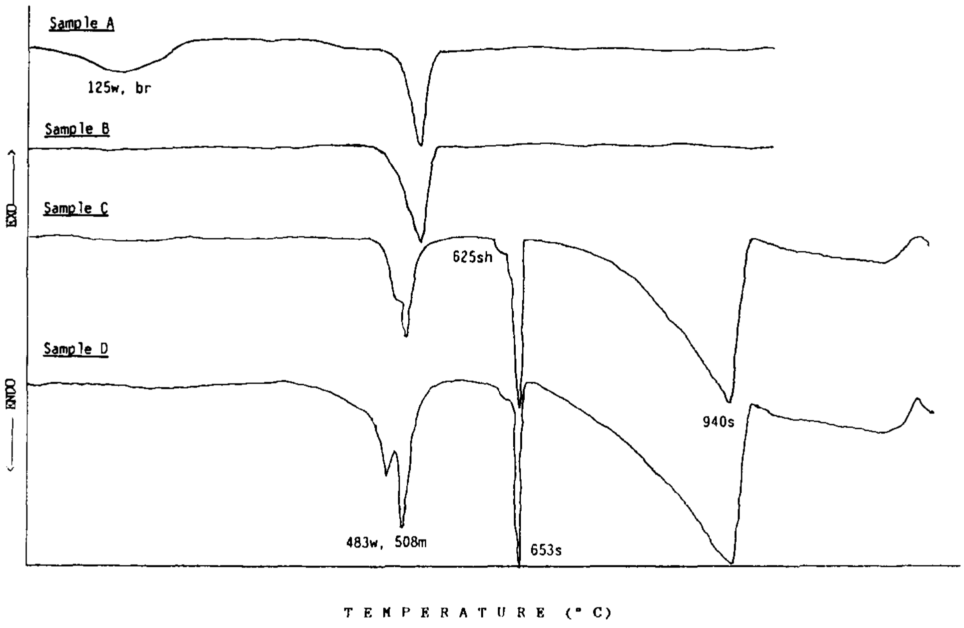

Fig. 1. DTA curves of samples A, B, C and D.

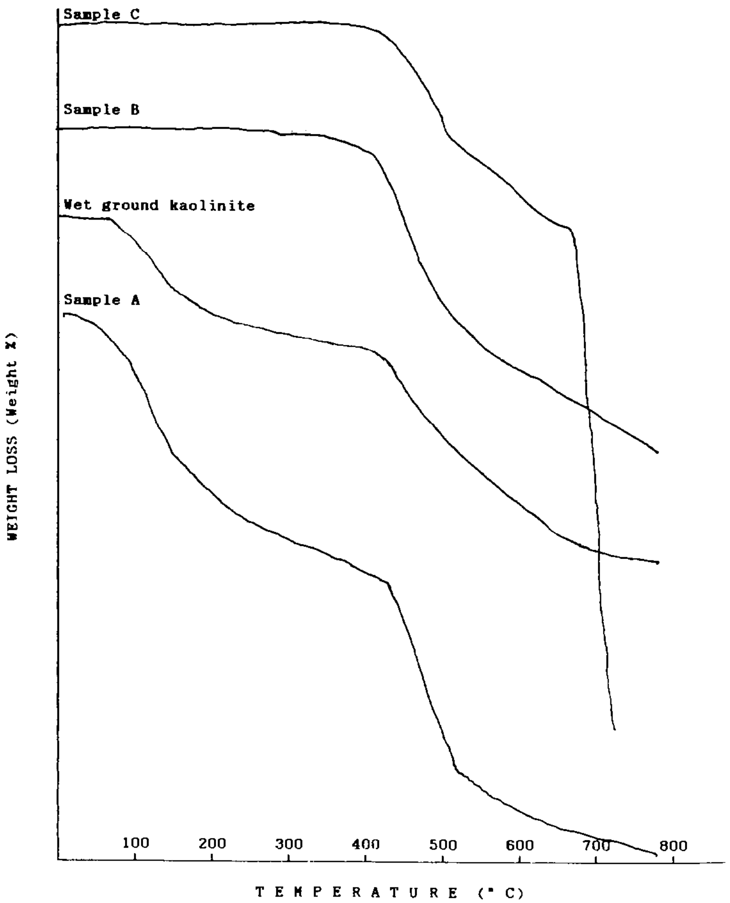

Fig. 2. TG curves of samples A, B and C and of wet ground kaolinite.

very small amount of strongly bound intercalated water which is evolved only at elevated temperatures.

The most significant difference between samples A and B is the appearance of an endothermic peak at 125°C for sample A. The absence of this peak from the DTA curve of sample B, and the fact that this sample did not show any loss of mass below 300°C, indicate that sample B did not contain this type of water. For comparison, the TG curve of kaolinite wet ground in the absence of CsCl is also shown in Fig. 2. This sample contains water adsorbed at the crystal edges exposed during the grinding of the clay. This water is lost below 300°C, but the weight loss is much smaller than that for sample A, which implies that the high weight loss of sample A is associated with the elimination of weakly bound intercalated water which is not present in sample B.

Samples C and D did not show any weight loss below 400°C. However, they do contain excess CsCl that was adsorbed by the solids when they

TABLE 1

TG regions, temperature ranges, weight loss percentage (calculated on the basis of kaolinite) and DTA endothermic peaks in the thermal analysis curves of untreated kaolinite and samples A, B, and C

	TG region	Temperature range/°C	Weight loss/%	DTA peak temp/°C
Kaolinite	1st	r.t.–170		
	2nd	170–400	0.3	
	3rd	400–590	8.2	530m
	4th	590–685	2.1	
	5th	685–950	0.3	
Sample A	1st	r.t.–250	11.2	125w, br
	2nd	250–430	3.0	
	3rd	430–550	10.8	525m
	4th	550–800	6.8	
Sample B	1st	r.t.–250		
	2nd	250–430	1.8	
	3rd	430–550	9.4	525m
	4th	550–800	6.2	
Sample C	1st	r.t.–400		
	2nd	400–430	0.7	
	3rd	430–525	5.5	483w, 508m
	4th	525–630	3.0	625sh
	5th	630–680	0.8	653s
	6th	680–970	115.6	940s

Key: w, weak; m, medium; s, strong; br, broad; sh, shoulder; r.t., room temperature.

were aged in CsCl solution; this is shown by the appearance of endothermic peaks at 483, 653, and 940°C which respectively correspond to the phase transition, melting, and boiling of the CsCl salt and the high weight loss in the 6th TG region. In these two samples, as is the case in sample B, only CsCl is intercalated into the kaolinite, perhaps with very small amounts of strongly bound water.

IR spectra

The photoacoustic IR spectra of untreated kaolinite and of samples A, B, and C are shown in Fig. 3, while Table 2 summarizes the frequencies and the assignments of the bands. The diffuse reflectance spectra of these samples are quite similar to those shown in this figure. Further, it should be noted that the spectra of samples B, C, and D closely resemble one another, but differ substantially from the spectrum of sample A.

The spectra of samples B–D also differ from the spectrum of untreated kaolinite in several regions (Fig. 3). In the OH stretching region, bands

A, B, C and D of kaolinite (due to either inner surface or inner hydroxyl groups) are virtually absent from the spectra of the complexes, which instead display three new bands in the 3500–3600 cm^{-1} region, as well as a very weak band near 3380 cm^{-1}. above 3600 cm^{-1}, band Z persists near 3670 cm^{-1} in the spectra of all three samples, while band A was observed only for sample C. At lower frequencies, all of the bands that arise from Al–O and AlO–H vibrations are also perturbed, and are shifted either to lower (band I) or to higher (bands H and M) frequencies. The Si–O bands, however, are only slightly affected by complexation.

The most noticeable difference between the spectrum of sample A and those of samples B–D involves the relative intensity and definition of the bands in the 3500–3585 cm^{-1} region. Two bands, at 3508–3522 cm^{-1} and at 3582 cm^{-1}, develop with the grinding of the kaolinite/CsCl mixture and its ageing in air [3]. They are relatively weak and very broad in the spectrum of sample A, and are the only bands which can be assigned to the antisymmetric and symmetric stretching vibrations of intercalated H_2O molecules which are evolved at temperatures below 250°C [3]. (The deformation of the intercalated water occurs at 1640 cm^{-1}.) In contrast, the two bands in the 3500–3585 cm^{-1} region in the spectra of samples B–D are very intense and well defined, and occur at slightly lower frequencies than the water stretching vibrations. Since these samples may contain only very small amounts of water, these bands (like band A′ at 3600 cm^{-1}) must arise

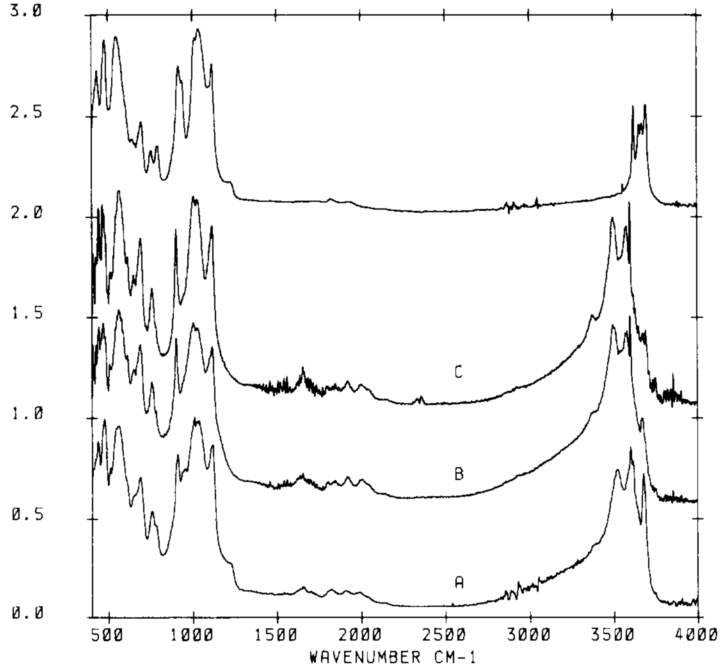

Fig. 3. Photoacoustic IR spectra of samples A, B and C, and of kaolinite (top curve). Samples B and C were air ground, leading to partial hydration (see text). The spectra have been rescaled and offset vertically for clarity.

from perturbed OH groups of kaolinite: their similarity with the H_2O bands of sample A is coincidental.

Band D is intense in the spectrum of kaolinite, but appears only as a shoulder in the spectrum of sample A, and weakly or not at all in the spectra of samples B–D. This band arises from inner hydroxyls, and it is therefore expected that it will not be affected by the intercalation of proton acceptors. However, in our previous curve-fitting study of the OH stretching bnads in spectra of kaolinite/CsCl intercalation complexes [4],

TABLE 2

Assignment of observed bands (in cm^{-1}) in photoacoustic and diffuse reflectance IR spectra of kaolinite and kaolinite/CsCl complexes

Assignment	Symbol	Natural clay	Sample [a]		
			A	B	C
AlO–H stretching	A	3692			3692
	Z	3686	3672	3670	3667
	B	3666			
	C	3653			
	D	3622	3616		
FeO–H stretching		3601			
AlO–H stretching	A′		3599	3600	3600
Intercalated H_2O O–H stretching			3582		
AlO–H stretching	D′			3576	3577
Intercalated H_2O O–H stretching			3508		
AlO–H stretching	A″			3503	3502
Surface H_2O O–H stretching				3376	3375
Intercalated H_2O H–O–H bending			1641	1639	1657
Si–O stretching	E	1117	1111	1117	1117
	P	1099			
	F	1040	1030	1032	1031
	G	1013	1009	1005	1006
AlO–H deformation	H	939		947	945
	I	918	903	903	903
	J		779	785	780
	K	756	760	759	759
	L	694	690	690	691
Al–O deformation	M	552	565	572	569
Si–O deformation	N	476	471	474	473
	O	434	440	443	443

[a] Sample A: kaolinite/CsCl/H_2O; samples B and C: kaolinite/CsCl. Preparation and characterization of these samples are described in the text.

we found that the intensity of band D is in fact weakened with intercalation. It is therefore logical to assume that the new bands in the 3500–3600 cm^{-1} region should have a contribution from both inner-surface hydroxyls and inner hydroxyls.

An additional, very weak band appears near 3380 cm^{-1} in the spectra of samples B–D. When the samples were air ground, or ground together with a small drop of water, the intensity of this band increased; it decreased again when the sample was reheated at 250°C. (The spectra of samples B and C after grinding in air are depicted in Fig. 3.) Thus it is reasonable to attribute this band to the small amounts of water which are held by the intercalation complex up to the dehydroxylation of the clay, or to surface water molecules, held by the edges of the clay layers ("broken-bond" adsorption).

DISCUSSION

In the spectrum of sample A, all of the bands which are due to O–H, AlO–H, Al–O, and Si–O vibrations are perturbed, whereas in the spectra of samples B–D only those vibrations which arise from O–H, AlO–H, and Al–O groups are affected. Samples B–D do not contain interlayer water, but rather only Cs^+ and Cl^- ions. The chloride ion can act as a proton acceptor; thus hydrogen bonds are formed with the inner-surface hydroxyls, leading to the perturbation of the vibrations which are associated with these OH groups (bands A, B, C, H, I and M). Caesium ions also contribute to the perturbation of these bands, because of the electrostatic repulsion betweenthem and the protons of the OH groups. Sample A contains tremendous amounts of intercalated water in addition to Cs^+ and Cl^-. Caesium ions are water "structure breakers" and the resulting non-clustered water molecules form hydrogen bonds with the oxygen plane and inner-surface hydroxyl plane, leading to the perturbation of the vibrations which are associated with these Si–O and OH groups.

Sample A was obtained by a mechanochemical process in which the kaolinite is delaminated by grinding, and freshly exposed oxygen and hydroxyl planes adsorb water molecules and Cs^+ and Cl^- ions. The shapes and sizes of the spaces between the aluminosilicate layers are determined by the grinding process. The adsorbed water molecules and ions fill these interlayer spaces. Therefore, clusters obtained by this technique do not show any preferred orientation, and no peak occurs in the X-ray diffraction curve.

Sample B was prepared by heating sample A at 250°C. Water molecules are evolved during heating, and new clusters are formed with parallel aluminosilicate layers intercalated by Cs^+ and Cl^- ions. The diameters of the Cs^+ (c.n. = 8) and Cl^- ions are 0.348 and 0.362 nm, respectively. A spacing of 1.065 nm allows these ions to be located in the interlayer with a very small "keying" of the Cl^- inside the ditrigonal cavity of the oxygen plane. It can be assumed that the penetrated Cl^- interacts with the inner hydroxyl, thus resulting in the changes in band D.

Sample C was obtained by ageing sample a at 60°C in an aqueous CsCl solution. This transformation can be regarded as a recyrstallization process in which unstable clusters with non-parallel layers are disaggregated in the aqueous phase, and new clusters are obtained with a preferred orientation of parallel layers. In contrast, sample D was prepared by ageing untreated kaolinite at 60°C in an aqueous CsCl solution. The product from this treatment is very similar to sample C, the only difference being the presence of small amounts of the hydrated kaolinite phase that gives a 0.810 nm peak in the X-ray diffraction curve. Because of its low concentration relative to that of kaolinite/CsCl, this phase was detected only by X-ray diffraction, and not by DTA or IR spectroscopy.

It should be noted that, although samples C and D were obtained from an aqueous phase, the resulting CsCl intercalation complex is almost anhydrous. This is an indication that a system with inter-water hydrogen bonds is more stable than one with hydrogen bonds between water molecules and silioxane and hydroxyl groups of kaolinite. Clustered water molecules are more restricted translationally and rotationally in their motion than monomers weakly bonded to the siloxanes and hydroxyls of kaolinite, and therefore have lower entropy. Thus during the mechanochemical treatment, when the water content is low, intercalation of water by kaolinite is favoured by entropy; in aqueous systems, where the water content is high, water clustering is favoured by enthalpy stabilization of the cluster.

CONCLUSIONS

In the crystal structure of the kaolinite/CsCl/H_2O intercalation complex obtained by grinding kaolinite with CsCl, the kaolin-like layers are not arranged in any preferred orientation. The thermal treatment of this complex at 250°C results in the evolution of most of the intercalated water and the formation of an intercalation complex with parallel aluminosilicate layers and a *c*-spacing of 1.065 nm. The same complex is obtained by the ageing of the kaolinite/CsCl/H_2O intercalation complex, or of untreated kaolinite, in a concentrated aqueous CsCl solution at 60°C for three weeks. These results imply that a system with hydrogen bonds between water molecules is more stable than one with bonds between water molecules and the siloxanes and hydroxyls of the kaolin-like layer.

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REFERENCES

1 S. Yariv, J. Chem. Soc. Faraday Trans. 1, 71 (1975) 674.
2 S. Yariv, Int. J. Trop. Agric., 4 (1986) 310.
3 K.H. Michaelian, S. Yariv and A. Nasser, Can. J. Chem., 69 (1991) 749.
4 K.H. Michaelian, W.I. Friesen, S. Yariv and A. Nasser, Can. J. Chem., 69 (1991) 1786.
5 S. Yariv, E. Mendelovici and R. Villalba, in B. Miller, (Ed.) Proc. Seventh Int. Conf. Therm. Anal., Kingston, Canada, 1982, Vol. 1, John Wiley, Chichester, 1982, p. 533.
6 S. Yariv, A. Nasser, Y. Deutsch and K.H. Michaelian, J. Therm. Anal., 37 (1991) 1373.
7 B.K.G. Theng, The Chemistry of Clay Organic Reactions, Adam Hilger, London, 1974, p. 239.
8 A. Weiss, W. Thielepape and H. Orth, Proc. Int. Clay Conf., Jerusalem, 1966, Vol. 1, Israel Program for Scientific Translations, Jerusalem, 1966, p. 277.
9 P.M. Costanzo, R.F. Giese, Jr. and M. Lipsicas, Clays Clay Miner., 32 (1984) 419.
10 M. Lipsicas, C. Straley, P.M. Costanzo and R.F. Giese, Jr., J. Colloid Interface Sci., 107 (1985) 221.
11 R.F. Giese, Jr. and P.M. Costanzo, Geochemical Processes at Mineral Surfaces, Am. Chem. Soc. Symp. Ser., 323 (1986) 37.
12 P.M. Costanzo and R.F. Giese, Jr., Clays Clay Miner., 33 (1985) 415.