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Effect of water on the formamide-intercalation of kaolinite

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Abstract

The molecular structures of low defect kaolinite completely intercalated with formamide and formamide–water mixtures have been determined using a combination of X-ray diffraction, thermoanalytical techniques, DRIFT and Raman spectroscopy. Expansion of the kaolinite to 10.09 Å was observed with subtle differences whether the kaolinite was expanded with formamide or formamide–water mixtures. Thermal analysis showed that greater amounts of formamide could be intercalated into the kaolinite in the presence of water. New infrared bands were observed for the formamide intercalated kaolinites at 3648, 3630 and 3606 cm^{−1}. These bands are attributed to the hydroxyl stretching frequencies of the inner surface hydroxyls hydrogen bonded to formamide with water, formamide and interlamellar water. Bands were observed at similar positions in the Raman spectrum. At liquid nitrogen temperature, the 3630 cm^{−1} Raman band separated into two bands at 3633 and 3625 cm^{−1}. DRIFT spectra showed the hydroxyl deformation mode at 905 cm^{−1}. Changes in the molecular structure of the formamide are observed through both the NH stretching vibrations and the amide 1 and 2 bands. Upon intercalation of kaolinite with formamide, bands are observed at 3460, 3344, 3248 and 3167 cm^{−1} attributed to the NH stretching vibration of the NH involved with hydrogen bonded to the oxygens of the kaolinite siloxane surface. In the DRIFT spectra of the formamide intercalated kaolinites bands are observed at 1700 and 1671 cm^{−1} and are attributed to the amide 1 and amide 2 vibrations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DRIFT spectroscopy; Formamide; Kaolinite; Intercalation; Raman microscopy; Molecular structure; Thermal analysis

1. Introduction

Kaolinite can be expanded, when chemically reacted in aqueous solutions with molecules such

as formamide, urea or potassium acetate, which insert between the kaolinite layers [1–4]. Such a process is known as intercalation. Intercalation may take place through several mechanisms depending on the point of interaction of the inserting molecule and the kaolinite surface. This mechanism depends on the disruption of the hydrogen bonding between the kaolinite layers and

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the replacement with hydrogen-bonding with the inserted molecule. For molecules such as potassium acetate, interaction occurs through the acetate anion and the hydroxyls of the gibbsite like surface often referred to as inner surface hydroxyls [5–8]. In this case additional hydroxyl stretching frequencies are observed at positions between 3595 and 3605 cm^{-1} . Such bands reflect the hydrogen bond formation between the carboxylate group and the inner surface hydroxyls.

In the case of urea, interaction occurs through the NH_2 groups [5,6]. The insertion of the urea molecules breaks the hydrogen bonds between the gibbsite-like hydroxyls and the oxygens of the next adjacent siloxane surface with the subsequent formation of hydrogen bonds between the hydrogens of the urea and the oxygens of the siloxane layer. Molecules such as formamide and acetamide may interact through several interaction sites, either through the C=O group, the lone pair of nitrogen electrons or through the amide group. A previous study [1] has shown that formamide readily intercalates kaolinite and the proposal was made that the intercalation process depended upon whether the kaolinite was ordered (low-defect) or disordered (high-defect) in terms of layer stacking [9]. Halloysites and kaolinites intercalate with formamide at different rates. Therefore, intercalation of kaolinite/halloysite mixtures with formamide is used as a standard technique for the determination of halloysite in the presence of kaolinite [9]. Kaolinites from Washington County, Georgia, with varying defect structures have been intercalated with formamide and additional Raman bands have been observed at 3610 and 3627 cm^{-1} [9]. The extent of intercalation of these kaolinites was incomplete and changes in the molecular structure of the inserting formamide molecule were not investigated. The objectives of this paper are, therefore: (a) to report the molecular structure of kaolinites fully intercalated with formamide; (b) to study the effect of water on the intercalation of formamide; and (c) to investigate the changes in the molecular structure of the formamide molecule upon insertion between the kaolinite layers.

2. Experimental

2.1. The kaolinite intercalates

The clay mineral used in this study is a highly ordered, low-defect kaolinite from Kiralyhegy, Hungary. Intercalation of the air-dried clay was carried out according to the formulation of Weiss et al. [10,11]. Three milligram portions of the kaolinite were mixed with 5 cm^3 of formamide (analytical grade, Reanal, Budapest, Hungary) as well as with 5 cm^3 of 1:1 by weight ratio of formamide:water solution and stirred for 80 h at room temperature. The intercalates were separated from the solution by centrifugation and allowed to dry at room temperature for a week.

2.2. X-ray powder diffraction

XRD analyses were carried out on a Philips wide angle PW 1050/25 vertical goniometer equipped with a graphite diffracted beam monochromator. The d -spacing and intensity measurements were improved by application of a self developed computer aided divergence slit system, enabling constant sampling area irradiation (20 mm long) at any angle of incidence. The goniometer radius was enlarged from 173 to 204 mm. The radiation applied was $\text{CuK}\alpha$ from a long fine focus Cu tube, operating at 40 kV and 40 mA. The samples were measured at 50% relative humidity in stepscan mode with steps of $0.02^\circ 2\theta$ and a counting time of 2 s. Measured data were corrected with the Lorentz polarisation factor (for oriented specimens) and for their irradiated volume.

2.3. Diffuse reflectance infrared spectroscopy

Diffuse reflectance Fourier transform infrared spectroscopic (commonly known as DRIFT) analyses were undertaken using a Bio-Rad 60A spectrometer. Five hundred and twelve scans were obtained at a resolution of 2 cm^{-1} with a mirror velocity of 0.3 cm s^{-1} . Spectra were co-added to improve the signal to noise ratio. Approximately 3 wt% kaolinite or intercalated kaolinite was dispersed in 100 mg oven dried spectroscopic grade

KBr with a refractive index of 1.559 and a particle size of 5–20 μm . Reflected radiation was collected at $\approx 50\%$ efficiency. Background KBr spectra were obtained and spectra ratioed to the background. The diffuse-reflectance accessory used was designed exclusively for Bio-Rad FTS spectrometers. It is of the so-called ‘praying monk’ design, and is mounted on a kinematic baseplate. It includes two four-position sample slides and eight sample cups. The cup (3 mm deep, 6 mm in diameter) accommodates powdery samples mixed with KBr using an agate mortar and pestle in 1–3% concentration. The collection efficiency of this adaptor (part number: 099-093 1) is approximately 50%.

The reflectance spectra expressed as Kubelka–Mink unit versus frequency curves are very similar to absorbance spectra and can be evaluated accordingly. The advantage of using DRIFT measurements over the pellet technique is that in this case the likely interference of the mulling agent (intercalation of KBr in a liquid phase under pressure) can be avoided.

2.4. Raman microprobe spectroscopy

Very small amounts of the kaolinite or the intercalated clay mineral were placed on a polished metal surface on the stage of an Olympus BHSM microscope, equipped with $10\times$, $20\times$, and $50\times$ objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge-coupled device detector (CCD). Raman spectra were excited by a Spectra-Physics model 127 He/Ne laser (633 nm) and recorded at a resolution of 2 cm^{-1} and were acquired in sections of approximately 1000 cm^{-1} for 633 nm excitation. Repeated acquisitions using the highest magnification, were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The best method of placing the kaolinites on this metal surface was to take a very small amount on the end of the spatula and then tap the crystals on to the metal surface.

Spectra at low temperatures were obtained us-

ing a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Samples were placed on a circular glass disc, which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. It was found that the best method of obtaining 77 K was to cool rapidly at 50 K min^{-1} until 100 K was obtained and then cool slowly at 1 K min^{-1} until 77 K was obtained. Samples were held at this temperature for 30 min to ensure thermal equilibrium. In order to measure several samples under the same conditions, three small aluminium cups were placed in the quartz holder, enabling three samples to be measured without warming to room temperature and cooling again. Because of the increased optical path, spectra at 77 K are noisier and require longer accumulation times. Spectra were obtained using 12 s scans for 20 min using the special short 50X (UWLD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This combined with the spherical aberration of the stage window, resulted in decreased signal.

Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel ‘Peakfit’ software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995. Graphics are presented using Micro-soft excel.

2.5. Thermal analysis

Simultaneous thermogravimetric, differential-

thermogravimetric, differential thermal analysis (TG-DTG-DTA) measurements of the intercalates were performed in a Derivatograph PC-type thermoanalytical instrument (Hungarian Optical-Works, Budapest, Hungary) in nitrogen atmosphere at a heating rate of $5^{\circ}\text{C min}^{-1}$. Thermogravimetric-mass spectrometry (TG-MS) runs were performed by means of a Netzsch 209 thermobalance coupled with a Balzers MSC 200 ThermoCube type mass spectrometer connected via a fused silica capillary for sample introduction. Samples of a few mg were heated in helium atmosphere at a rate of $10^{\circ}\text{C min}^{-1}$.

3. Results and discussion

3.1. XRD analyses

When kaolinites are intercalated with an inserting molecule, expansion occurs along the *c*-axis direction. Fig. 1 displays the X-ray diffraction patterns of the formamide-intercalated kaolinites and the deintercalated kaolinites after thermal treatment at 300°C . The kaolinite has an initial *d*(001) spacing of 7.14 \AA and is a well-ordered kaolinite with a Hinckley index of 1.39. Upon intercalation with formamide and formamide–water mixtures, the kaolinite expands to slightly different *d*-spacings of 10.13 and 10.09 \AA . No intensity remains in the 7.14 \AA peak after intercalation. This expansion is in good agreement with previous results [1]. Thus, based on X-ray diffraction results, the well-ordered kaolinite is 100% intercalated. Slight differences were observed in the *d*-spacings for the kaolinite expanded with 100% formamide and with 50% formamide–water mixtures. The *d*(001) peak shows strong asymmetry on the high angle side for both expanded kaolinites. The *d*(001) peak profile may be curve fitted and a second peak identified at 10.34 \AA for the 100% formamide intercalated kaolinite and 10.28 \AA for the water–formamide-intercalated kaolinite. The relative areas of the two peaks at 10.13 and 10.34 \AA for the formamide-intercalated kaolinite are 50.1 and 49.9%. It is apparent that there are subtle differences in the expansion of the kaolinite with formamide and formamide–water

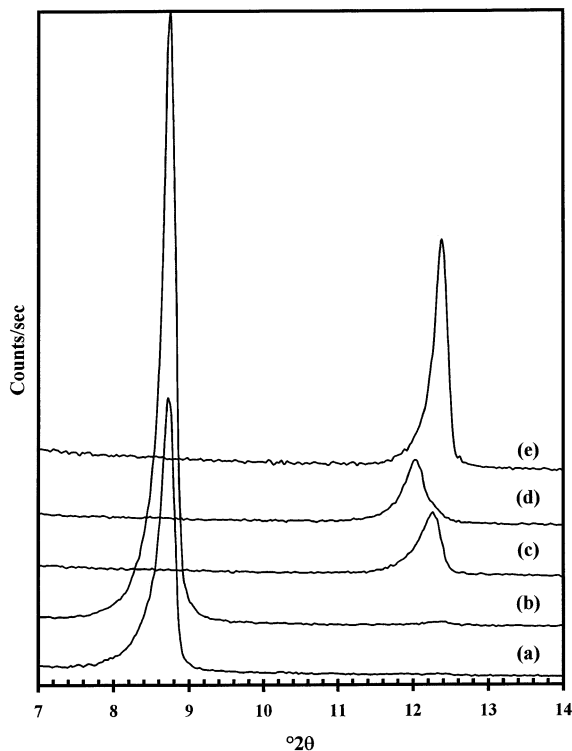


Fig. 1. X-ray diffraction of: (a) formamide-intercalated kaolinite; (b) formamide–water intercalated kaolinite; (c) deintercalated formamide-intercalated kaolinite after heating to 300°C ; (d) deintercalated formamide–water intercalated kaolinite after heating to 300°C ; (e) untreated kaolinite.

mixtures. Two interpretations may be given to the observation of the two peaks. Firstly, the kaolinite expands on a regular basis to two different structures. This would indicate two different structures for the formamide between the kaolinite layers. Secondly, the kaolinite expands unevenly with greater expansion at the edges of the kaolinite layers than in the middle. Such an observation has been observed for the expansion of kaolinites at the edges, with water under high pressures and elevated temperatures [12]. The peak widths of the 10.34 and 10.13 \AA peaks for the formamide-intercalated kaolinite are 0.362 and $0.169^{\circ} 2\theta$. The peak widths of the 10.28 and 10.086 \AA peaks for the formamide–water-intercalated kaolinite are 0.327 and $0.158^{\circ} 2\theta$. The peak width of the untreated kaolinite was $0.125^{\circ} 2\theta$.

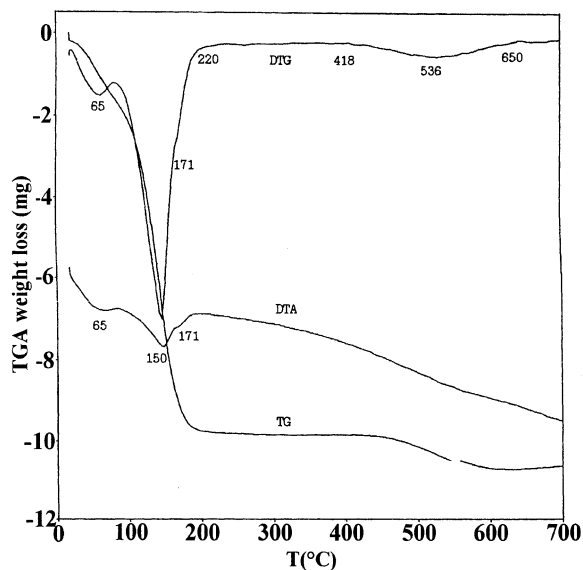


Fig. 2. Simultaneous TG-DTG-DTA curves of 31.81 mg kaolinite intercalated with formamide.

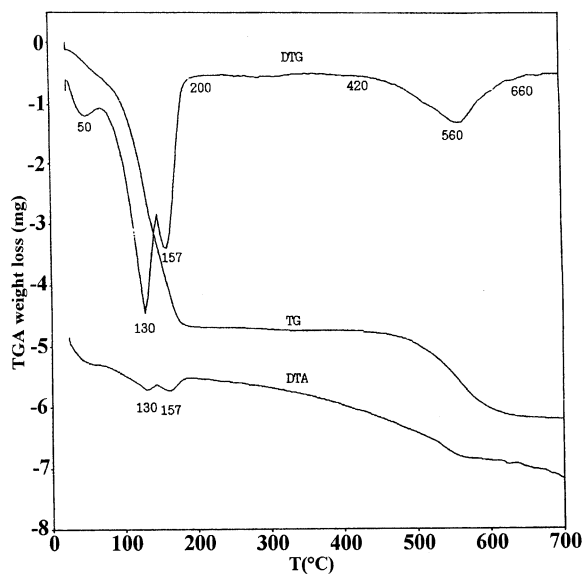


Fig. 3. Simultaneous TG-DTG-DTA curves of 34.87 mg kaolinite intercalated with 1:1 formamide–water mixture.

Thus upon intercalation the peak widths increased. Such an observation supports the concept of an increased range of structures and thus the kaolinite has become more disordered upon intercalation.

XRD traces in Fig. 1 c and d show the kaolinite $d(001)$ spacing after deintercalation. No intensity remains in the 10.09 Å peak. However the two kaolinites collapse upon deintercalation to different spacings from the original $d(001)$ spacing. The formamide-intercalated kaolinite contracts to a d -spacing of 7.20 Å and the formamide–water intercalated kaolinite to 7.35 Å upon thermal treatment. The $d(001)$ peaks are also strongly asymmetric on the high angle side after deintercalation. Two peaks are observed at 7.20 and 7.34 Å with relative areas of 44.3 and 55.7% for the formamide-intercalated kaolinite. For the formamide–water-intercalated kaolinite, two peaks are observed at 7.35 and 7.42 Å with relative intensities of 71.0 and 29.0%. The significance of the collapse of the expanded layers to values greater than the 7.14 Å is that the kaolinite is becoming more disordered after deintercalation. The layers after expansion are unable to pack as closely together after deintercalation as for the original kaolinite. The observation of two $d(001)$ spacings suggests that two types of collapsed structures exist after deintercalation.

3.2. Thermoanalytical investigations

The TG-DTG-DTA curves of kaolinite intercalated with formamide are shown in Fig. 2. Comparing the thermal analysis curves, it is found that the amount of water liberated up to 50°C was 1.76%. The loss of formamide from the heated complex took place in two closely overlapping stages up to 130 and 157°C. The dehydroxylation of the kaolinite took place between 420 and 660°C with a maximum release rate at 560°C. Considering the fact that 1 mol of dehydroxylation water is formed from the removal of 2 mol of inner (and inner surface) OHs, and that in the unit cell there are three inner surface and one inner OH groups of which only the inner surface hydroxyls can normally be accessed by the intercalating molecules, the amount of the intercalated formamide molecules per inner surface OH group can be calculated. This value is 0.77 mol formamide per mole inner surface OH.

The thermal decomposition curves of the formamide–water intercalate (Fig. 3) show a signifi-

cantly different pattern. On the one hand, the amount of water liberated at 65°C is 4.56%, which is some 2.6 times more than with formamide alone. On the other hand, the intercalated formamide is released at a temperature some 20°C higher than in the previous case. It means that formamide is bonded more strongly, i.e. the thermal deintercalation requires a more aggressive treatment. As a consequence, it is suggested that the deintercalated clay will be less ordered as is also evidenced by the XRD results. The fact that dehydroxylation took place with a maximum rate at 536°C (rather than at 560°C) indicate a stronger interaction between the kaolinite layers and the reactive molecules. The most striking difference in this case is the fact that the amount of intercalated formamide is 2.38 mol formamide per mol inner surface OH group. This means that water can increase the amount of intercalated formamide by more than three times. Mass spectrometric detection of the evolved gases showed that water was released from the samples in the first step, only. It means that the amount of formamide calculated from the TG curves between 80 and 220°C is correct. It, of course, does not mean that water cannot co-intercalate with

formamide. It only means that water is much less strongly bound in the structure and that the presence of water in the intercalating solution can significantly enhance the introduction of formamide into the clay structure.

3.3. DRIFT spectroscopy of the hydroxyl-stretching region

X-ray diffraction provides information about the unit cell and the expansion of the unit cell upon intercalation. Intercalation of kaolinites can also be followed by spectroscopic techniques, where molecular information may be obtained. In particular, both infrared and Raman spectroscopy provide information on the molecular structure and the changes in that molecular structure brought about through the insertion of the molecule between the kaolinite layers. Two types of information may be obtained: (a) the changes to the molecular structure of the kaolinite; and (b) changes to the molecular structure of the inserting molecule, in this case, formamide. Fig. 4 displays the DRIFT spectra of the untreated kaolinite and the formamide and formamide–water intercalates, clearly illustrating the changes brought about in

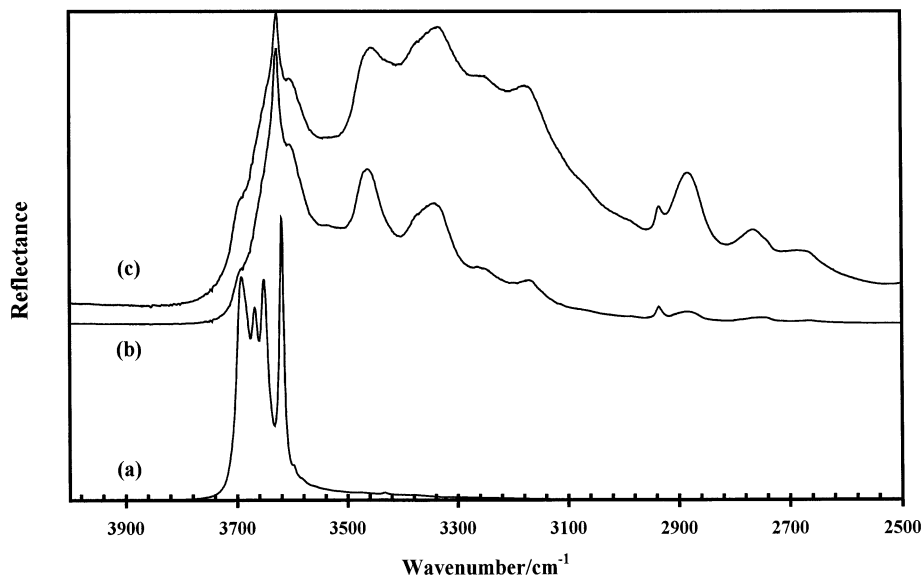


Fig. 4. DRIFT spectra of the hydroxyl stretching region of: (a) low defect kaolinite; (b) formamide-intercalated kaolinite; and (d) formamide–water-intercalated kaolinite.

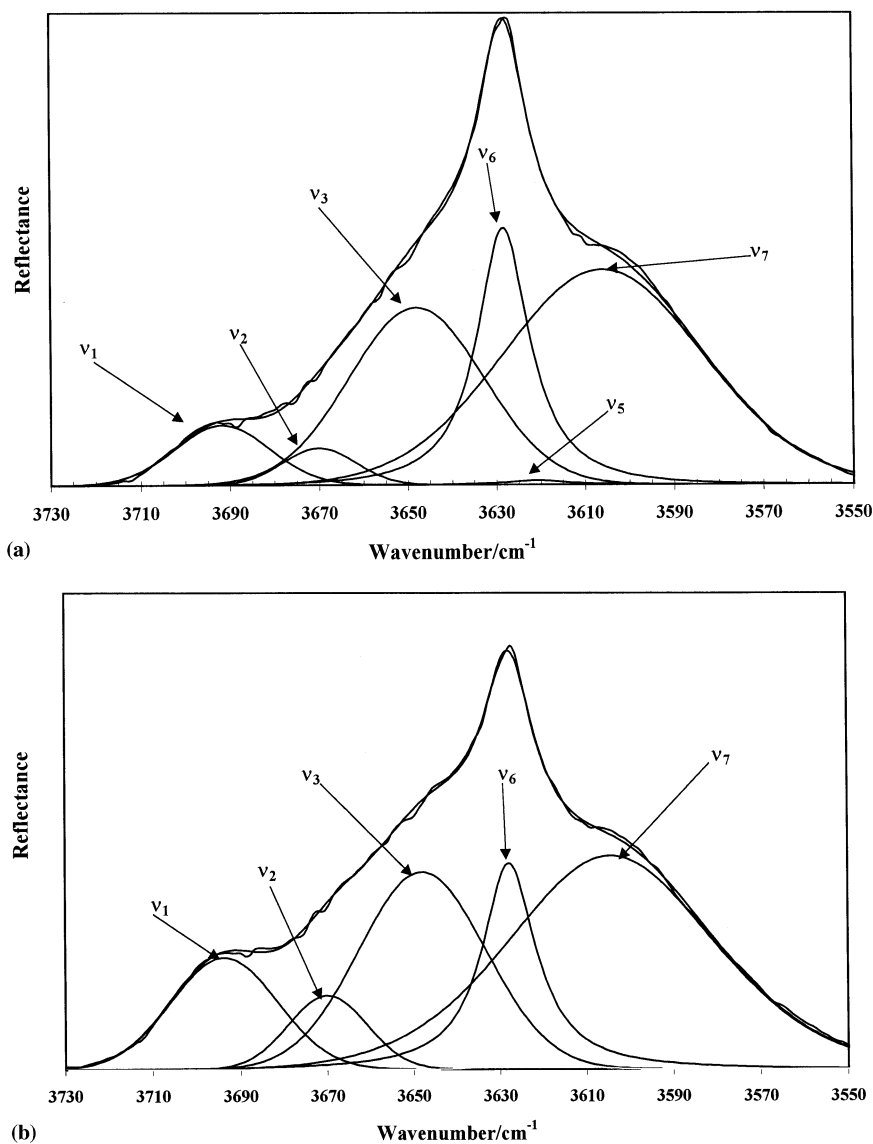


Fig. 5. (a) Band component analysis of the DRIFT spectrum of the hydroxyl stretching region of formamide-intercalated kaolinite. (b) Band component analysis of the DRIFT spectrum of the hydroxyl stretching region of formamide–water-intercalated kaolinite.

kaolinite spectra through the intercalation with formamide. Changes in the NH and CH stretching spectra of the inserting molecule are also observed. The spectra show that the intensity of the NH and CH bands is greater for the formamide–water intercalated kaolinite than in the formamide-intercalated kaolinite. This observation fits well with the TGA data where intercalation of the kaolinite with water increased the

amount of formamide intercalated into the kaolinite.

DRIFT spectroscopy of the hydroxyl stretching region of untreated kaolinite shows five bands at 3693, 3681, 3667, 3651 and 3619 cm⁻¹ with relative intensities of 28.0, 9.3, 8.6, 31.9 and 21.1%. The first four bands are assigned to the hydroxyl stretching frequencies of the inner surface hydroxyls and the band at 3619 cm⁻¹ to the inner

hydroxyl [13,14]. Fig. 5 a and b display the band component analyses of the DRIFT spectra of the hydroxyl-stretching region of formamide and formamide–water intercalated kaolinite. Upon intercalation of the kaolinite with formamide bands are observed at 3692, 3670, 3648, 3628 and 3606 cm^{-1} with relative intensities of 6.0, 2.9, 25.6, 18.6 and 46.4%. It should be noted that the fitting of the hydroxyl-stretching region is a function of the base line fitting process and some variation in the band parameters can occur. However no band could be fitted in the spectrum at 3620 cm^{-1} without a great deal of difficulty and the fitting iteration process always minimised a band in this position.

Intercalation with formamide has resulted in the loss of intensity of the bands assigned to the in-phase vibrations of the inner surface hydroxyls [13,14]. The band at 3693 cm^{-1} decreased in intensity from 28 to 6.0% relative intensity. The band at 3682 cm^{-1} is also no longer observed. An additional band at 3628 cm^{-1} was observed with relative intensity of 18.6%. A second new band was observed at 3606 cm^{-1} with 46.6% relative intensity. It is interesting that XRD showed the kaolinite to be totally intercalated, yet on the molecular scale, some intensity remains for some of the inner surface hydroxyls (6.0%). If the assumption is made that all of the inner surface hydroxyls are bonding with the formamide, then this intensity can be attributed to the edge and 'outer' hydroxyls. The observation that some intensity remains in the hydroxyl-stretching modes suggests that no formamide was adsorbed on the kaolinite 'outer' surfaces. Remarkably the band assigned to the inner hydroxyl is not observed at the normal position of 3620 cm^{-1} . One possible explanation is that the amide unit fits into the ditrigonal cavity of the siloxane layer and interacts with the inner hydroxyl. If this is so then a hydrogen bond could be formed between the amide group and the inner hydroxyl, which results in the shift of the 3620 cm^{-1} band to 3628 cm^{-1} . Significant intensity remains in a band at 3648 cm^{-1} and this band may be attributed to the interaction of the C=O unit of the formamide with the inner surface hydroxyl groups.

Upon intercalation of the kaolinite with a 50% mix of formamide and water, bands are observed at 3694, 3670, 3648, 3628, 3621 and 3605 cm^{-1} . The relative intensities of these bands are 11.2, 5.5, 24.4, 14.6, 4.0 and 43.8%. The relative intensity of the 3694 cm^{-1} band is almost twice that for the formamide-intercalated kaolinite. The intensity of the 3670 cm^{-1} band is approximately 50% of the intensity of the 3694 cm^{-1} band. The intensity of the 3648 cm^{-1} band is almost the same for both intercalates. The intensity of the 3628 cm^{-1} band is slightly less (14.6%) compared with the value for the formamide-intercalated kaolinite (18.6%). The intensity of the 3605 cm^{-1} band of the formamide–water-intercalated kaolinite is 43.8% compared with 46.4% for the formamide-intercalated kaolinite.

The limitations of the band fitting process should be recognised. Firstly it is difficult to fit a base line to the hydroxyl-stretching region because of the underlying water and amide bands. Secondly some variation in peak position may occur because of the widths of the fitted bands. So the accuracy of the peak position is estimated to be $\pm 2 \text{ cm}^{-1}$. Nevertheless the trends in the changes in intensity and the observation of additional bands are believed to be real.

3.4. Raman spectroscopy of hydroxyl stretching vibrations

The hydroxyl-stretching region of kaolinites is easily studied using Raman spectroscopy [14]. Fig. 6 shows the Raman spectra of the NH and hydroxyl-stretching region of formamide and formamide–water intercalates at 298 and 77 K. Two points need to be made from the point of view of spectroscopy: firstly there is an intensity decrease of $\approx 70\%$ when obtaining spectra at 77 K, because of the additional optics and secondly the Raman spectrum of kaolinites with increased disorder as occurs when kaolinites are intercalated with formamide, is more difficult to determine [15]. The band component analyses of the spectra are shown in Fig. 7. Table 1 reports the band component analyses of these spectra together with that of the Raman spectrum of the untreated kaolinite. The Raman spectrum of a low-defect

Table 1
Results of the band component analysis of the DRIFT and Raman spectra of the hydroxyl stretching region of kaolinite intercalated with 100% formamide and with 50:50% formamide–water mixtures

Kaolinite	Spectrum	ν_1	ν_4	ν_2	ν_3	ν_6	ν_5	ν_7
Low defect	DRIFT	Band centre cm ⁻¹	3693	3681	3667	3651	3619	Absent
		% Area	28.0	9.3	8.6	31.9		21.1
		Bandwidth cm ⁻¹	19.2	15.9	11.8	18.4		9.1
100% formamide intercalated Kaolinite	DRIFT	Band centre cm ⁻¹	3692	Absent	3670	3648	3628	3606
		% Area	6.0		2.9	25.6	18.6	46.4
		Bandwidth cm ⁻¹	25.0		19.3	35.7	14.0	53.0
50% formamide–water intercalated Kaolinite	DRIFT	Band centre cm ⁻¹	3694	Absent	3670	3648	3628	3605
		% area	11.2		5.5	24.4	14.6	43.8
		Bandwidth cm ⁻¹	21.2		21.2	34.7	14.9	55.5
Low-defect kaolinitet	Raman	Band centre cm ⁻¹	3693	3684	3668	3649	3620	Absent
		% Area	17.0	31.0	15.4	14.5	20.8	
Untreated	At 298 K	Bandwidth cm ⁻¹	15.2	9.5	15.1	11.5	5.7	
100% Formamide intercalated kaolinite	Raman	Band centre cm ⁻¹	Absent	Absent	3678	3648	3630	3605
		% Area			5.8	18.2	58.7	17.0
	At 298 K	Bandwidth cm ⁻¹			35.7	26.9	7.5	31.7
100% Formamide intercalated kaolinite	Raman	Band centre cm ⁻¹	Absent	3681	3660	Absent	3633	3588
		% Area		9.2	1.3		42.7	46.7
	at 77 K (Estimates)	Bandwidth cm ⁻¹		12.4	7.9		14.6	18.3
50% Formamide–water intercalated kaolinite	Raman	Band centre cm ⁻¹	3706	Absent	Absent	3647	3630	3605
		% Area	3.1			17.9	52.8	26.1
	At 298 K	Bandwidth cm ⁻¹	19.9			27.6	8.0	38.5
50% Formamide–water intercalated kaolinite	Raman	Band centre cm ⁻¹	3701	Absent	3660	3642	3632	3590
		% Area	2.7		18.1	3.3	37.1	14.0
	At 77 K	Bandwidth cm ⁻¹	11.0		Broad	45.0	5.1	7.1

kaolinite such as the Kiralyhegy kaolinite shows bands at 3693, 3684, 3668, 3649 and 3620 cm^{-1} with relative intensities of 17.0, 31.0, 15.4, 14.5 and 20.8%. Upon intercalation of kaolinite with formamide, no intensity is observed in the bands at 3693, 3684, 3668 and 3649 cm^{-1} attributed to the inner surface hydroxyls. Three bands are now observed at 3648, 3630 and 3605 cm^{-1} with relative intensities of 18.2, 58.7, and 17.0%. No inner hydroxyl band was observed at 3620 cm^{-1} . This observation is consistent with the DRIFT results. It is proposed that two types of interactions exist between the inner surface hydroxyl groups and the formamide resulting in two bands at 3648 and 3630 cm^{-1} . It is proposed that these two interactions depend upon the conformation of the formamide and the gibbsite-like surface. Two types of interactions could occur firstly through the C=O group and secondly through the lone pair of electrons on the nitrogen. Two bands are observed because of a difference in hydrogen-bond strength. Further the 3620 cm^{-1} band is shifted to higher frequencies upon intercalation. Thus it is suggested that the band at 3630 cm^{-1} is actually composed of two coincident overlapping bands.

Upon intercalation of the kaolinite with the 50% formamide–water mixture, bands are observed at 3647, 3630 and 3605 cm^{-1} with 17.9, 52.8 and 26.1% relative intensity, respectively. Bands are observed in the same positions and with approximately the same intensity irrespective of whether the kaolinite was intercalated with 100% formamide or with 50% formamide–water. One significant difference is the increase in intensity of the band at 3605 cm^{-1} . The intensity of this band is 17.0% for the formamide-intercalated kaolinite and is 26.1% for the formamide–water intercalate. Such results suggest this band is attributable to the hydroxyl stretching frequency of interlamellar water. The intensity of the 3630 cm^{-1} band is 10% greater for the formamide–water intercalate than the formamide-intercalate. It is suggested that the 3630 cm^{-1} band involves an interaction between the formamide hydrogen bonded to the inner surface hydroxyls of the kaolinite gibbsite-like surface. In the DRIFT spectra of the hydroxyl stretching region two intense bands are observed at 3628 and 3648 cm^{-1} . The 3648 cm^{-1} band is infrared active and Raman active. Such a result can be explained if the intercalation complex involves both formamide and water. The band at 3630 cm^{-1} , which is both

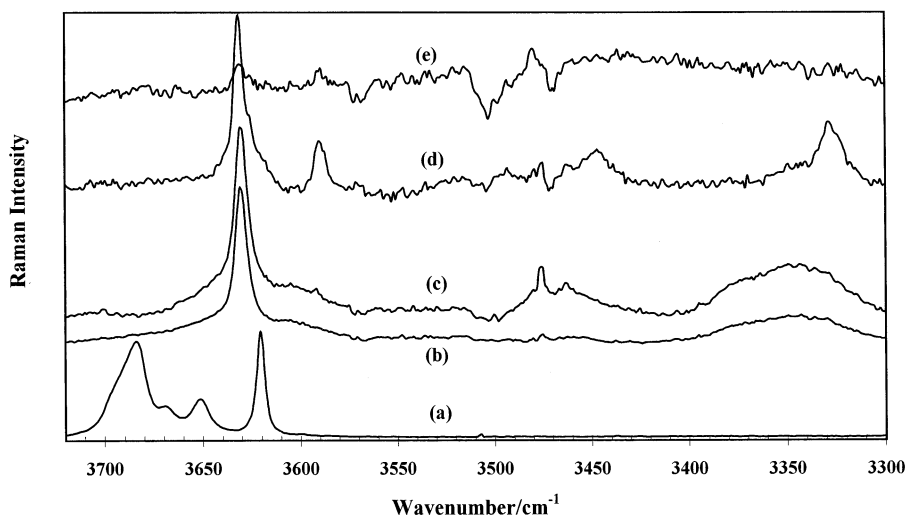


Fig. 6. Raman spectra of the hydroxyl-stretching region of: (a) untreated kaolinite; (b) formamide-intercalated kaolinite at 298 K; (c) formamide–water-intercalated kaolinite at 298 K; (d) formamide-intercalated kaolinite at 77 K; and (e) formamide–water-intercalated kaolinite at 77 K.

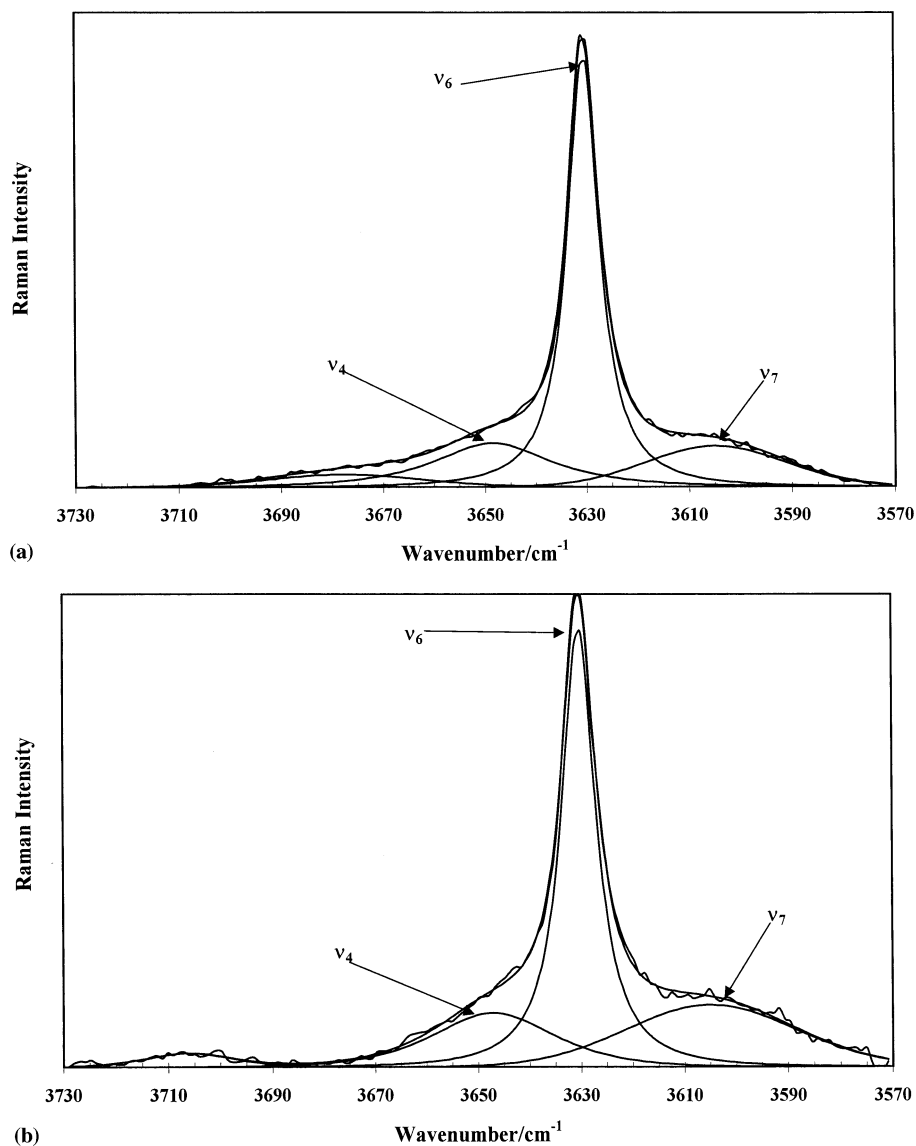


Fig. 7. (a) Band component analysis of the Raman spectrum of the hydroxyl stretching region of formamide-intercalated kaolinite. (b) Band component analysis of the Raman spectrum of the hydroxyl stretching region of formamide–water-intercalated kaolinite. (c) Band component analysis of the Raman spectrum of the hydroxyl stretching region of formamide–water-intercalated kaolinite at 77 K.

Raman and infrared active, involves only the hydrogen bonding of the formamide with the inner surface hydroxyls. The difference in the two peak positions is accounted for by the strength of the hydrogen bonds formed between the formamide or the formamide–water unit. The weaker hydrogen bonding results in the observa-

tion of the hydroxyl stretching bands at high frequencies (3648 cm^{-1} compared with 3630 cm^{-1}).

Upon obtaining the Raman spectra of the hydroxyl stretching region of the formamide–water intercalated kaolinite at 77 K, bands are observed at 3632 , 3625 and 3590 cm^{-1} with relative intensi-

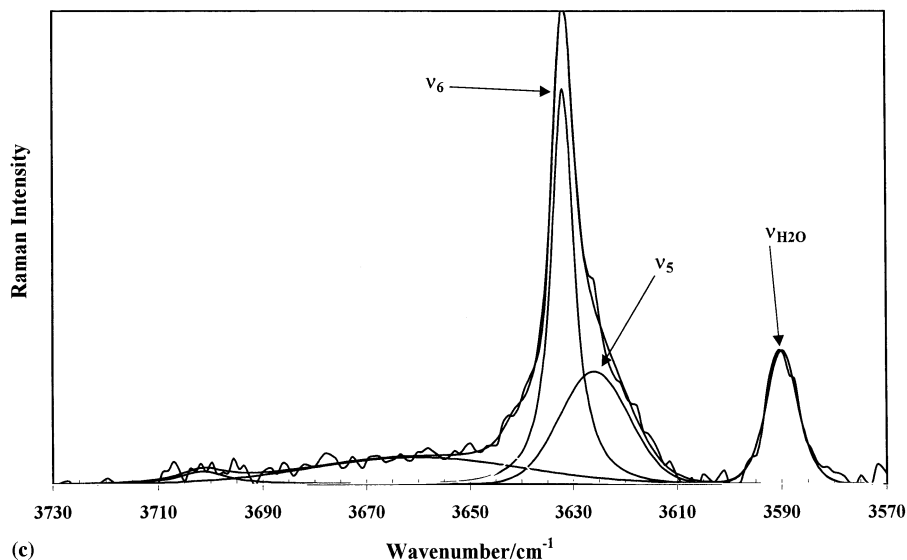


Fig. 7. (Continued)

ties of 37.1, 24.7 and 14.0%, respectively. It is noteworthy that by obtaining spectra at liquid nitrogen temperature, separation of the two coincident bands at 3630 cm^{-1} in the 298 K spectra occurs. Two bands are now observed at 3632 and 3625 cm^{-1} . It is only by obtaining the spectra at liquid nitrogen temperature that the two coincident bands at 3630 cm^{-1} can be separated. Firstly the bands become narrower and secondly the band attributed to the inner hydroxyl, frequency shifted from 3620 to 3630 cm^{-1} through the interaction of the lone pair of nitrogen electrons and the inner hydroxyl, becomes separated from the inner surface hydroxyl band at 3630 cm^{-1} frequency shifted to 3633 cm^{-1} . The other bands in the spectral profile are broad bands, which make up part of the base line. The ν_7 band has shifted from 3605 to 3590 cm^{-1} and the bandwidth decreased significantly from 31.7 to 7.1 cm^{-1} upon cooling to liquid nitrogen temperature. Two bands in the hydroxyl-stretching region are observed for the formamide-intercalated kaolinite at 3633 and 3588 cm^{-1} . These bands correspond well with the bands for the formamide–water-intercalated kaolinite. However, the spectrum of the hydroxyl-stretching region of the formamide-intercalated kaolinite at liquid ni-

trogen temperature is of such poor quality, that further inferences cannot be made. The fact that the 3628 cm^{-1} band shifts to 3633 cm^{-1} upon reaching liquid nitrogen temperature suggests that this band is attributable to the inner surface hydroxyls hydrogen bonded to the formamide. Such shifts have been previously observed for intercalation complexes with DMSO and formamide studied by the authors [19,20].

3.5. Spectroscopy of the NH stretching region

When kaolinite is intercalated with an inserting molecule such as formamide, not only do changes occur in the spectrum of the kaolinite, significant changes in the spectrum of the inserting molecule also occur. Table 2 reports such changes to formamide upon its insertion between the kaolinite layers. The infrared spectrum of formamide shows very broad bands centred at 3365, 3184, and 3027 cm^{-1} attributed to the NH stretching vibrations [5,6]. Upon intercalation of kaolinite with formamide, bands are observed at 3460, 3344, 3248 and 3167 cm^{-1} with relative intensities of 33.7, 53.5, 1.9 and 7.7%. The bands at 3460 and 3344 cm^{-1} are attributed to the NH stretching vibration of the NH involved with hydrogen bonded to

Table 2
Results of the band component analysis of the DRIFT and Raman spectra of the NH stretching region of kaolinite intercalated with 100% formamide and with 50% formamide/50% water mixtures

Kaolinite	Spectrum	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
100% Formamide only	DRIFT	Band centre cm ⁻¹ % Area Bandwidth					3365		3027	3184
		cm ⁻¹					Broad		Broad	Broad
100% Formamide intercalated kaolinite	DRIFT	Band centre cm ⁻¹ % Area Bandwidth			3460			3344	3248	3167
		cm ⁻¹						53.5 59.9	1.9 24.8	7.7 36.4
50% Formamide–water intercalated kaolinite	DRIFT	Band centre cm ⁻¹ %Area Bandwidth		3457			3340	3242	3177	3106
		cm ⁻¹					51.0 152.0	5.9 55.1	17.6 81.0	17.0 108.0
100% Formamide intercalated kaolinite	RAMAN at 298 K	Band centre cm ⁻¹ % Area Bandwidth		3522	3463		3376	3341		
		cm ⁻¹					22.5 36.2	59.4 49.2		
50% Formamide–water intercalated kaolinite	RAMAN at 298 K	Band centre cm ⁻¹ % Area Bandwidth		3522	3476	3454	3375	3342		
		cm ⁻¹					15.2 30.0	52.8 45.3		
50% Formamide–water intercalated kaolinite	Raman at 77 K	Band centre cm ⁻¹ % Area Bandwidth		3524	3485	3449	3379	3350	3327	
		cm ⁻¹					1.4 15.0	12.5 24.7	44.5 21.9	

the oxygens of the kaolinite siloxane surface. It is suggested that the NH bonds are involved in two different conformations with different hydrogen bond strengths. It is proposed that the two molecular arrangements involve the intercalation of the formamide with and without water. The concept of two such conformations fits well with the observation of two hydrogen-bonded hydroxyl bands at 3648 and 3628 cm^{-1} as is observed in the DRIFT spectra. Here it is argued that the 3648 cm^{-1} band results from the intercalation of formamide with water and the 3628 cm^{-1} band from the intercalation of formamide only. The NH bands at 3248 and 3167 cm^{-1} are probably due to non-hydrogen bonding NH units.

When the kaolinite is intercalated with a formamide–water mixture, bands are observed at 3457, 3340, 3242, 3177 and 3106 cm^{-1} with relative intensities of 5.4, 51.0, 5.9, 17.6 and 17.0%. Significant differences in intensity of the NH bands are observed between the two intercalates. The 3460 cm^{-1} band intensity decreases from 33.7 to 5.4%. The intensity of the $\approx 3340 \text{ cm}^{-1}$ band remains unchanged but significantly increases in the 3242, 3177 and 3106 cm^{-1} bands are observed. It is suggested that for the formamide–water intercalate, the high energy conformation is minimised and significant NH groups are not hydrogen bonded. The additional 3106 cm^{-1} band, which may correspond with the very broad 3028 cm^{-1} band of formamide, is attributed to NH units hydrogen bonded to water. The Raman spectra of the NH stretching region for the formamide-intercalated kaolinite show bands at 3463, 3376 and 3341 cm^{-1} with relative intensities of 8.2, 22.5 and 59.4%. Some intensity is also observed for bands at 3550 and 3522 cm^{-1} . These bands are attributed to water molecules in the intercalation complex. It is suggested that the band at 3463 cm^{-1} is the antisymmetric stretching mode, which is strong in the DRIFT spectrum but weak in intensity in the Raman spectrum. The band observed at 3376 cm^{-1} is due to the symmetric NH stretching mode, which is observed in the Raman spectrum but not in the infrared spectrum. The Raman spectrum of the formamide–water intercalated kaolinite shows bands at 3476, 3454, 3375 and

3342 cm^{-1} with relative intensities of 18.7, 13.8, 15.2 and 52.8%. Upon cooling to liquid nitrogen temperature, the Raman spectrum of the formamide–water intercalated kaolinite shows bands at 3485, 3449, 3379, 3350 and 3327 cm^{-1} with relative intensities of 9.0, 28.1, 1.4, 12.5, and 44.5%.

It is suggested that by obtaining the spectra at liquid nitrogen temperature, the bands at 3476, 3375 and 3342 cm^{-1} shift to 3449, 3350 and 3327 cm^{-1} . In addition it appears the 3476 cm^{-1} band splits into two bands at 3485 and 3449 cm^{-1} . Both the Raman and DRIFT spectra show significant changes in the molecular structure of the NH units upon intercalation with formamide.

3.6. DRIFT spectroscopy of the hydroxyl deformation modes

Another means of studying the changes in the structure of kaolinite upon intercalation with formamide is the complementary study of the hydroxyl deformation mode [16]. These bands are centred on 915 cm^{-1} [16]. The spectra of the hydroxyl deformation modes are shown in Fig. 8. The band component analysis of the DRIFT spectra of the formamide-intercalated and formamide–water-intercalated kaolinites are shown reported in Table 3. For the low defect kaolinite three deformation bands are observed at 939, 924 and 913 cm^{-1} with relative intensities of 1.0, 11.0 and 57.7%. The 913 cm^{-1} band is attributed to the hydroxyl deformation modes of the inner hydroxyl and 924 and 939 cm^{-1} bands to the hydroxyl deformation modes of the inner surface hydroxyl groups. Upon intercalation of the kaolinite with formamide, bands are observed at 971, 913 and 905 cm^{-1} . A second band fit with only two bands at 971 and 905 cm^{-1} also gives a good fit. So the question arises as to which fit is correct. The first fit is the more logical with the band at 913 cm^{-1} assigned to the hydroxyl deformation of the inner hydroxyl with the second component at 905 cm^{-1} attributed to the inner surface hydroxyl deformation mode. The second fit suggests that there is only one band at 905 cm^{-1} . This fits well with the observation of only one band at 3628 cm^{-1} in the hydroxyl-stretching

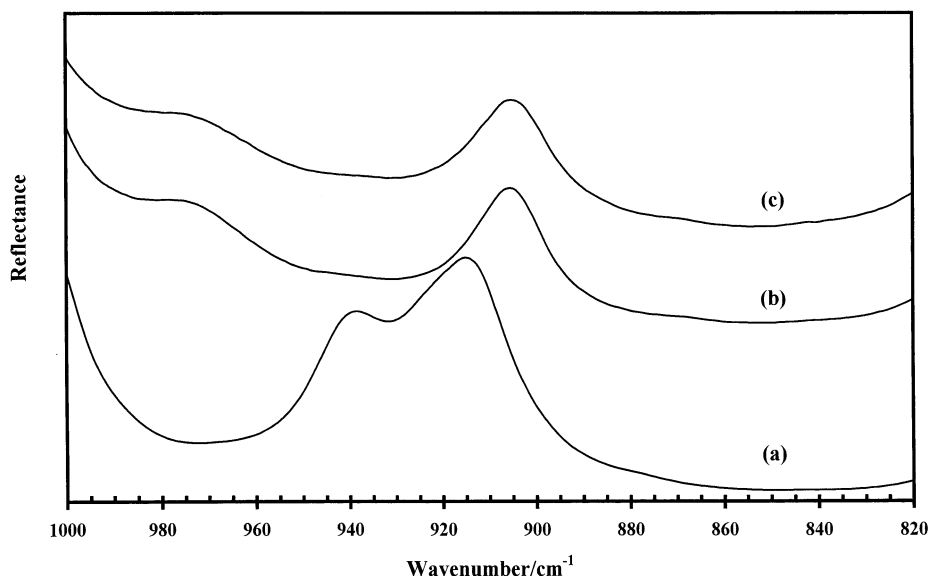


Fig. 8. DRIFT spectra of the hydroxyl deformation modes of: (a) kaolinite; (b) formamide-intercalated kaolinite; (c) formamide–water-intercalated kaolinite.

Table 3

Results of the band component analysis of the DRIFT spectra of the hydroxyl deformation region of the ordered and disordered kaolinites and their formamide intercalates

Kaolinite		Formamide	$\nu_{1-\text{def}}$	$\nu_{2-\text{def}}$	$\nu_{3-\text{def}}$	$\nu_{4-\text{def}}$
Low defect	Band centre cm^{-1}		939	924	913	
	% Area		31.0	11.0	57.7	
	Bandwidth cm^{-1}		18.4	14.9	15.0	
100% Formamide intercalated kaolinite	Band centre cm^{-1}	971			913	905
	% Area	13.6			11.6	74.8
	Bandwidth cm^{-1}	15.0			17.1	15.5
50% Formamide–water intercalated kaolinite	Band centre cm^{-1}	971			913	905
	% Area	11.7			11.3	77.0
	Bandwidth cm^{-1}	16.0			16.8	16.7

region. Thus the argument would be that both the inner and inner surface hydroxyl deformation modes occur at 905 cm^{-1} . The relative intensities of the 971 , 913 and 905 cm^{-1} bands are 13.6, 11.6, and 74.8%, respectively. Significantly the intensities of the bands attributed to the hydroxyl deformation of the inner surface hydroxyls at 939 and 924 cm^{-1} are reduced in intensity to 0.0%. Thus as with the hydroxyl stretching frequencies, the intensity of the hydroxyl deformation vibrations of the inner surface hydroxyls have been reduced to zero intensity. Such a finding fits well

with the XRD data which showed the kaolinite was fully intercalated with formamide.

An additional band at 905 cm^{-1} with 74.8% of the total intensity is attributed to the hydroxyl deformation vibration of the inner surface hydroxyls hydrogen bonded to the C=O of the formamide [17]. The band at 971 cm^{-1} is attributed to an out-of plane CH wag [17]. The major advantage of using the hydroxyl deformation modes is that these bands are not overlapped with the water OH and amide NH stretching bands. When the kaolinite is intercalated with the 50% for

amide–water mixture, bands are observed at similar positions. The relative intensities of the 971 cm^{-1} band decreased from 13.6 to 11.7% and the relative intensity of the 905 cm^{-1} band increased from 74.8 to 77.0%. The fact that the 905 cm^{-1} band increased in intensity with the increased concentration of water may suggest that this band is associated with the bonding of water or at least a bonding of a formamide–water complex.

3.7. Amide and water bands

The best means of identifying the presence of water in the intercalates is to determine the water bending vibration at 1630 cm^{-1} . One of the difficulties in studying the water-bending region of amide-intercalated kaolinites is the overlap of some of the amide bands with the water bending vibration. The DRIFT spectra of the $1500\text{--}1800\text{ cm}^{-1}$ region of the form amide-intercalated kaolinites are shown in Fig. 9 and the results reported in Table 4. In the DRIFT spectra of the formamide intercalated kaolinites bands are observed at 1700 , and 1671 cm^{-1} and are attributed to the amide 1 (1715 cm^{-1}) and amide 2 vibra-

tions (1674 cm^{-1}) [18]. The 1700 cm^{-1} band is attributed to the C=O stretching vibration. The normal position of the C=O band is between 1640 and 1680 cm^{-1} . A substantial shift in this frequency is observed upon intercalation of the formamide into the kaolinite. The bands at 1695 and 1674 cm^{-1} are attributed to the NH deformation of a primary amide [17,18]. The band observed at 1674 cm^{-1} belongs to NH deformation vibration. The band at 1630 cm^{-1} is attributed to adsorbed water. The remaining band observed at 1595 cm^{-1} is attributed to the HOH bending frequency of water, i.e. of non-hydrogen bonded water molecules. Liquid water normally has a band at 1630 cm^{-1} . It is concluded that the water is not hydrogen bonded and simply functions as a space-filling molecule in the expanded interlayer space. The relative intensity of the 1630 cm^{-1} band is 5.6% for the formamide-intercalated low defect kaolinite. In the XRD discussion above, spaces in the form amide-intercalated kaolinites were suggested. The role of the nonhydrogen-bonded water may well fill these spaces. A similar set of results is obtained for the formamide–water-intercalated high defect kaolinite. However the intensity of the 1595 cm^{-1} band is significantly

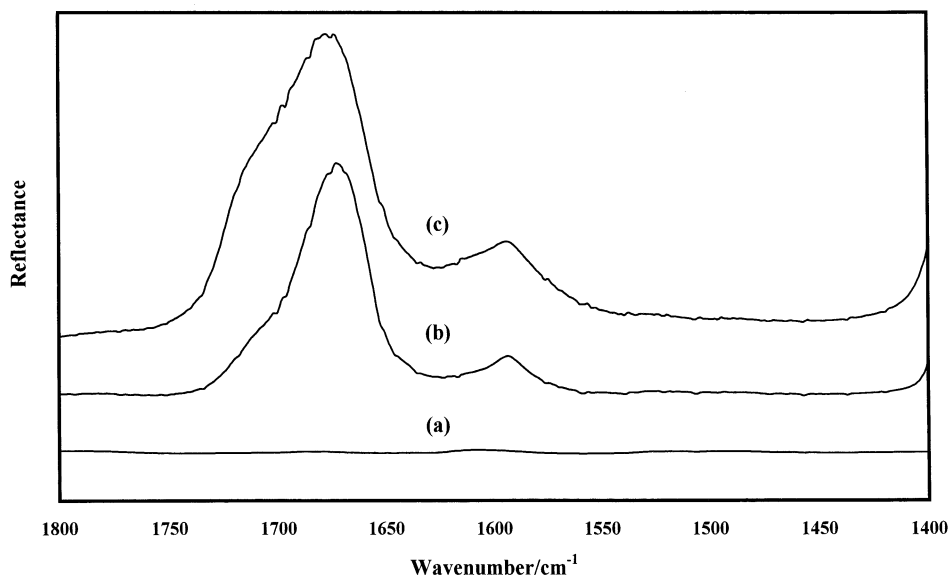


Fig. 9. DRIFT spectra of the water bending modes for: (a) kaolinite; (b) formamide intercalated kaolinite; (c) formamide–water-intercalated kaolinite.

Table 4
Results of the band component analysis of the DRIFT spectra of the 800–1000 cm⁻¹ region of kaolinite intercalated with 100% formamide and with 50% formamide–water mixture

Kaolinite	Spectrum	Formamide C=O stretch	NH def	NH def	$\nu_{\text{H}_2\text{O}-1}$	$\nu_{\text{H}_2\text{O}-2}$	$\nu_{\text{H}_2\text{O}-2}$
100% Formamide intercalated kaolinite	DRIFT	Band centre cm ⁻¹	1700	1671	1630	1595	
		% Area	24.7	58.4	5.6	11.1	
		Bandwidth cm ⁻¹	38.6	30.0	42.1	24.2	
50% Formamide–water intercalated kaolinite	DRIFT	Band centre cm ⁻¹	1710	1675	1630	1595	
		% Area	23.9	48.9	5.5	21.7	
		Bandwidth cm ⁻¹	35.2	39.2	36.9	44.1	
	DRIFT	Band centre cm ⁻¹			–1630		
		% area			100		
		Bandwidth cm ⁻¹			45.0		
100% Formamide intercalated kaolinite	Raman at 298 K	Band centre cm ⁻¹		1679	1665	1593	
		% Area		24.6	34.3	41.0	
		Bandwidth cm ⁻¹		28.0	20.0	15.3	
50% Formamide–water intercalated kaolinite	Raman at 298 K	Band centre cm ⁻¹		1693	1668	1591	
		% Area		29.4	25.5	45.1	
		Bandwidth cm ⁻¹		44.1	25.9	28.5	
50% Formamide–water intercalated kaolinite							
16.0	Raman at 77 K	Band centre cm ⁻¹		1690	1656	1595	1553
		% Area		22.4	23.6	16.0	37.5
		Bandwidth cm ⁻¹		54.4	30.5	23.2	48.2

greater as would be expected with the increased amount of water.

Two NH deformation vibrations are observed in the Raman spectrum of the formamide-intercalated kaolinite at 1679 and 1665 cm^{-1} with relative intensities of 24.6 and 34.3%. For the formamide–water-intercalated kaolinite, the bands are observed at 1693 and 1668 cm^{-1} with 29.4 and 25.5% relative intensity. No band was observed at the 1665 cm^{-1} position in the DRIFT spectrum, thus it is suggested that this band is a Raman active-infrared inactive in-plane NH deformation mode. Whereas the band at 1679 cm^{-1} is both Raman and infrared active and is attributed to the out-of-plane NH deformation mode. The band at 1593 cm^{-1} is attributed to the water-bending mode. It is unusual to observe this water band in the Raman spectrum. This suggests that the water deformation mode has a degree of symmetry and therefore shows Raman activity. Upon obtaining the Raman spectrum at liquid nitrogen temperature, bands are observed at 1690, 1656, 1595 and 1553 cm^{-1} with relative intensities of 22.4, 23.6, 16.0 and 37.5%. The out-of-plane NH deformation mode shows a shift of 3 cm^{-1} upon cooling to liquid nitrogen temperature, whereas the 1668 cm^{-1} band shifts to 1656 cm^{-1} . It is apparent that the water-bending mode shifts to 1553 cm^{-1} . It must be kept in mind that the water is interlayer water, which is non hydrogen bonded to other water molecules. This is why the hydroxyl stretching frequency occurs at the high frequency of 3595 cm^{-1} .

4. Conclusions

The intercalation of kaolinites with formamide can be followed by using a combination of X-ray diffraction, thermal analysis and spectroscopic techniques. X-ray diffraction provides information on the unit cell whereas vibrational spectroscopy provides information on the molecular structure of both the kaolinite and the inserting molecule. Intercalation of a low-defect kaolinite with formamide was found to be complete and caused an increase in the defect structures in the kaolinite. Upon intercalation of the kaolinite with

either formamide or formamide–water mixtures, additional infrared bands are observed at 3628 and 3606 cm^{-1} . The band at 3628 cm^{-1} is sharp and is attributed to the hydroxyl stretching frequency of the inner surface hydroxyls hydrogen bonded to the carbonyl group of the formamide. Even though a significant decrease in the intensity of the inner surface hydroxyls, and X-ray diffraction shows the kaolinite to be fully intercalated, some intensity of the hydroxyl stretching frequencies remain. The band at 3606 cm^{-1} was attributed to the hydroxyl frequencies of non-hydrogen bonded water involved in the intercalate structure. The Raman spectra of the formamide-intercalated kaolinites show no intensity in the bands attributed to the normal inner surface hydroxyl stretching frequencies. Only two bands were observed in the Raman spectra at 3630 and 3605 cm^{-1} attributed to the inner surface hydroxyls hydrogen bonded to the C=O group of the formamide and the inner hydroxyl, respectively.

Another means of showing changes in the kaolinite structure upon intercalation with formamide is to study, the hydroxyl deformation modes centred on 915 cm^{-1} . Intercalation results in the deformation modes occurring at frequencies below 915 cm^{-1} . The band observed at 905 cm^{-1} is assigned to the hydroxyl deformation vibration of the inner surface hydroxyls hydrogen bonded to the formamide carbonyl group. Water also plays a significant role in the intercalation process and is observed by band at 1595 cm^{-1} , which corresponds to the bending mode frequency of water vapour. Thus the water functions as a space-filling molecule as this frequency corresponds to non-hydrogen bonded water molecules. Intercalation of formamide into kaolinite provides a number of conformation structures for the incorporation of the formamide unit into the interlayer spaces of the kaolinite. Two interactions involving bonding of the formamide either through the carbonyl or lone pair of electrons is proposed. The effect of water content on the intercalation process is to increase the amount of formamide incorporated into the structure. The NH groups bond to the oxygens of the siloxane surface.

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