Clays and Clay Minerals, Vol. 34, No. 6, 635–644, 1986.

MOLECULAR MOTIONS, SURFACE INTERACTIONS, AND STACKING DISORDER IN KAOLINITE INTERCALATES

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Abstract—Intercalates of Georgia well-crystallized kaolinite with formamide, N-methylformamide (NMF), and dimethylsulfoxide (DMSO) were prepared at room temperature by dispersing the clay in the organic liquid. Several physical and chemical properties of the intercalated organic molecules and the clay, while intercalated and after de-intercalation, were examined using nuclear magnetic resonance (NMR), infrared (IR), and electron paramagnetic resonance spectroscopy (EPR), and specific heat (C_p) measurements. The chemical bonding between the inner-surface hydroxyls and the organic molecules, as indicated by IR, was strongest for DMSO and weakest for formamide. The distortion of the kaolinite layer, as shown by EPR, also was greatest for DMSO and least for formamide. NMR T_1 measurements indicated a relatively strong DMSO-kaolinite surface interaction that slowed down the methyl group reorientation comparable to that in bulk solid DMSO. T_1 measurements indicated a weaker interaction for NMF. De-intercalation by mild heating did not return the kaolinite to its original structural state as shown by EPR and C_p. The greatest disorder was found for the DMSO de-intercalate and the least for the formamide de-intercalate. These experiments show that for sufficiently strong bonding between the clay inner surface and the intercalating molecule, the structure of the clay is capable of distortion, which is partly temporary and partly permanent. The permanent changes probably involve the introduction of stacking faults.

Key Words—Dimethyl sulfoxide, Electron paramagnetic resonance, Formamide, Infrared spectroscopy, Intercalate, Kaolinite, N-methylformamide, Nuclear magnetic resonance, Specific heat.

INTRODUCTION

Study of the static and dynamic properties of an intercalated molecule can yield information about the environment of the molecules, and, indirectly, about the surface properties and structure of the clay. Few studies of intercalated kaolins have attempted to examine the range of time scales which are available with modern experimental techniques. Costanzo *et al.* (1984) and Lipsicas *et al.* (1985) used very long (X-ray powder diffraction and heat-capacity measurements), medium (nuclear magnetic resonance relaxation-time measurements), and very short (infrared absorption) time scales to study the static and dynamic properties of water intercalated into kaolinite. A similarly broad examination of the properties of intercalated organic molecules has not been carried out. This is unfortunate because of the importance of clay-organic interactions in catalysis and clay diagenesis, in the use of intercalation to distinguish types of kaolins, and perhaps, even in the origin of organic life.

The present study was designed to investigate the degree of interaction between a single kaolinite mineral and several organic intercalating molecules. The range of time scales was broad and included infrared (IR), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and heat capacity (C_p) measurements. The aim was to determine the relative strengths of interaction between the organic molecule and the clay over a wide time scale and to correlate these strengths with the properties of the organic molecules.

BACKGROUND

Infrared absorption spectroscopy (IR) has been traditionally used to estimate the strength of the bonding between clay minerals and intercalated molecules. Intercalated guest molecules may be perturbed by the close proximity of the clay, which will be reflected in shifts in the IR bands of the molecule. Similarly, the bands due to the inner-surface hydroxyls of a kaolin mineral will reflect changes due to the introduction of the intercalated molecules. Presumably, the greater the change in the IR bands upon intercalation, the stronger the bonding between the organic molecules and the clay.

Interaction between the organic molecule and its host clay can be seen in changes in the correlation times for molecular motions which are reflected in the nuclear spin relaxation times. Such changes have been shown for water in kaolinites (Lipsicas *et al.*, 1985) and halloysite (Cruz *et al.*, 1978).

Barrios *et al.* (1977) observed increased stacking disorder in kaolinite that resulted from a cycle of hydrazine intercalation and de-intercalation. No comparable study has investigated the relative effectiveness of different intercalating agents. In addition to X-ray powder

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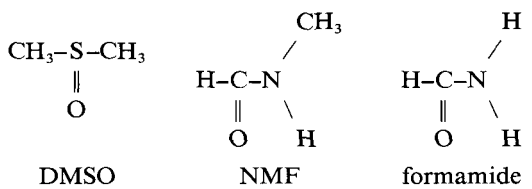
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diffraction and infrared spectroscopy, the degree of disorder in a kaolin mineral also can be seen, albeit indirectly, from measurements of the heat capacity (C_p). The changes in stacking order resulting from intercalation followed by de-intercalation can be readily followed in this manner.

Subtler changes in the structure of the kaolinite layers may be observed by techniques that rely on the symmetry of specific sites in the layers. One such technique that has been extensively exploited is electron paramagnetic resonance spectroscopy (EPR). The bulk of the EPR research to date deals with comparisons between kaolin samples from different localities having different chemical and structural properties (Mestdagh *et al.,* 1982). EPR is potentially useful in examining the changes which take place during intercalation; this application has not been previously exploited.

SAMPLE PREPARATION

Well-crystallized kaolinite from Georgia (KGa-1 from the Source Clay Repository of The Clay Minerals Society) was intercalated with dimethylsulfoxide (DMSO), N-methylformamide (NMF), and formamide. All intercalates had two molecules per unit cell.



Because the addition of small amounts of water accelerates the intercalation reaction (Olejnik *et al.,* 1968), all intercalates, except for the DMSO-intercalate studied by NMR, were prepared by dispersing 3 g of clay in 20 ml of an 8–9% water-organic solution. The suspensions were continuously stirred at 25°C for one week. The clay-organic suspensions are commonly heated to increase the rate of intercalation but, because heating may change the bonding between the clay and intercalated organic, the samples in this study were intercalated and then air dried under ambient conditions. XRD showed that all samples were at least 95% intercalated.

The presence of water in an intercalated clay is a problem for proton NMR experiments on organic molecules; the proton signal from the organic may be difficult to distinguish from that from water, and the water may perturb the organic molecular motions. To minimize these problems, one of the NMR samples was prepared using anhydrous DMSO; full intercalation required 36 days under a nitrogen atmosphere. The sample, dried under flowing nitrogen and then vacuum pumped at room temperature for several hours to remove excess DMSO, remained >95% intercalated, but about 15% of the total DMSO in the clay sample was present as non-intercalated bulk material. It was possible to discriminate against the proton signal of the non-intercalated DMSO inasmuch as the signal was relatively weak and had a short relaxation time that was essentially independent of temperature.

EXPERIMENTAL

Infrared spectroscopy

IR spectra were recorded with a PYE-UNICAM 3-300 double beam spectrometer. The samples were prepared as mulls with a fluorinated hydrocarbon, and the mulls were deposited on 1-mm-thick polycrystalline silicon discs.

Electron paramagnetic resonance

EPR measurements were made with a Varian E 109 spectrometer operating at X band (~9 GHz). The spectrometer was equipped with a Varian H_{011} cavity capable of variable temperature operation. The best spectral resolution was attained at 98 K; hence, only these results will be presented. Temperature cycling showed that the EPR signal at room temperature and at 98 K was completely reproducible. The EPR first derivative signal was accumulated and signal averaged in a DEC/MINC computer system.

Proton nuclear magnetic resonance

Proton NMR measurements of spin-lattice (T_1) relaxation times were made as a function of temperature with a Bruker CXP100 spectrometer. T_1 measurements on the NMF intercalate were carried out at 90 MHz and 25 MHz using a π–$\pi/2$ inversion pulse sequence. T_1 measurements on the DMSO were made at 90 MHz and 32 MHz using a saturation technique—a closely spaced sequence of $\pi/2$ pulses followed by a single $\pi/2$ "inspection" pulse. The choice of technique was determined by the magnetization decay of the samples.

Specific heat

C_p measurements were made with a Perkin-Elmer differential scanning calorimeter (DSC-2) equipped for low-temperature operation. Using liquid nitrogen as the coolant, the calorimeter operated easily between 110 and 300 K. The sample and reference assembly were enclosed in a glove box purged with dry nitrogen to prevent frost accumulation, and the sample and reference cups were flushed with dry helium.

The heat capacity of a sample was determined by comparing the power necessary to heat, individually, the sample and a standard material at a predetermined rate (Daniels, 1973). Benzoic acid (Fisher Certified Primary Standard for Calorimetry) was the standard, and its C_p values were taken from Ginnings and Furukawa (1953). A temperature calibration was made using the solid phase transition (186.1 K) and melting point (279.7 K) of high purity cyclohexane. At temperatures be-

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tween these transitions, temperatures are accurate to within 1 K; at other temperatures the error is probably less than 3 K.

Samples of the intercalated clay (5–10 mg) were weighed and hermetically sealed in aluminum sample pans. All scans were made at a heating rate of 5 K/min over a 2-K range. While heating at a constant rate, the difference between the power input to the sample and the benzoic acid is proportional to the difference in the heat capacities of the two materials. The power difference was measured by the displacement of the chart recorder pen at the end of the 2° scan with reference to the isothermal pen position at the same temperature. For each data point, at least three and as many as seven replicate measurements of the clay sample, the benzoic acid standard, and a blank (empty pan) were made. Erratic readings were discarded, and the mean of the remaining readings was used for the C_p calculation. To ensure that the intercalated clay was stable between 100 and 300 K, a complete scan from 300 to 100 K was made. No C_p anomalies were observed, and XRD showed that samples which had been cycled down to 100 K and back to 300 K were still intercalated. The C_p of the de-intercalated clay was measured using the intercalated clay sample after its sample pan was first carefully punctured and heated at 600 K for several hours to drive off the organic material. Overall accuracy of the technique, as estimated by measurements of high purity sapphire and indium, was in the range of 2–3%.

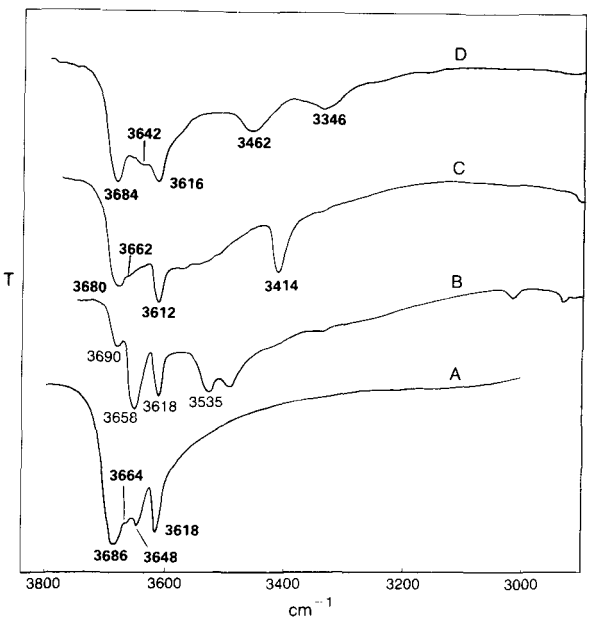


Figure 1. Infrared spectra of (A) Georgia well-crystallized kaolinite (KGa-1), (B) its intercalates with dimethylsulfoxide, (C) N-methylformamide, and (D) formamide. Samples were prepared as mulls with a fluorinated hydrocarbon on polycrystalline silicon discs.

RESULTS

Infrared spectroscopy

Because the 3686-, 3664-, and 3648-cm^{-1} bands are due to the inner-surface hydroxyls, they should be sensitive to changes in the interlayer bonding and should reflect any interaction between the hydroxyl surface and intercalated molecules. Compared with sample KGa-1, the spectrum of the DMSO intercalate (Figure 1B) is different in the 3700–3630-cm^{-1} region. The three inner-surface bands of the kaolinite have been replaced by two bands at 3690 and 3658 cm^{-1}, and the high frequency band is much reduced in intensity. The IR spectrum of the DMSO-kaolinite intercalate is essentially identical to that reported by Olejnik *et al.* (1968).

The NMF intercalate spectrum (Figure 1C) is similar to, but not identical with that reported by Cruz *et al.* (1969). The spectrum of Cruz *et al.* showed a strong, broad absorption between 3695 and 3550 cm^{-1}, whereas the sample examined in this study had a spectrum that more closely resembled that of the original kaolinite in the OH-stretching region (Figure 1A). The shift toward 3550 cm^{-1} of the kaolinite inner-surface OH vibrations in the Cruz *et al.* sample indicated that the bonding from the clay surface to the NMF molecules was stronger than in the intercalate of the present study.

Except for a weak band at about 3580 cm^{-1}, little difference was noted between the spectrum of the formamide-KGa-1 intercalate and that of sample KGa-1 in the OH-stretching region (Figure 1D), indicating that the hydrogen bonds from the hydroxyls to the organic molecule have the same strength as they have in the parent clay. On the other hand, the IR spectra of Cruz *et al.* (1969) show that the surface hydroxyls of their intercalated kaolinite were significantly perturbed.

The observed differences between the formamide and NMF intercalates of the present study and those of Cruz *et al.* probably result from different preparative procedures. Cruz *et al.* used a kaolinite-hydrazine intercalate as the starting material and replaced the hydrazine by exposure of the sample to heated NMF and formamide vapor. In the present study, the samples were intercalated directly from the liquid at room temperature.

Electron paramagnetic resonance

The EPR signal of kaolinite has been studied extensively by a number of workers (Angel *et al.*, 1974; Jones *et al.*, 1974; Meads and Maulden, 1975; Mesdagh *et al.*, 1982). The signal in the $g \approx 4$ region is due to Fe^{3+} in the high-spin state ($S = 5/2$). Four resonances have been observed in the $g \approx 4$ region; an isotropic line, referred to as I, with $g \approx 4.2$, and the E triplet with

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Table 1. Electron paramagnetic resonance results for Georgia well-crystallized kaolinite (KGa-1) untreated, intercalated (with dimethylsulfoxide (DMSO), N-methyl formamide (NMF), or formamide), and de-intercalated (by mild heating or methanol washing).

Sample	I line		
	Area (%)	Width (G)	g_I[3]
Untreated KGa-1 clay	30.6	185	4.23
Intercalated with DMSO	61.4	180	4.14
Intercalated with NMF	35.8	180	4.19
Intercalated with formamide	33.9	195	4.24
DMSO intercalate, heated[1]	41.7	190	4.20
DMSO intercalate, MeOH wash, 3 times	48.3	180	4.15
DMSO intercalate, MeOH wash, 6 times	43.3	203	4.19
DMSO intercalate, MeOH wash, 9 times	41.7	190	4.17
NMF intercalate, heated[2]	38.2	195	4.23
Formamide intercalate, heated[2]	34.7	195	4.24

[1] 110°C for 4 hr.
[2] 110°C for 48 hr.
[3] See text.

components $g_z \approx 4.7$, $g_x \approx 3.8$, and $g_y \approx 3.4$. Only at temperatures near 100 K have g_x and g_y been resolved. It is generally agreed that both E and I Fe substitute for Al in octahedral sites (Komusinski *et al.*, 1981). The I line is due to Fe^{3+} in an orthorhombic symmetry site, whereas the E lines are produced by Fe in higher symmetry sites. There is some disagreement in the literature regarding the correlation of the Fe^{3+} EPR signal with kaolinite crystallinity. One suggestion is that only the I line correlates with crystallinity (Mestdagh *et al.*, 1980), however, Jones *et al.* (1974) and Komusinski *et al.* (1981) suggested that both I and E lines reflect the state of crystallinity of the kaolinite.

The EPR first-derivative signal was integrated to give the EPR spectrum, which in turn was iteratively fitted to four Gaussian peaks by a least squares procedure. The solutions of the least squares equations were found to be unique for all samples, and the g values for the four peaks corresponded to the values expected for g_x, g_y, g_z, and g_I. The area of the peak corresponding to g_I (the area of the I line obtained from the Gaussian curve) was expressed as a percentage of the total area under the spectrum. In Table 1 the areas (%), width at half height, and g_I values for the untreated, intercalated, and de-intercalated clay are listed.

Intercalation led to an increase in the I line area, the increase being greatest for DMSO and least for formamide. De-intercalation of the DMSO intercalate led to a significant decrease in the I line area, but the residual value was appreciably greater than that of the untreated clay. De-intercalation of the NMF and formamide intercalates led to small and possibly insignificant increases in the I line area. The residual I line area for both intercalates was greater than that of the untreated clay. The g_I value for the untreated clay was very close to the values cited in the literature. Intercalation of DMSO produced a significant drop in g_I, and de-intercalation led to a residual value somewhat smaller than that of the untreated clay. The changes in the value of g_I following intercalation and de-intercalation of NMF and formamide were insignificant. The line width was not significantly affected by intercalation or de-intercalation by any of the organic molecules.

Nuclear magnetic resonance

Both the hydroxyl protons of the kaolinite and the protons of the intercalated molecules contribute to the observed proton NMR signal. Protons from the two sources can be discriminated because the signal from the hydroxyls decays very rapidly (within about 50 μs), leaving a signal which is entirely due to the intercalated molecules. This latter signal was studied as a function of temperature.

The NMR signal of DMSO is due to the methyl protons. The two methyl groups per molecule in pure DMSO solid are not crystallographically equivalent (Thomas *et al.*, 1966). Pajak *et al.* (1974) have shown that the two methyl groups reorient about their C_3 axes at different frequencies; two correspondingly different activation energies, 3.8 and 3.0 kcal/mole, were also determined. In the gas and liquid phases the two methyl groups are equivalent.

The mechanism of spin-lattice relaxation of the intercalated DMSO protons is a modulation of the proton dipolar interaction caused by reorientation of the methyl groups about their C_3 axes. Because the KGa-1 kaolinite contained about 900 ppm Fe^{3+}, proton dipolar interactions with these paramagnetic centers had to be considered as well as interactions between protons of the same or adjacent methyl groups. The Fe^{3+} ions occupy sites in the octahedral sheets of the clay layers and are close to the intercalated molecules. The spin-lattice relaxation rates for proton-proton and proton-paramagnetic ion interactions, respectively, are (Solomon, 1955):

$$\frac{1}{T_1} = C_1\left[\frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2\tau_c^2}\right] \quad (1)$$

$$\frac{1}{T_1} = C_2\frac{\tau_c}{1 + \omega_0^2\tau_c^2}, \quad (2)$$

where τ_c is the correlation time for the methyl group motion, $\omega = 2\pi\nu$, ν is the NMR Larmor frequency, and C_1 and C_2 are the respective mean-squared magnetic fields at the proton due to the dipolar interaction (the second moment). Eq. (1) predicts that the relaxation rate due to the proton-proton dipolar interaction reaches a maximum value at $\omega_0\tau = 0.62$. The corresponding minimum value of T_1 is

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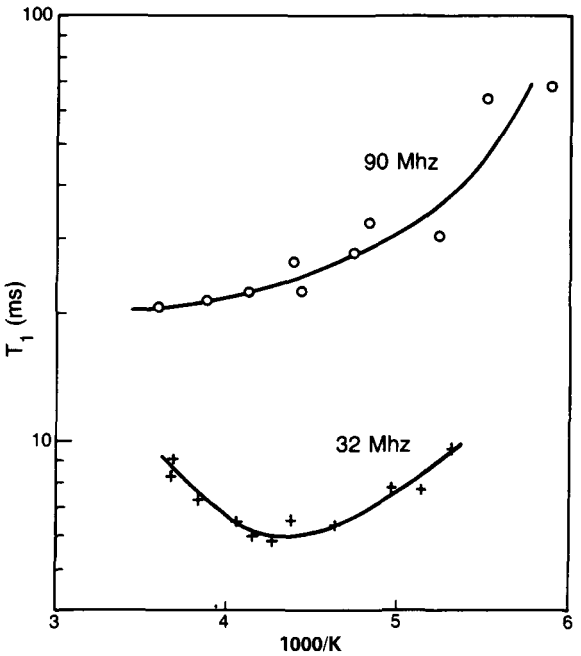


Figure 2. 90-MHz and 32-MHz values of T_1 for intercalated dimethylsulfoxide protons plotted against inverse temperature.

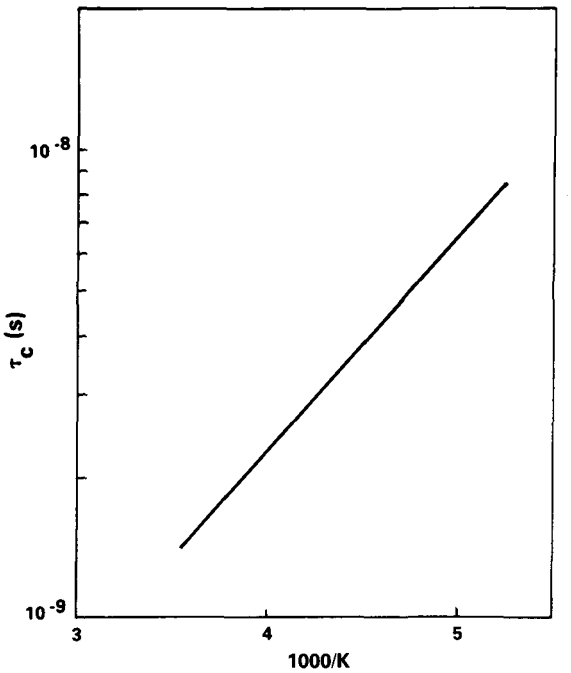


Figure 3. Correlation time, τ_c, for methyl group reorientation in intercalated dimethylsulfoxide plotted against inverse temperature. τ_c values were calculated from T_1 values as described in text.

$$(T_{1_{p-p}})_{min} = \frac{0.7\omega_0}{C_1} . \quad (3)$$

Similarly, from Eq. (2)

$$(T_{1_{para}})_{min} = \frac{2\omega_0}{C_2} , \quad (4)$$

but this occurs at $\omega_0\tau = 1$. In the $(T_1)_{min}$ regime, the correlation frequency $(1/\tau_c)$ of the methyl group reorientation is comparable with the NMR angular frequency, ω_0. Experimentally, the correlation frequency may be varied by varying the sample temperature, and the NMR frequency can be changed by changing the applied (Zeeman) magnetic field intensity.

The experimental values of the proton T_1 for the DMSO kaolinite intercalate are plotted as a function of 1000/T in Figure 2. The 90 MHz data showed that, over the experimental temperature range, the correlation frequency of the methyl group orientation was lower than ω_0 (=5.65 × 10^8 rad/s). By reducing the NMR frequency to 32 MHz (ω_0 = 2 × 10^8 rad/s), the same temperature range scanned the regime $\omega_0\tau_c < 1$ to $\omega_0\tau_c > 1$. A value of 6 × 10^{-3} s was obtained for $(T_1)_{min}$ at $1000/T_1 = 4.3$ (T = 233 K). Substituting this value into Eq. (3) yielded a value for C_1 of 2.3 × 10^{10} rad²/s². This second moment value compares with calculated values of 4.7 × 10^9 rad²/s² for a pair of methyl groups rapidly reorienting and 1.7 × 10^{10} rad²/s² for the "rigid lattice" second moment (Dufourq *et al.*, 1967). Thus, the value of the second moment, C_1, deduced from the experimental data for intercalated DMSO, is higher than expected if it were due entirely to proton-proton interactions. A more reasonable assumption is that there was an additional contribution from paramagnetic relaxation and that $1/T_1 = (1/T_1)_{p-p} + (1/T_1)_{para}$. Eq. (3) was used, however, with C_1 = 2.3 × 10^{10} rad²/s², to analyze the experimental data at 32 MHz so as to estimate the correlation times and activation energy for the methyl group reorientation. This approximation leads to an uncertainty in activation energy of about 10% or less and as much as a factor of two in τ_c. The correlation times deduced from the T_1 data are plotted against 1000/T in Figure 3. The activation energy for methyl group reorientation, deduced from the slope of the plot in Figure 3 is 2.1 kcal/mole. At 90 MHz, $(T_1)_{min}$ should have been observed when τ = 1.06 × 10^{-9} s which, according to Figure 3, corresponds to 1000/T = 3.25. This value is in reasonable agreement with the 90 MHz experimental data.

The T_1 minimum at 90 MHz appears to be broader than that at 32 MHz, and the estimated value of $T_{1_{min}}$ at this frequency is somewhat higher than that calculated from the ratio of the frequencies. This observation suggests a distribution of correlation times at each temperature associated with the 90 MHz measurements. The measurements at 32 MHz were made on the same sample as those at 90 MHz but several weeks later. During this interval, the intercalated molecules

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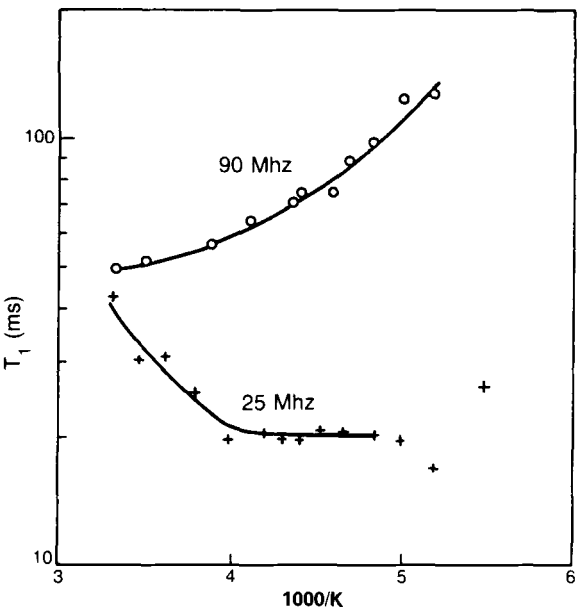


Figure 4. 90-MHz and 25-MHz values of T_1 for intercalated N-methylformamide protons plotted against inverse temperature.

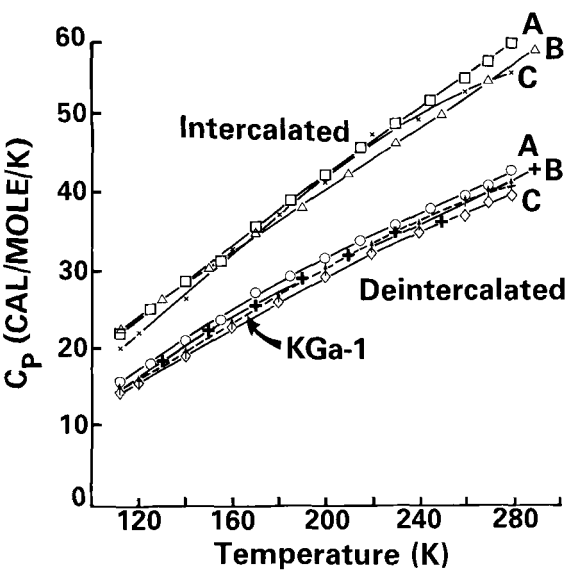


Figure 5. Heat capacity values for Georgia well-crystallized kaolinite (KGa-1) intercalated with (A) dimethylsulfoxide, (B) N-methylformamide, and (C) formamide (upper group of curves). Lower group of curves shows heat capacity of same intercalates after removal of organic molecules by mild heating. Fourth (dashed) curve in lower group shows heat capacity for untreated Georgia kaolinite.

may have reoriented, converting the disordered structure into a somewhat more ordered arrangement. As a result the bonding of the DMSO to the clay increased in strength, thereby narrowing the spectrum of correlation times (Resing, 1967).

No evidence was found in the 90-MHz and 32-MHz T_1 data for a second T_1 minimum region in the temperature range of the measurements, as would be expected if the two methyl groups of the intercalated DMSO were non-equivalent. A recent structure determination (Thompson and Cuff, 1985) of an ordered kaolinite : DMSO intercalate showed that the two methyl groups occupy very different sites in the interlayer region; one methyl group is keyed into the ditrigonal hole and the other lies between the interlayer bounding surfaces. The equivalence of the two methyl groups inferred from the T_1 data for the material studied in the present work suggests that the DMSO in the sample was disordered. Alternatively, the displacement of the two minima in temperature could have exceeded the temperature range of the measurements.

At room temperature, $\tau_c = 1.1 \times 10^{-9}$ s which corresponds to a reorientation frequency about four orders of magnitude lower than that of a free, classical methyl group rotor. At 230 K, the value of τ_c is comparable with that in solid DMSO at this temperature (Pajak *et al.*, 1974). Thus, reorientation of the methyl groups in DMSO was strongly hindered in the interlayer space. The inter-molecular proton-proton dipolar interaction and the deuteron quadrupolar interaction (for CD_3) for this strongly motionally hindered system is of great interest and is currently being studied by other NMR techniques.

The experimental values for the proton T_1 for the NMF kaolinite intercalate are plotted against 1/T in Figure 4. Interpretation of the proton measurements is considerably more difficult than for the DMSO intercalate, principally because of the presence of some intercalated water and the existence of protons on the carbon and nitrogen. The N–C bond has a substantial amount of double-bond character which inhibits free rotation about this axis. The signal strength and range of measured T_1 values strongly suggest that this proton relaxation is due to methyl protons. The main point of interest in Figure 4 is the flat minimum for T_1 measured at 25 MHz. As mentioned above, this indicates a distribution of correlation times for the methyl reorientation due to variations in the strength of the interaction of different molecules with the clay surface. The weaker interaction strength between NMF and the clay surface, as compared to DMSO, is consistent with the IR data outlined earlier.

Heat capacity

Heat capacity measurements were made for four groups of samples; the KGa-1 kaolinite intercalated with the three organic molecules, the same samples but heated to drive off the organic molecules, the bulk organic molecules, and the unreacted KGa-1 kaolinite. The C_p values of the intercalated and de-intercalated

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clays are shown in Figure 5 along with the C_p values of sample KGa-1. Each set of data points was fitted to a cubic equation. The intercalated and non-intercalated clays fall into two distinct groups; the intercalated clays having the larger C_p values at all temperatures. The vertical distance between the data sets is proportional to the C_p of the intercalated molecules. The measured heat capacities increase smoothly with increasing temperature, as expected.

The ranking of the intercalated clays (upper group of curves in Figure 5) in terms of C_p has no special significance because they are different materials. All three materials show nearly the same slope at low temperatures, and the DMSO and NMF intercalates are subparallel throughout the temperature range. The heat capacity of the formamide intercalate rises less rapidly at temperatures greater than 220 K. Inasmuch as formamide is physically the smallest of the three molecules, the rollover of the C_p may be due to a more rapid increase in molecular motion compared to the larger molecules.

The lower group of curves in Figure 5 shows the variation of C_p vs. temperature for the three de-intercalated clays and the original KGa-1 sample. All four curves have the same general form: a monotonic, nearly linear increase of C_p with increasing temperature. The process of intercalation followed by de-intercalation changes the C_p of the KGa-1 clay; the change is different for each organic molecule. The C_p values for sample KGa-1 treated with DMSO are consistently higher than the C_p values for the untreated clay; the values for the NMF treated KGa-1 sample are not significantly different from the original clay, and the formamide sample has a smaller heat capacity than the original clay.

Cruz *et al.* (1978) showed that the C_p of intercalated molecules can be derived from the heat capacities of the intercalated and de-intercalated clay. For an intercalated clay, clay(int), having weight fraction of guest molecule, x, the weight fraction of clay is $(1 - x)$ and $C_p(\text{int}) = (1 - x)C_p(\text{clay}) + xC_p(\text{guest})$. Using this procedure, the C_p values for the intercalated organics were determined. These values are plotted in Figure 6 along with C_p measurements of the three organics in bulk form. No special effort was made to purify the formamide, NMF, or DMSO. All contained small amounts of water, as verified by IR.

All three organics are solids at temperatures <225 K. The heat capacity of the bulk DMSO increased nearly linearly with temperature to about 220 K where it began to rise rapidly as melting began. The great increase in C_p made it impossible to continue the measurements to >260 K. A similar behavior was shown by both formamide and NMF at the lowest temperatures, but each underwent what is probably a two-step melting of a eutectic mixture followed by the melting

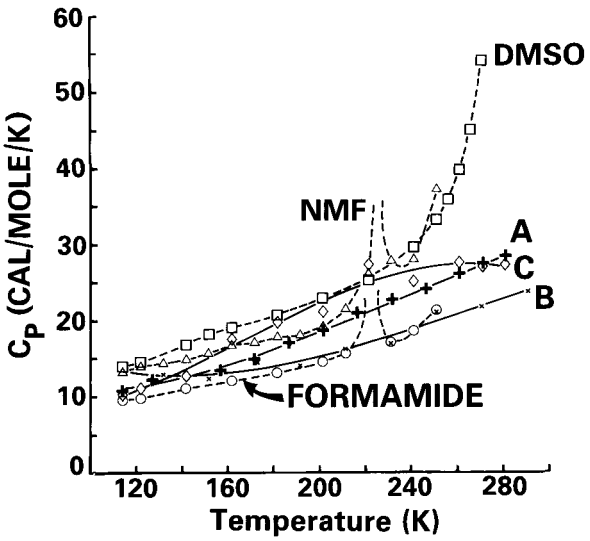


Figure 6. Comparison of heat capacities of bulk organics (dashed lines) with values calculated for intercalated molecules as described in text; (A) dimethylsulfoxide (+); (B) N-methyl formamide (×); (C) formamide (◇).

of the remaining organic molecules. The low-temperature endotherm was at ~220 K for formamide and at ~225 K for NMF. At higher temperatures, both produced large endotherms. As with DMSO, the increase in C_p at the higher temperatures was so great that measurements could not be made.

The curves of C_p vs. T for the intercalated organic molecules do not show the phase changes that are present in the curves of the bulk organic liquids. The absolute values of C_p for the intercalated molecules differed from the bulk values, two being lower (DMSO and NMF) and one higher (formamide). These differences could be an artifact due to the fact that the C_p for the silicate part of the intercalated kaolinite (i.e., C_p of the clay) is not really known; this quantity was estimated by the C_p for the de-intercalated clay and is subject to some uncertainty (Sposito and Prost, 1982). Another possible complication resulted from the fact that the amount of water in the bulk organic was likely to be different than that in the intercalated clay. Even if the absolute values of C_p for the intercalated organic molecules were not very meaningful, the change in C_p with temperature is. The absence of endothermic reactions in the intercalated organics is valid and is important in understanding the bonding of organic molecules to the clay matrix.

DISCUSSION

DMSO is an aprotic, highly associated liquid at room temperature. NMF has a single protic hydrogen and, because of the extra methyl group, is larger than the formamide molecule. The latter has two protic hydrogens on the nitrogen. All three molecules contain an

https://doi.org/10.1346/CCMN.1986.0340603 Published online by Cambridge University Press

oxygen making them good hydrogen bond acceptors. In general, the bonding from the clay to the organic molecule involves the inner-surface hydroxyls which bond to the carbonyl oxygen, and, for NMF and formamide, the protic hydrogen on the molecule can donate a hydrogen bond to the basal oxygens of the adjacent kaolinite surface. Thus, the environment about the intercalated molecules is highly different from that found in the bulk liquid or, at low temperatures, the bulk solid. In view of the different chemical and physical properties of the molecules and the probable differences in the way in which they are attached to the kaolinite surfaces when intercalated, it is not surprising that the present study indicates that the three molecules interact to different degrees with the clay surface. The observed differences between the clay surface interaction with DMSO and with the other organic molecules, however, are striking.

Each of the experimental techniques examined a different time scale and different parts of the organic-clay system. Thus, no single technique was capable of describing all the properties of the intercalated kaolinite. The IR results show the following: (1) The perturbation of the inner-surface hydroxyls on kaolinite was greatest for intercalated DMSO and least for intercalated formamide. These results are consistent with the facts that the electron donor character of the oxygen of DMSO (i.e., the basicity of DMSO) is considerably greater than that of either of the other two molecules, and that the basicity of the amides should increase with increasing number of methyl groups. (2) The spectra for the NMF and formamide of this study and those reported by Cruz *et al.* (1969) are different. The samples examined in the present study were significantly less perturbed than those of Cruz *et al.* The simplest explanation of these differences is that the two-stage intercalation process used by Cruz *et al.,* along with the mild heating they used to promote intercalation, substantially increased the strength of the hydrogen bonding between the inner-surface hydroxyls and the intercalated molecules. The increase in bonding strength resulting from mild heating indicates that heating increases the order of the intercalated molecules in the interlayer space as has already been demonstrated for kaolinite : DMSO (Thompson and Cuff, 1985) and halloysite : DMSO (Costanzo and Giese, 1986).

The precise orientations of the formamide, NMF, and DMSO molecules in disordered kaolinite intercalates are not known. Cruz *et al.* (1969) proposed two alternative orientations for the formamide and NMF molecules, each with a different hydrogen bonding scheme: one orientation placed the C=O bond perpendicular to the clay surface allowing two hydrogen bonds to form from the hydroxyl and only one hydrogen bond being formed. The difference between the two orientations is about 30°, and for each the carbonyl oxygen is the hydrogen bond acceptor. The molecular orientations with respect to the *a* and *b* axes were not specified. Based on steric considerations, Cruz *et al.* (1969) proposed that the C–N parallel orientation would be most likely for formamide while the C=O bond perpendicular orientation would be preferred by NMF. This orientation has been confirmed by crystal structure studies of dickite : formamide (Adams and Jefferson, 1976) and dickite : NMF (Adams, 1979) intercalates. These two structures show, however, that both orientations allow three hydrogen bonds to form, based on interatomic distances. In disordered intercalates of the three molecules examined here, it is reasonable to assume that each molecule adopted about the same orientation with respect to the clay layers as in the ordered structure. Thus, the lack of three dimensional order is probably due to an orientational disorder of the molecules with respect to *a* and *b*.

The EPR results of the present work show that the width of the I line and the g value for the line did not vary significantly, but that the area of the I line (expressed as a percentage of the total area) varied substantially due to the intercalation of DMSO. The increase was smaller for NMF, and still smaller for formamide. Inasmuch as the EPR signal was directly related to the symmetry of the octahedral sites of the kaolinite, the introduction of the DMSO between the kaolinite layers clearly changed the local symmetry more than did either NMF or formamide. The increase in I area (and a concomitant decrease in E area) indicates that intercalation resulted in a lowering of site symmetry for many of the Fe^{3+} ions. These structural changes argue for a much stronger interaction between the hydroxyl surface of the kaolinite and the DMSO molecules. Gradual removal of the DMSO by repeated washing of the fully intercalated clay with methanol (as indicated by a shift in the 001 XRD peak) resulted in a gradual decrease in the area of the I line from the fully intercalated value (61.4% of the total area) to a value (41.7%) substantially greater than that noted for the original clay (30.6%). Heating the intercalate to drive off the DMSO also resulted in an I line area substantially greater than that of the original clay. Some DMSO could have remained between the kaolinite layers, but the XRD and IR data indicated that such was not the case.

The EPR results show that the structure of the kaolinite layer was perturbed the most by DMSO intercalation, and that the residual perturbation of the structure after de-intercalation was greatest for the DMSO intercalate. Hence, NMF was more disruptive than formamide, but the difference was much less than the effects created by the intercalation of DMSO.

A detailed proton NMR study of the three molecules intercalated into the KGa-1 kaolinite is complex and beyond the scope of this investigation. It would require

https://doi.org/10.1346/CCMN.1986.0340603 Published online by Cambridge University Press

partial deuteration of the molecules in order to separate the behavior of different protons on the same molecule. T_1 measurements for the protons of the intercalated DMSO molecules showed that the methyl group reorientation was hindered to about the same extent as in solid bulk DMSO. Correlation times of $\sim 10^{-9}$ s and an activation energy of 2.1 kcal/mole were determined for this motion. A weaker molecule-surface interaction for the NMF kaolinite intercalate was indicated by the flat minimum for T_1 observed for this intercalate. Thus, the NMR data gave additional evidence for the stronger bonding of DMSO to the surface than NMF and provided quantitative information on the concomitant slowing down of the reorientation of intercalated methyl groups.

Figures 5 and 6 show that the C_p values for the de-intercalated kaolinites are ordered, with DMSO the largest and formamide the smallest. The difference in C_p is not great but, in view of the corroborating evidence from IR and EPR, it is significant. The observation that the de-intercalated DMSO sample had a greater C_p than the other de-intercalated samples suggests that the introduction of the DMSO followed by its loss on heating resulted in a permanent increase in the disorder of the stacking of kaolinite layers much as was observed by Barrios *et al.* (1977) for a kaolinite : hydrazine intercalate. The degree of disorder created by the intercalation-de-intercalation process could not be discerned from the C_p measurements alone.

The lack of phase changes in the C_p values for the intercalated molecules indicates that they were held rather strongly by the kaolinite surfaces and were not able to freely rotate and translate as they would have in the bulk. These results are in agreement with the NMR results of this study and are similar to the observations of the properties of water intercalated in kaolinite (Costanzo *et al.,* 1984; Costanzo *et al.,* 1982; Lipsicas *et al.,* 1985).

CONCLUSIONS

The examination of several chemical and physical properties of both the organic and clay constituents of intercalated kaolinites under a variety of time scales indicates that the strength of bonding between the clay and the organic molecules varies from one molecular species to the other. The order of strength of bonding is consistent with the electron donor character of the oxygen on the three molecules, i.e., with their basicity with respect to the oxygen. Furthermore, the stronger the bonding between the organic molecules and the clay, the greater the deformation of the clay layer while intercalated and after de-intercalation. An increase in layer stacking faults in the de-intercalated kaolinite with increasing strength of bonding is also evident. Slowing down of methyl-group reorientation due to intercalation was also observed; in DMSO the slowing down was comparable to that in the bulk solid.

The formation of bonds between the organic molecules and the clay is, at least in the molecules studied, sensitive to the temperature at which intercalation was performed, probably related to the degree of order of the intercalated molecules in the interlayer voids.

ACKNOWLEDGMENT

The research was partially supported by the National Science Foundation through grants EAR8213888 and EAR8307685 to R.F.G. and P.M.C.

REFERENCES

Adams, J. M. (1979) The crystal structure of a dickite : N-methylformamide intercalate [$Al_2Si_2O_5(OH)_4HCON \cdot HCH_3$]: *Acta Crystallogr.* **B35,** 1084–1088.

Adams, J. M. and Jefferson, D. A. (1976) The crystal structure of a dickite : formamide intercalate $Al_2Si_2O_5(OH)_4 \cdot HCONH_2$: *Acta Crystallogr.* **B32,** 1180–1183.

Angel, B. R., Jones, J. P. E., and Hall, P. L. (1974) Electron spin resonance studies of doped synthetic kaolinite. I: *Clay Miner.* **10,** 247–255.

Barrios, J., Plançon, A., Cruz, M. A., 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. and Giese, R. F. (1986) Ordered halloysite : dimethyl sulfoxide intercalate: *Clays & Clay Minerals* **34,** 105–107.

Costanzo, P. M., Giese, R. F., and Lipsicas, M. (1984) Static and dynamic structure of water in hydrated kaolinites: Part I. The static structure: *Clays & Clay Minerals* **32,** 419–428.

Costanzo, P. M., Giese, R. F., Lipsicas, M., and Straley, C. (1982) Synthesis of a quasi-stable kaolinite and capacity of interlayer water: *Nature* **296,** 549–551.

Cruz, M., Laycock, Z., and White, J. L. (1969) Perturbation of OH groups in intercalated kaolinite donor-acceptor complexes. I. Formamide-, methyl formamide-, and dimethyl formamide-kaolinite complexes: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1,* L. Heller, ed., Israel Univ. Press, Jerusalem, 775–789.

Cruz, M., Letellier, M., and Fripiat, J. J. (1978) NMR study of adsorbed water. II. Molecular motions in the monolayer hydrate of halloysite: *J. Chem. Phys.* **69,** 2018–2027.

Daniels, T. (1973) *Thermal Analysis:* Wiley, New York, 272 pp.

Dufoureq, J., Chezeau, J.-M., and Lemanceau, B. (1967) Etude par résonance magnétique du mouvement des groupes méthyles du diméthylsulfoxyde solide: *C. R. Acad. Sci. Paris* **265,** 761–764.

Ginnings, D. C. and Furukawa, G. (1953) Heat capacity standards for the range 14–1200°K: *J. Amer. Chem. Soc.* **75,** 522–527.

Jones, J. P. E., Angel, B. R., and Hall, P. L. (1974) Electron spin resonance studies of doped synthetic kaolinite. II: *Clay Miner.* **10,** 257–270.

Komusinski, J., Stoch, L., and Dubiel, S. M. (1981) Application of electron paramagnetic resonance and Mössbauer spectroscopy in the investigation of kaolinite-group minerals: *Clays & Clay Minerals* **29,** 23–30.

Lipsicas, M., Straley, C., Costanzo, P. M., and Giese, R. F. (1985) Static and dynamic structure of water in hydrated kaolinites: Part II. The dynamic structure: *J. Coll. Interface Sci.* **107,** 221–230.

https://doi.org/10.1346/CCMN.1986.0340603 Published online by Cambridge University Press

Meads, R. E. and Malden, P. J. (1975) Electron spin resonance in natural kaolinites containing Fe^{3+} and other transition metal ions: *Clay Miner.* **10,** 313–345.

Mestdagh, M. M., Herbillon, A. J., Rodrique, L., and Rouxhet, P. (1982) Evaluation du rôle du fer structural sur la cristallinite des kaolinites: *Bull. Mineral.* **105,** 457–466.

Mestdagh, M. M., Vielvoye, L., and Herbillon, A. J. (1980) Iron in kaolinite: II. The relationship between kaolinite crystallinity and iron content: *Clay Miner.* **15,** 1–13.

Olejnik, S., Aylmore, L. A. G., Posner, A. M., and Quirk, J. P. (1968) Infrared spectra of kaolin mineral-dimethyl sulfoxide complexes: *Clay Miner.* **8,** 421–434.

Pajak, Z., Jurga, K., and Jurga, S. (1974) Molecular dynamics of solid dimethylsulfoxide studied by NMR pulse technique: *Acta Physica Polonica* **A45,** 837–842.

Resing, H. A. (1967) Nuclear magnetic resonance relaxation of molecules adsorbed on surfaces: in *Adv. Molecular Relaxation Processes* **1,** 109–154.

Solomon, I. (1955) Relaxation processes in a system of two spins: *Phys. Review* **99,** 559–565.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on smectites: *Chem. Reviews* **82,** 553–573.

Thomas, R., Shoemaker, C. B., and Klaas, E. (1966) The molecular and crystal structure of dimethyl sulfoxide, $(H_3C)_2SO$: *Acta Crystallogr.* **21,** 12–20.

Thompson, J. G. and Cuff, C. (1985) The crystal structure of the kaolinite : dimethysulfoxide intercalate: *Clays & Clay Minerals* **33,** 490–500.

(Received 17 December 1985; accepted 9 September 1986; Ms. 1549)

https://doi.org/10.1346/CCMN.1986.0340603 Published online by Cambridge University Press