

INTERPRETATION OF SOLID STATE ^{13}C AND ^{29}Si NUCLEAR MAGNETIC RESONANCE SPECTRA OF KAOLINITE INTERCALATES

JOHN G. THOMPSON

Geology Department, James Cook University of North Queensland
Townsville, Queensland 4811, Australia

Abstract— ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy with magic-angle spinning has been used to study the short-range ordering and bonding in the structures of intercalates of kaolinite with formamide, hydrazine, dimethyl sulfoxide (DMSO), and pyridine-*N*-oxide (PNO). The ^{29}Si chemical shift indicated decreasing levels of bonding interaction between the silicate layer and the intercalate in the order: kaolinite: formamide ($\delta = -91.9$, ppm relative to tetramethylsilane), kaolinite: hydrazine (-92.0), kaolinite: DMSO (-93.1). The ^{29}Si signal of the kaolinite: PNO intercalate (-92.1) was unexpectedly deshielded, possibly due to the aromatic nature of PNO. The degree of three-dimensional ordering of the structures was inferred from the ^{29}Si signal width, with the kaolinite: DMSO intercalate displaying the greatest ordering and kaolinite: hydrazine the least. ^{13}C resonances of intercalating organic molecules were shifted downfield by as much as 3 ppm in response to increased hydrogen bonding after intercalation, and in the kaolinite: DMSO intercalate the two methyl-carbon chemical environments were non-equivalent ($\delta = 43.7$ and 42.5).

Key Words—Dimethylsulfoxide, Formamide, Hydrazine, Intercalate, Nuclear magnetic resonance, Ordering, Pyridine-*N*-oxide.

INTRODUCTION

Solid-state ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS/NMR) spectroscopy has proven to be sensitive to the short range ordering of minerals. In particular, the ^{29}Si chemical shift in synthetic and natural silicates and aluminosilicates is sensitive to: (1) the chemical nature of the atoms directly attached to oxygens of the silicate tetrahedra, also described as the second coordination sphere of silicon (Lippmaa *et al.*, 1980; Mägi *et al.*, 1981); (2) interatomic distances (Smith and Blackwell, 1983; Higgins and Woessner, 1982) and angles (Smith and Blackwell, 1982); and (3) hydrogen bond strength (Thompson, 1984b). Solid state ^{13}C MAS/NMR, however, has not provided significantly more information than was available from solution studies, though a chemical shift non-equivalence not observable in solution has commonly been observed in the solid (Wasylishen and Fyfe, 1982).

In this present work the above two techniques have been combined to investigate further the structures of and bonding in a selection of well-documented kaolinite intercalates: kaolinite:formamide (Adams *et al.*, 1976; Ledoux and White, 1966), kaolinite:dimethyl sulfoxide (DMSO) (Jacobs and Sterckx, 1970; Olejnik *et al.*, 1968; Sanchez and Gonzalez, 1970), kaolinite:pyridine-*N*-oxide (PNO) (Olejnik *et al.*, 1971; Weiss and Orth, 1973), and kaolinite:hydrazine (Weiss *et al.*, 1963; Ledoux and White, 1966). Solid-state ^{13}C and ^{29}Si MAS/NMR spectroscopy should provide complementary information to the infrared spectroscopic data and to the one- and three-dimensional structural data

already obtained. Conversely, the infrared and structural data should be indispensable in the interpretation of the NMR data.

EXPERIMENTAL

The material chosen for intercalation was kaolinite #4, Oneal pit, Macon, Georgia, supplied by Ward's Natural Science Establishment, Rochester, New York. It was chosen for its low iron content ($<0.5\%$ as Fe_2O_3), and narrow ^{29}Si NMR resonance (signal width at half height ($\Delta\nu_{1/2}$) = 83 Hz). This kaolinite is relatively poorly crystallized, with a Hinckley crystallinity index of 0.43 (Hinckley, 1963), and was found to intercalate more readily than well-crystallized kaolinites. The measured cation-exchange capacity (CEC) is 11.2 meq/100 g of kaolinite. The only contaminating phase present is about 5% smectite ($d = 14.8 \text{ \AA}$).

The intercalates with formamide (kaolinite:formamide), DMSO (kaolinite:DMSO), and hydrazine (kaolinite:hydrazine) were prepared by immersing the clay in the pure reagent (lab. grade) at 60°C for 2 weeks, 1 week, and 24 hr, respectively. The first two products were subsequently dried at 60°C for 48 hr and then left to stand for several weeks. The hydrazine intercalate, due to its instability in air, was prepared and dried immediately prior to analysis. The intercalate with PNO (kaolinite:PNO) was prepared by entrainment with hydrazine; i.e., kaolinite:hydrazine was saturated in liquid PNO at 70°C for 24 hr, and dried at 100°C for 24 hr to evaporate the hydrazine. The excess PNO was removed by rapid washing with chloroform.

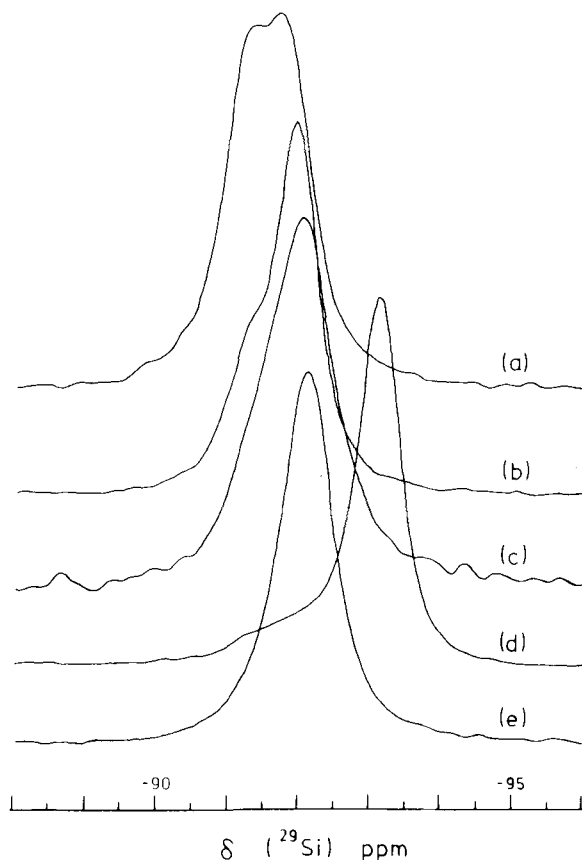


Figure 1. ^{29}Si CP/MAS NMR spectra of (a) untreated Georgia kaolinite, (b) kaolinite:formamide, (c) kaolinite:hydrazine, (d) kaolinite:DMSO, and (e) kaolinite:PNO intercalates. Spectra were obtained at 59.61 MHz on a Bruker CXP-300 spectrometer using ^1H and ^{29}Si r.f. fields of 10 and 50 G, respectively. Samples were packed in Delrin rotors and spun at 3–4 kHz. The spectra (b)–(e) display minor contributions from unexpanded kaolinite at $\delta = -91.5$.

The process of intercalation was monitored by X-ray powder diffraction (XRD) analysis with a Rigaku horizontal, wide-angle goniometer diffractometer (model No. CN2155DS) using Mn-filtered $\text{FeK}\alpha$ radiation. Intercalation of the kaolinite was greater than 90% for all compounds, with each kaolinite intercalate displaying a residual 7.17-Å reflection in the XRD pattern. The basal reflections for the four intercalates were: kaolinite:formamide 10.1 Å, kaolinite:hydrazine 10.4 Å, kaolinite:DMSO 11.2 Å, kaolinite:PNO 12.6 Å. The level of intercalation and magnitude of the basal spacing for each of the four intercalates are in good agreement with the results of the authors mentioned above.

Solid state NMR spectra were collected on a Bruker CXP-300 NMR spectrometer at the Brisbane NMR Centre, Griffith University, Queensland. ^{29}Si spectra

Table 1. ^{29}Si NMR chemical shifts and signal widths at half height ($\Delta\nu_{1/2}$).

	Chemical shift (ppm relative to TMS)	$\Delta\nu_{1/2}$ (Hz)
Georgia kaolinite	-91.5	83
Kaolinite:formamide intercalate	-91.9	50
Kaolinite:hydrazine intercalate	-92.0	71
Kaolinite:DMSO intercalate	-93.1	43
Kaolinite:PNO intercalate	-92.1	55

were obtained at 59.61 MHz. Cross-polarization with magic-angle spinning (CP/MAS) was used with r.f. fields for ^1H and ^{29}Si of 10 and 50 kHz, respectively. Approximately 200 free induction decays (f.i.d.) were collected with an experimental repeat time of 10 sec. For the ^{13}C spectra, obtained at 75.46 MHz, both CP/MAS and dipolar ^1H decoupling (DD/MAS) were employed. The CP/MAS experiments were performed with r.f. fields for ^1H and ^{13}C of 12.5 and 50 G, respectively. In each experiment between 150 and 350 f.i.d.s were collected with a repeat time of 2 sec for CP/MAS and 5 sec for DD/MAS. The ^{13}C solution spectra were obtained at 15.0 MHz on a JEOL JNM FX60Q NMR spectrometer with ^1H decoupling.

RESULTS

The ^{29}Si NMR spectra of the four kaolinite intercalates are displayed in Figure 1 together with the corresponding spectrum of the untreated Georgia kaolinite. Kaolinite exhibits two ^{29}Si resonances (Barron *et al.*, 1983b) which have been explained by either differences in hydrogen bond interactions or by differences in Si–Al distances (Thompson, 1984a). The latter explanation was supported by the recent refinement of the kaolinite structure by Switch and Young (1983). The coeval refinement by Adams (1983), however, arrived at a different result using another kaolinite and favored neither of the above explanations. The ^{29}Si spectra of the kaolinite intercalates all exhibit a single resonance. The chemical shift of the ^{29}Si resonances relative to tetramethylsilane (TMS) for each of the intercalates is listed in Table 1 together with the width at half height of each signal ($\Delta\nu_{1/2}$) in Hz. The degeneracy of the silicon environments by expansion of the kaolinite structure further suggests that Si–Al interactions between the layers is the principal cause of silicon site differentiation.

The ^{13}C NMR spectra of the three kaolinite:organic intercalates are shown in Figures 2–4; both the cross-polarized (CP/MAS) and dipolar ^1H decoupled (DD/MAS) spectra are presented. Under the experimental conditions described above, the ^{13}C resonances of the intercalated organic molecules were enhanced in the CP/MAS spectra, whereas the DD/MAS spectra allowed all of the resonances to be observed, particularly

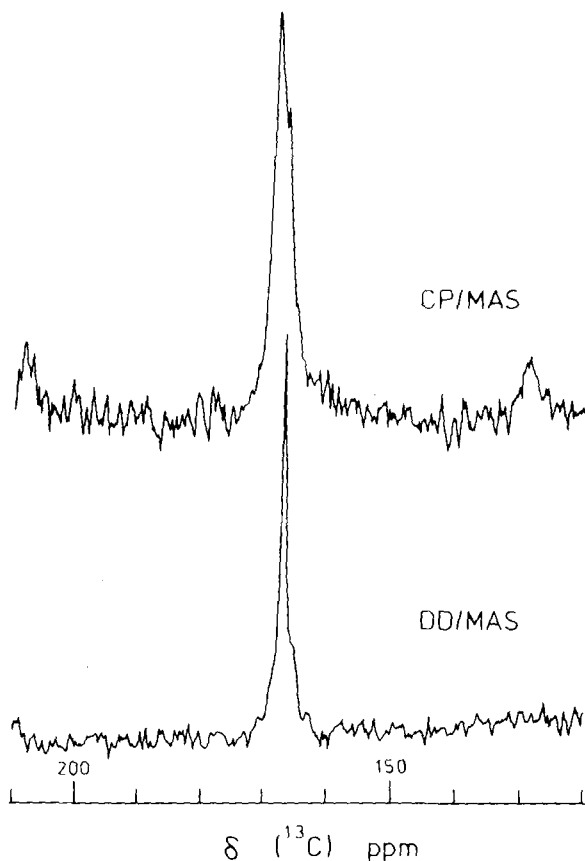


Figure 2. ^{13}C DD/MAS and CP/MAS spectra of the kaolinite:formamide intercalate. The former displays a strong resonance at $\delta = 166.7$ due to adsorbed formamide, with a shoulder at $\delta = 164.8$ resulting from residual liquid formamide. In the latter, the strong resonance at $\delta = 168.2$ is due to intercalated formamide, with lesser contributions from the adsorbed and liquid formamide.

those due to adsorbed and excess (more mobile) organic molecules.

The kaolinite:formamide intercalate displays three resonances (Figure 2). The resonance at $\delta = 164.8$ (relative to TMS) is due to excess formamide and corresponds to a literature value of $\delta = 164.9$ (Stothers, 1972). The resonance at $\delta = 166.7$, which dominates the DD/MAS spectrum, is due to formamide adsorbed via the amine functional group. The resonance dominating the CP/MAS spectrum at $\delta = 168.2$ is that of the intercalating formamide bonded at each end. Broadening of this ^{13}C resonance is likely due to ^{14}N quadrupolar coupling, as described by Hexem *et al.* (1981).

The spectrum of the kaolinite:DMSO intercalate similarly displays three resonances. The resonance at $\delta = 40.3$, more intense in the DD/MAS spectrum, is due to excess DMSO and corresponds within experimental error with the literature value of $\delta = 40.4$ (Stothers, 1972). The resonances at $\delta = 43.7$ and 42.5

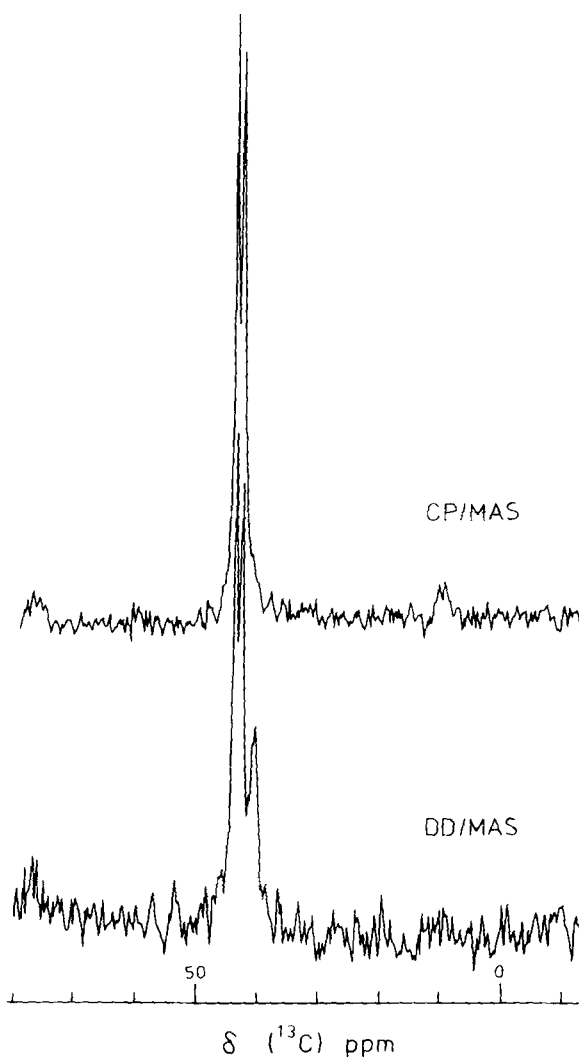


Figure 3. ^{13}C DD/MAS and CP/MAS spectra of the kaolinite:DMSO intercalate. Both spectra display resonances at $\delta = 43.7$ and 42.5 due to nonequivalent methyl carbon chemical environments. The signal due to residual DMSO at $\delta = 40.3$ is enhanced in the DD/MAS spectrum.

of almost equal intensity are those of the intercalating DMSO.

The ^{13}C CP/MAS spectrum of the kaolinite:PNO intercalate displays strong resonances at $\delta = 137.4$ and 128.2 , together with several weaker signals. With reference to solution ^{13}C NMR data for PNO (Anet and Yavari, 1976), the strong signals are assigned to the α - and β -carbons, respectively, in the kaolinite:PNO intercalate. The DD/MAS spectrum of kaolinite:PNO, displaying signal pairs at $\delta = 139.4$ and 137.6 , and $\delta = 127.1$ and 125.6 , is almost identical to the DD/MAS spectrum of pure, solid PNO (not shown) suggesting that this spectrum is completely dominated by residual PNO carbon resonances.

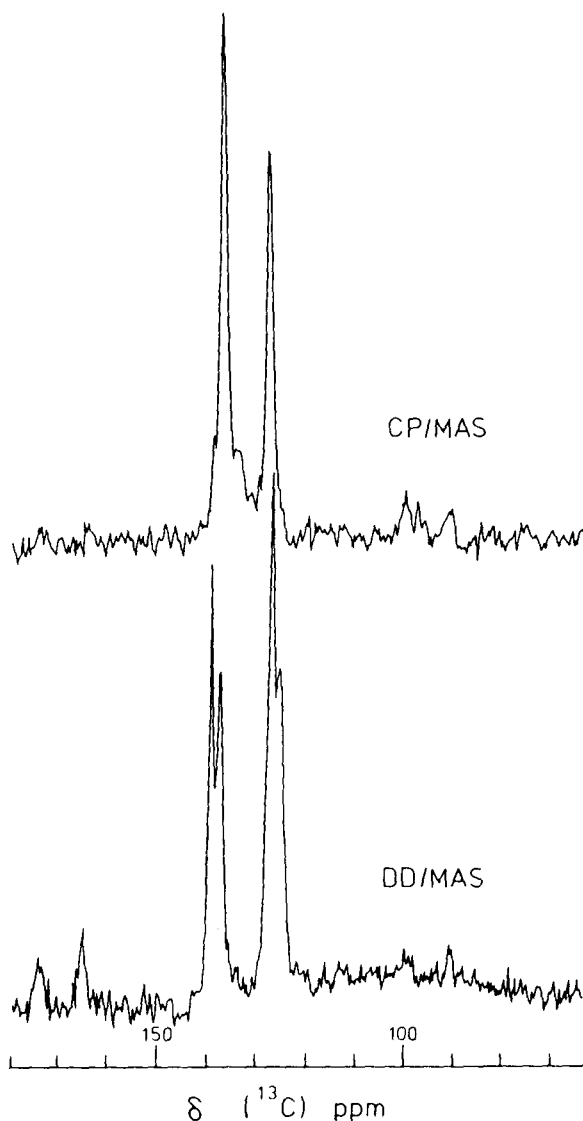


Figure 4. ^{13}C DD/MAS and CP/MAS spectra of the kaolinite:PNO intercalate. In the CP/MAS spectrum the resonances at $\delta = 13.74$ and 128.2 are assigned to the α - and β -carbons of kaolinite:PNO, respectively. The DD/MAS spectrum is completely dominated by residual PNO carbon resonances with signal pairs at $\delta = 139.4$ and 137.6 , and $\delta = 127.1$ and 125.6 .

DISCUSSION

Kaolinite:formamide intercalate

In the ^{29}Si spectrum of the kaolinite:formamide intercalate (Figure 1), the strong signal at $\delta = -91.9$ is due to the intercalate with a downfield shoulder at $\delta = -91.5$ from residual Georgia kaolinite. The added shielding is interpreted as a weakening of the hydrogen bond interaction with the tetrahedral layer and therefore a lessening of the electron-withdrawing effect on the tetrahedrally coordinated silicon atoms. Similar

effects have been observed in alkylammonium-smectite complexes (Thompson, 1984b).

Structural studies on kaolinite:formamide (Adams *et al.*, 1976) and dickite:formamide intercalates (Adams and Jefferson, 1976) suggested the existence of only one hydrogen bond per formamide molecule with the adjacent tetrahedral silicate layer. The recently refined structure of kaolinite (Sutch and Young, 1983) indicated that all of the inner-surface hydroxyls appear to bond to the adjacent layer. This decrease in the number of hydrogen bonds upon intercalation with formamide is a plausible explanation of the observed added shielding. Alternatively, the difference in nuclear shielding of ^{29}Si can be explained in terms of the relative electronegativities of oxygen and nitrogen, the O-H...O hydrogen bond being stronger than the N-H...O bond. Similar weak N-H...O hydrogen bonds have been observed in primary alkylammonium-vermiculite complexes (Laby and Walker, 1970).

The observed ^{13}C spectra of the kaolinite:formamide intercalate and the other organic intercalates are most easily interpreted by comparison with the shifts of the organic compounds observed in dilute solution of deuterated solvents, typically chloroform. Difficulties arise, however, when trying to compare these spectra with the chemical shifts observed in the pure organic compound. These difficulties are not surprising considering that factors influencing ^{13}C chemical shifts are at best only qualitatively understood (Wehrli and Wirthlin, 1978).

Infrared studies of the kaolinite:formamide intercalate (Ledoux and White, 1966) demonstrated a net increase in hydrogen bond participation by formamide on intercalation relative to dilute formamide in chloroform. In the present study a deshielding of the ^{13}C resonance at $\delta = 168.2$ was observed compared with $\delta = 165.6$ for dilute formamide in deuterated chloroform. The downfield shift due to increased hydrogen bonding for the carbonyl carbon in formamide agrees well with recent work on hydroxybenzaldehydes (Imashiro *et al.*, 1983). Taken alone, this evidence suggests a direct relationship between ^{13}C deshielding and hydrogen bond strength; however, consideration of the ^{13}C resonance in pure formamide indicates otherwise. Infrared data (Ledoux and White, 1966) have shown that the hydrogen bonds in pure formamide are significantly stronger than in the kaolinite:formamide intercalate. Contrary to the relationship implied above, the ^{13}C resonance in pure formamide is not further deshielded but occurs upfield by 3.3 ppm ($\delta = 164.9$).

Clearly, no simple relationship applying to all systems exists between ^{13}C NMR resonance and the level of hydrogen bonding. Some justification exists, however, for inferring such a relationship between the carbonyl ^{13}C resonance of dilute formamide in chloroform and that of the kaolinite:formamide intercalate. Obviously in pure formamide very significant amide-res-

onance effects are present which are reflected in the differences in formamide bond lengths observed between the solid (Ladell and Post, 1954) and the dickite intercalate (Adams and Jefferson, 1976).

Kaolinite:hydrazine intercalate

The ^{29}Si spectrum of the kaolinite:hydrazine intercalate displayed a single resonance at $\delta = -92.0$ (Figure 1) which is significantly broader ($\Delta\nu_{1/2} = 71$ Hz) (Table 1) than those of the kaolinite:formamide ($\Delta\nu_{1/2} = 50$ Hz), kaolinite:DMSO ($\Delta\nu_{1/2} = 43$ Hz), and kaolinite:PNO intercalates ($\Delta\nu_{1/2} = 55$ Hz). The ^{29}Si chemical shift was not significantly different from that of the kaolinite:formamide intercalate, suggesting similar N-H . . . O hydrogen bonding interactions. The increased signal width, however, probably corresponded to a greater variation in the chemical environment of the silicon nuclei. This greater variation is interpreted as a decrease in three-dimensional ordering of this intercalate compared with the kaolinite:formamide intercalate. Such an interpretation is consistent with the one-dimensional Fourier projections of the two intercalates obtained by Weiss *et al.* (1963), which indicated a double layer of oriented hydrazine molecules. Also, the greater mobility of the small hydrazine molecules in the kaolinite:hydrazine intercalate would contribute to a decrease in ordering.

Kaolinite:DMSO intercalate

The ^{29}Si spectrum of the kaolinite:DMSO intercalate displayed a narrow ($\Delta\nu_{1/2} = 43$ Hz) resonance at $\delta = -93.1$. The narrowness of this resonance suggests a high degree of equivalence of the silicon chemical environments, which is consistent with three-dimensional ordering within the structure. The observed chemical shift of the kaolinite:DMSO ^{29}Si resonance was identical to that of halloysite at $\delta = -93.1$ (Mägi *et al.*, 1981), though significantly deshielded relative to pyrophyllite at $\delta = -95.0$ (Mägi *et al.*, 1981). In pyrophyllite only relatively weak ionic and van der Waals interactions (Giese, 1975) are present, whereas in halloysite, interlayer water hydrogen bonds to the tetrahedral silicate layers (Hendricks and Jefferson, 1938) and results in a deshielding of the ^{29}Si resonance. The ^{29}Si chemical shift observed in the kaolinite:DMSO intercalate supports the existence of a bonding (electron-withdrawing) interaction stronger than van der Waals forces alone as suggested by Adams (1978). Such bonding interaction would be between the sulfur and the oxygens of the tetrahedral silicate layer, as the existence of C-H . . . O hydrogen bonds is not supported (see Tensmeyer *et al.*, 1960). Orientation of the DMSO molecule with the sulfur-oxygen bond approximately normal to the *ab* plane, as proposed by Adams (1978) and Jacobs and Sterckx (1970), provides optimum sulfur-oxygen distances, although this orientation results

in the methyl groups being unacceptably near to the silicate layer.

The ^{13}C spectra of kaolinite:DMSO (Figure 3) displayed a free DMSO resonance at $\delta = 40.3$ and two methyl resonances, of almost equal intensity, from intercalated DMSO deshielded by 3.4 and 2.2 ppm. The deshielding of the ^{13}C nuclei paralleled the observations for the kaolinite:formamide intercalate. The two equally intense methyl carbon resonances at $\delta = 43.7$ and 42.5 were due to nonequivalent chemical environments. In the liquid state the two methyl carbons are chemically equivalent. Additionally, a solid state ^{13}C NMR study by Pines *et al.* (1972) did not discern inequivalence in nuclear shielding of the two methyl carbons, though more recent ^1H NMR lineshape studies have detected methyl group inequivalence in the solid state (Ripmeester, 1981). It is likely that when DMSO is complexed with kaolinite the two methyl groups are held in chemically nonequivalent positions, paralleling the explanation of the two ^{29}Si resonances observed for untreated kaolinite (Thompson, 1984a). Alternatively, in the solid state, the two methyl carbons are nonequivalent due to a difference in C-S bond lengths as in solid DMSO (0.05 Å) (Thomas *et al.*, 1966). Either way, the absence of the symmetric $\nu(\text{CS})$ vibration (Olejnik *et al.*, 1968) in the infrared spectrum of the intercalate can be interpreted as having resulted from a lowering of the DMSO symmetry after intercalation.

The interpretation of the OH-stretching bands in kaolinite and its intercalates is often a matter of conjecture. For the kaolinite:DMSO intercalate, however, the formation of the uncharacteristically sharp peaks at 3658, 3535, and 3499 cm^{-1} (Olejnik *et al.*, 1968) suggests the formation of relatively strong and regular hydrogen bonds between the inner-surface hydroxyls and the sulfonyl oxygen. The relationship between $\nu(\text{OH})$ -stretching frequency and O-H . . . O bond length in solids described by Nakamoto *et al.* (1955) confirms that a shift to lower frequency correlates well with an overall shortening and thus strengthening of the O-H . . . O hydrogen bonds.

The ^{13}C resonances of the kaolinite:DMSO intercalate ($\delta = 43.7$ and 42.5) were deshielded relative to both dilute DMSO in deuterated chloroform ($\delta = 41.0$) and pure DMSO ($\delta = 40.4$). Increased electron withdrawal on the methyl carbons due to an increase in hydrogen bonding by the sulfonyl oxygen accounts for the observed deshielding, although the infrared evidence (Olejnik *et al.*, 1968) does not support this proposed explanation. Jacobs and Sterckx (1970), however, interpreted their $\nu(\text{SO})$ data as indicating the formation of such strong hydrogen bonds in the kaolinite:DMSO intercalate.

Overall, the narrowness of the ^{29}Si NMR single resonance, the apparent resolution of the two methyl chemical environments by ^{13}C NMR, and the forma-

tion of significant hydrogen bonds between the inner-surface hydroxyls and the sulfonyl oxygen suggests a high degree of short-range ordering in the kaolinite:DMSO intercalate. That the kaolinite:DMSO intercalate is a highly ordered structure is further supported by the presence of strong, well-resolved, non-basal reflections in the XRD powder pattern obtained in this study, in agreement with the results of Jacobs and Sterckx (1970).

Kaolinite:PNO intercalate

The ^{29}Si spectrum of kaolinite:PNO displayed a single resonance at $\delta = -92.1$ ($\Delta\nu_s = 55$ Hz). Assuming that the ^{29}Si signal width is an indication of three-dimensional ordering, as discussed above, a value of 55 Hz suggests that the kaolinite:PNO intercalate has less ordering than the kaolinite:DMSO intercalate, but more than the kaolinite:hydrazine intercalate. From previous considerations of the effect of hydrogen bond interaction on the ^{29}Si chemical shift, the observed shift at $\delta = -92.1$ indicates that PNO is equally strongly hydrogen bonded to the adjacent silicate layer as are both hydrazine and formamide. On this basis the structure of kaolinite:PNO (Weiss and Orth, 1973) requires the formation of C–H . . . O hydrogen bonds. As discussed for the kaolinite:DMSO intercalate, the existence of C–H . . . O hydrogen bonds is not acceptable, and a significantly more shielded ^{29}Si resonance should be expected than was actually observed. The anomalously deshielded ^{29}Si resonance may be explained by considering the aromatic nature of PNO. The magnetically anisotropic aromatic ring deshields nuclei in the plane of the ring. Although the PNO rings are not strictly normal to the kaolinite layer (Weiss and Orth, 1973), they are sufficiently close to cause some deshielding of the neighboring silicon nuclei. A semi-quantitative estimate of the amount of deshielding experienced by the silicon nucleus can be derived from calculations by Johnson and Bovey (1958) for aromatic hydrocarbons. Assuming a distance of 4–5 Å between the center of the PNO ring and an adjacent silicon nucleus near to the plane of that ring (Weiss and Orth, 1973), the expected deshielding (~ 0.3 ppm) would be of the right order of magnitude to account for a significant part of the anomalous deshielding.

The ^{13}C spectra of the kaolinite:PNO intercalate (Figure 4) are more difficult to interpret. As it was not possible to collect a CP/MAS ^{13}C spectrum of pure PNO, the signals observed in the CP/MAS spectrum for kaolinite:PNO must have been almost entirely due to intercalated PNO. The chemical shift of the β -carbon in the kaolinite:PNO intercalate ($\delta = 128.2$) is comparable to that of the β -carbon of PNO in ethanol ($\delta = 127.9$) (see Anet and Yavari, 1976), a mildly polar solvent. The α -carbon in the kaolinite:PNO intercalate, however, was unexpectedly shielded by > 1.5 ppm relative to the α -carbon of PNO in solutions of wide-

ranging polarity and acidity. Other effects such as steric interactions and neighbor group anisotropy would predominate at the *ortho*-carbon (α) (Wehrli and Wirthlin, 1978).

The non-observance of a distinct γ -carbon resonance is not surprising in view of the results of solution studies. Depending on the solvent properties, the γ -carbon of PNO in solution resonated in the range $\delta = 123.2$ to 145.5. Minor variation in the hydrogen bonding between the kaolinite inner-surface hydroxyls and the PNO oxygen would result in modulation of the mesomeric effect, and consequently variation in the deshielding at the γ -carbon. It is possible that the γ -carbon contributed to the weak signals which appeared in the CP/MAS spectrum as shoulders at $\delta = 133$ and 139.

Overall, the ^{13}C spectra of the kaolinite:PNO intercalate confirm the formation of relatively strong hydrogen bonds between the kaolinite inner-surface hydroxyls and the PNO oxygen. The absence of a single, clearly resolved γ -carbon resonance in the ^{13}C CP/MAS spectrum correlates with the peak width of the ^{29}Si signal in that a high degree of three-dimensional ordering is lacking in the kaolinite:PNO crystal structure.

Extent of intercalation

From a cursory examination of the present results, ^{29}Si NMR spectroscopy appears to provide a more reliable indication of the extent of intercalation than does a consideration of the relative intensities of the $d(001)$ XRD reflections. The latter technique relies on the presence of long-range ordering, whereas NMR does not. For example, the XRD pattern of the kaolinite:DMSO intercalate, after correcting for structure factor differences and the Lorentz factor, indicates that the intercalation had proceeded to $\geq 95\%$ completion, whereas the ^{29}Si CP/MAS spectrum of the same sample demonstrates that 90–92% would have been a more reliable estimate. Similar lack of agreement between NMR and XRD data was observed for the other intercalates as well. In order that the ^{29}Si CP/MAS data be quantitative, the ^{29}Si –H internuclear distances and rates of relaxation for ^{29}Si must be the same for each sample (Barron *et al.*, 1983a).

It is reasonable to assume that the rates of relaxation are the same, because in each case the aluminosilicate structure and composition are the same. The experimental results, however, suggest that the ^{29}Si –H internuclear distances are *not* the same. Inasmuch as ^{29}Si in kaolinite:hydrazine appeared to cross-polarize much less efficiently (cf. signal-to-noise in Figure 1) than in the other intercalates protons from the intercalating compound must have been involved in cross-polarization. The ^{29}Si NMR results in this study demonstrate that significant differences in ^{29}Si –H internuclear distances must exist between the tetrahedrally coordinat-

ed silicon and protons from the intercalating compound. Therefore, a conclusion that the ^{29}Si CP/MAS spectra (sensitive to short-range ordering) of kaolinite intercalates provides a more reliable indication of the level of intercalation than XRD (sensitive to long-range ordering) is not justified. Nevertheless, the results obtained are consistent within the respective scope of each technique.

CONCLUSIONS

Solid-state ^{29}Si and ^{13}C NMR analyses of the four kaolinite intercalates could not be predicted from previous infrared or XRD investigations. This is not surprising given the different analytical capability of high-resolution MAS/NMR of solids, namely, sensitivity to the averaged chemical and magnetic environment of the subject nucleus.

Although unequivocal interpretations were not always possible the following conclusions can be made:

(1) Using ^{29}Si NMR it was possible to observe the level of bonding interaction between the silicate layer and the intercalate; however, it was necessary to consider influences not relating to bonding (e.g., neighboring-group anisotropy).

(2) The width of the ^{29}Si resonances ($\Delta\nu_{1/2}$) showed the level of three-dimensional, short-range ordering in the kaolinite intercalate.

(3) ^{13}C NMR in kaolinite:organic intercalates was generally difficult to interpret. Upon intercalation, organic molecules were susceptible to changes in bond length and angle. These changes were not a problem for ^{29}Si because distortion of the aluminosilicate structure after intercalation was not evident. These and other influences (Wehrli and Wirthlin, 1978) made interpretation of the ^{13}C spectra more difficult.

(4) ^{13}C chemical shifts appeared to be compatible with changes in hydrogen bond participation that can be inferred from infrared studies. Detail was obtainable regarding redistribution of electron density in the kaolinite:PNO intercalate and the non-equivalence of methyl-carbon chemical environments in the kaolinite:DMSO intercalate.

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Резюме—Спектроскопия ядерного магнетического резонанса ^{13}C и ^{29}Si использовалась для исследования короткодействующего упорядочения и связи в структуре прослоек каолинита с формамидом, гидразином, диметилевой сероокисью (ДМСО) и пиридином-*N*-окисью (ПНО). Химический сдвиг ^{29}Si указывал на уменьшающиеся уровни взаимодействия связи между силикатными слоями и включаемым веществом в порядке: каолинит:формамид ($\delta = -91,9$, частей на миллион по отношению к тетраметилсилану), каолинит: гидразин ($-92,0$), каолинит: ДМСО ($-93,1$). Сигнал ^{29}Si прослойки каолинит: ПНО ($-92,1$) оказался неожиданно не защищенным, вероятно, в результате ароматической природы ПНО. Степень пространственного упорядочения структур была обнаружена при помощи ширины сигнала ^{29}Si . Прослойка каолинит: ДМСО имела наибольшее упорядочение, а каолинит: гидразин—наименьшее. Резонансы ^{13}C включаемых органических молекул перемещались вниз на величину порядка 3 частей на миллион в результате увеличивающейся водородной связи после прослаивания. В случае прослойки каолинит: ДМСО, две химические группы метил-углерод были неравновесны ($\delta = 43,7$ и $42,5$). [E.G.]

Resümee— ^{13}C und ^{29}Si nuklearmagnetische Resonanzspektroskopie mit "Magic-angle Spinning" wurde verwendet, um die Nahordnung und die Bindung in den Strukturen von Wechsellagerungen von Kaolinit mit Formamid, Hydrazin, Dimethylsulfoxid (DMSO), und Pyridin-*N*-Oxid (PNO) zu untersuchen. Die chemische Verschiebung von ^{29}Si deutete auf abnehmende Niveaus der Bindungswechselwirkung zwischen der Silikatschicht und der Einlagerung hin, in der Reihenfolge: Kaolinit:Formamid ($\delta = -91,9$, ppm in Vergleich zu Tetramethylsilan), Kaolinit:Hydrazin ($-92,0$), Kaolinit:DMSO ($-93,1$). Das ^{29}Si -Signal der Kaolinit:PNO-Wechsellagerung ($-92,1$) war unerwartet wenig abgeschirmt, wahrscheinlich aufgrund der aromatischen Natur von PNO. Der Grad der dreidimensionalen Ordnung der Strukturen wurde aus der Breite des ^{29}Si -Signals abgeleitet, wobei die Kaolinit:DMSO-Wechsellagerung den höchsten Ordnungsgrad und die Kaolinit:Hydrazin-Wechsellagerung den niedrigsten zeigte. Die ^{13}C -Resonanzen der eingelagerten organischen Moleküle wurden bis zu 3 ppm nach geringerer magnetischer Feldstärke verschoben als Auswirkung einer zunehmenden Wasserstoffbindung nach der Einlagerung, und in der Kaolinit:DMSO-Wechsellagerung waren die zwei chemischen Methyl-Kohlenstoff-Milieus nicht gleich ($\delta = 43,7$ und $42,5$). [U.W.]

Résumé—La spectroscopie de résonance magnétique nucléaire de ^{13}C et de ^{29}Si avec spin d'angle magique a été utilisée pour étudier l'ordre à court terme et les liaisons dans les structures d'intercalates de kaolinite avec la formamide, l'hydrazine, la sulphoxide diméthyle (DMSO), et l'oxide-*N*-pyridine (PNO). Le déplacement chimique de ^{29}Si a indiqué des niveaux décroissants d'interaction de liaisons entre la couche silicate et l'intercalate dans l'ordre: kaolinite: formamide ($\delta = -91,9$, ppm relatives à la tétraméthylsilane), kaolinite: hydrazine ($-92,0$), kaolinite: DMSO ($-93,1$). Le signal ^{29}Si de kaolinite: hydrazine ($-92,1$) était découvert de manière inattendue, possiblement à cause de la nature aromatique de PNO. Le degré d'ordre à trois dimensions des structures a été inféré à partir de la largeur du signal ^{29}Si , avec l'intercalate kaolinite: DMSO montrant le plus grand ordre et la kaolinite: hydrazine, le plus petit. Les résonances ^{13}C de molécules organiques intercalantes étaient déplacées vers le bas du champ par autant que 3 ppm en réponse à une liaison d'hydrogene augmentée après l'intercalation, et dans l'intercalate kaolinite: DMSO, les deux environnements chimiques méthyl-carbone étaient non-équivalents ($\delta = 43,7$ et $42,5$). [D.J.]