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Characterization of an alkylammonium-montmorillonite-phenanthrene intercalation complex by carbon-13 nuclear magnetic resonance spectroscopy

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ABSTRACT: Low molecular weight polycyclic aromatic hydrocarbons can intercalate from the solid phase into montmorillonite (Mt) saturated with quaternary alkylammonium ions. However, the interaction and relationship between guest and host organic molecules in the interlayer space of the clay are not well understood. We have intercalated phenanthrene into tetradecyltrimethylammonium (TDTMA)-montmorillonite by a solid-solid reaction. The basal spacing of the original TDTMA-Mt complex is close to 1.8 nm, indicating the presence in the interlayer space of a double layer of TDTMA ions with the alkyl (polymethylene) chains lying parallel to the silicate layers, and the carbon zig-zags adopting an all-*trans* conformation. After intercalation of phenanthrene the basal spacing increases to about 3.4 nm, indicating a change in orientation of the alkyl chains with respect to the silicate layers. ¹³C-NMR spectroscopy shows that adding phenanthrene to TDTMA-Mt leads to a displacement by -3 ppm of the -(CH₂)_n- signal for TDTMA. This signal and that for interlayer phenanthrene are also broadened relative to the respective pure compounds. These observations, together with measurements of nuclear spin relaxation time constants, strongly suggest that in the complex with phenanthrene the polymethylene chains of TDTMA extend away from the silicate layers, and no longer assume a rigid all-*trans* carbon zig-zag conformation. Rather, the TDTMA chains become relatively disordered and intimately mixed with phenanthrene.

Polycyclic aromatic hydrocarbons (PAHs), of which phenanthrene is a member, are widespread in the environment. In particular, soils near disused gas works contain high levels of PAHs arising from the incomplete combustion of coal and oil (Byers *et al.*, 1994; Chen *et al.*, 1996). Concern about the persistence and genotoxicity of PAHs has stimulated much research into the bioremediation of contaminated sites (Durant *et al.*, 1995; Grosser *et al.*, 1995). In these sites PAHs are concentrated in coal tar and, therefore, can presumably be taken up, if not intercalated, into an organo-mineral matrix. However, the potential for the *in situ* containment of PAHs by entrapment or intercalation has not been explored. The adsorption of alkylammonium ions by 2:1 type layer silicates, notably mont-

morillonite and vermiculite, has been well documented (Theng, 1974; Lagaly, 1993). The process is essentially one of exchange between the inorganic cations (e.g. Na), initially present at the clay surface, and the organic cations in solution. Being hydrophobic, alkylammonium-exchanged clays have a larger propensity for sorbing non-ionic organic compounds (e.g. PAHs), than the parent (unmodified) materials (Jaynes & Boyd 1990; 1991). Nevertheless, the amount that can be taken up from aqueous solutions is limited because such compounds have a low solubility in water (Smith *et al.*, 1990).

This limitation may be overcome by mixing the non-ionic compound as a solid with dry alkylammonium-exchanged clays. In this way, Ogawa *et*

al. (1992; 1995) were able to intercalate up to 50% by weight of naphthalene, anthracene, and pyrene into montmorillonite saturated with long-chain quaternary ammonium ions. They suggested that the process was driven by hydrophobic interactions between the guest PAH molecules and the host alkylammonium ions. If so, we might expect the conformation and motion of the interlayer guest and host organic species to be substantially altered.

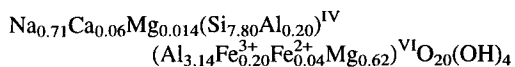
Nuclear magnetic resonance (NMR) spectroscopy has been useful in probing the dynamic behaviour of guest molecules in zeolites (Pfeifer, 1976; Lechert & Basler, 1989; Hong *et al.*, 1993; Qiang Xu *et al.*, 1996). To our knowledge, however, this technique has not been previously applied to characterize organic compounds in layer silicates. One obstacle has been the need to provide evidence that the NMR signals arise principally from the intercalated species rather than from the portion that is attached to external crystal surfaces. We have overcome this problem by intercalating phenanthrene from the solid phase into montmorillonite (Mt) saturated with tetradecyltrimethylammonium (TDTMA) ions using the method of Ogawa *et al.* (1992).

Following Cheung & Gerstein (1981) the intimacy of mixing (association) between phenanthrene and TDTMA in the interlayer space of the clay has been assessed through proton spin diffusion using NMR spectroscopy. We should stress that it is the proton spin information that diffuses, and not the protons themselves. This information, which is exchanged between pairs of neighbouring protons through interactions between the two magnetic dipoles, can diffuse over dimensions of the order of tens of nanometres over milliseconds, or 100 nm over a period of about 1 s (Zumbulyadis, 1983). Distinct proton spin relaxation constants for guest and host molecules can therefore be taken as evidence for a lack of mixing or heterogeneity on a scale of tens of nm or more. The test for heterogeneity can be further enhanced by observing proton spin diffusion processes through the effects on ^{13}C NMR signals (Zumbulyadis, 1983; Tekely *et al.*, 1989). The improved chemical shift dispersion of signals is then combined with the sensitivity of proton spin relaxation to probe changes in molecular dynamics.

MATERIALS AND METHODS

The montmorillonite used was a Na-rich specimen supplied by Kunimine Industries Co., Japan

marketed as 'Kunipia-F', and commonly abbreviated to 'KpF'. Its structural formula (Iwasaki & Onodera, 1995) is:



Tetradecyltrimethylammonium bromide of $\approx 99\%$ purity was obtained from Sigma Chemical Co. (St. Louis, Missouri, USA), and reagent-grade phenanthrene ($>98\%$) from Merck-Schuchardt (Hohenbrunn, Germany). Both compounds were used as received.

The cation exchange capacity (CEC) of the KpF sample was determined by leaching with 1 M ammonium acetate at pH 7, washing with 90% ethanol, displacing the ammonium with 1 M NaCl, and measuring the amount displaced with an autoanalyzer (Blakemore *et al.*, 1987). A CEC of 113 cmol(+) kg^{-1} was measured, in good agreement with the value of 115 cmol(+) kg^{-1} given by the manufacturer. Conversion to the TDTMA-exchanged form was achieved by shaking the clay with an aqueous solution of TDTMA-bromide for which the concentration of TDTMA ions was equivalent to the CEC. After removing excess electrolyte by repeated washing with deionized water, the TDTMA-Mt complex was dried in an oven at 30°C.

The TDTMA-Mt-phenanthrene intercalate was prepared by mixing three parts of the TDTMA-Mt complex with one part of solid phenanthrene for 10 min in an agate mortar and pestle, as described by Ogawa *et al.* (1992). The amount of TDTMA and phenanthrene present in the respective complexes was checked by carbon and nitrogen analysis using a Leco FP-2000 instrument and EDTA as a calibration standard. X-ray diffractometry (XRD) was carried out by air-drying an aqueous suspension of the samples on a glass slide, and scanning at a rate of 2° 2θ min^{-1} , using a Philips PW1010 diffractometer and Co- $K\alpha$ radiation (Whitton & Churchman, 1987). Infrared (IR) spectra were obtained from KBr discs using a Digilab FTS-7R Fourier-transform spectrophotometer.

The ^{13}C NMR spectra were obtained by packing 0.25–0.32 g of air-dry samples in a 7 mm diameter silicon nitride rotor, sealed at both ends with Kel-F caps, and spinning at 5 kHz in a magic-angle spinning (MAS) probe made by Doty Scientific (Columbia, SC, USA). Spectra were run at a frequency of 50.3 MHz using a Varian Inova-200 spectrometer. Each 90° proton preparation pulse of

5 μ s duration was followed by a 1 ms cross-polarization contact time, and 30 ms of data acquisition. The recovery delay was 1 s for both the TDTMA-Mt and TDTMA-Mt-phenanthrene complex, 2 s for TDTMA-bromide, and 600 s for phenanthrene. Signals were averaged over periods between 20 and 90 min. Chemical shifts were expressed relative to tetramethylsilane with the methyl signal of solid hexamethylbenzene at 17.4 ppm serving as a secondary reference.

Proton spin-lattice relaxation time constants, $T_1(H)$, were measured by applying a 10 μ s 180° pulse, and waiting for a variable relaxation interval before applying the cross-polarization sequence. Proton rotating-frame relaxation time constants, $T_{1\rho}(H)$, were measured by inserting a variable proton spin-locking interval between the 90° proton preparation pulse and the cross-polarization contact time. Values of the cross-polarization transfer time constant, T_{CH} , were measured by varying the contact time, and fitting ^{13}C NMR peak heights to a double-exponential function (Alla & Lippmaa, 1976):

$$\text{Height}(t) = K \left\{ \exp(-t/T_{1\rho}(H)) - \exp(-t/T_{CH}) \right\} / \left\{ 1/T_{CH} - 1/T_{1\rho}(H) \right\} \quad (1)$$

where K is an arbitrary scaling factor.

RESULTS AND DISCUSSION

Chemical and X-ray diffraction analyses

Table 1 gives the C and N contents of pure TDTMA-bromide and of TDTMA-Mt, both before and after intercalation of phenanthrene. The XRD patterns of TDTMA-Mt and its intercalate with phenanthrene are shown in Fig. 1.

The C and N contents of TDTMA-Mt agree to within 2% of the values calculated on the basis that

TABLE 1. Carbon and nitrogen contents of tetradecyltrimethylammonium bromide (TDTMA-bromide), TDTMA-exchanged K_pF montmorillonite (TDTMA-Mt), and TDTMA-Mt-phenanthrene intercalation complex.

Sample	Total C (%)	Total N (%)
TDTMA-bromide	60.5	4.16
TDTMA-Mt	17.65	1.22
TDTMA-Mt-phenanthrene	36.90	0.90

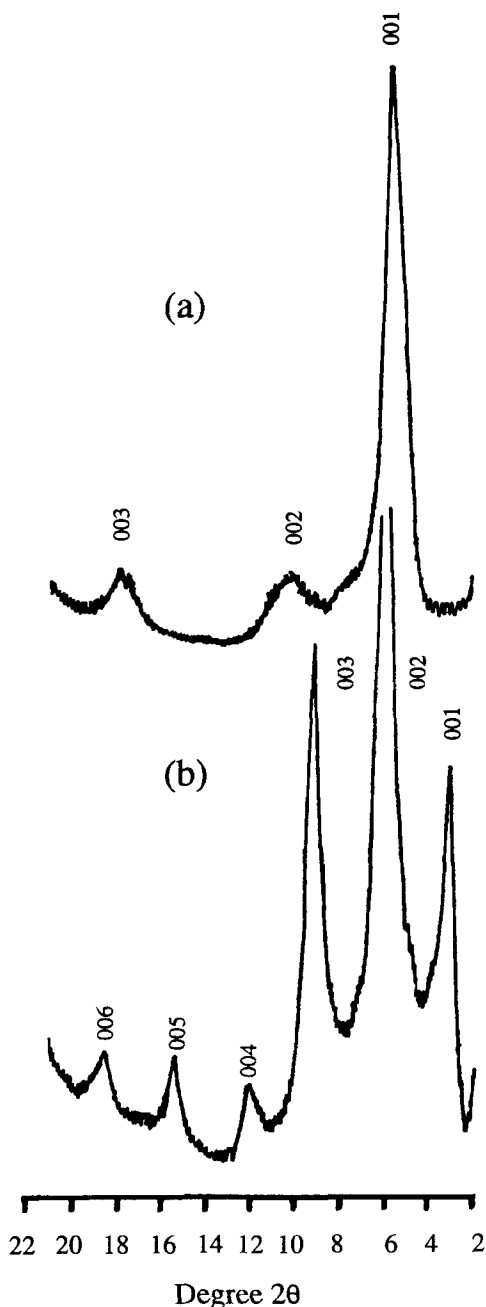


FIG. 1. X-ray diffraction patterns of (a) the interlayer complex of tetradecyltrimethylammonium (TDTMA) with montmorillonite (Mt); (b) the intercalation complex of TDTMA-Mt with phenanthrene.

all the exchange sites on the clay, that is $113 \text{ cmol}(+) \text{ kg}^{-1}$, were occupied by TDTMA ions. Since the thickness of an individual silicate layer is 0.96 nm (Theng, 1974), a basal or 001 spacing of 1.82 nm (Fig. 1a) for the TDTMA-Mt complex corresponds to an interlayer separation (Δ -value) of 0.86 nm . This value accords with the presence in the interlayer space of a double layer of TDTMA ions with the polymethylene chain lying parallel, and the all-*trans* carbon zig-zag plane perpendicular, to the silicate layers (Theng, 1974; Lagaly, 1993).

In this orientation, a TDTMA ion occupies about 1.12 nm^2 of surface area. By taking a crystallographic area of $752 \text{ m}^2 \text{ g}^{-1}$ for montmorillonite (van Olphen, 1977), and an interlayer surface area of $700 \text{ m}^2 \text{ g}^{-1}$, we may assign $105 \text{ cmol}(+) \text{ kg}^{-1}$ of TDTMA ions, that is 93% of the total CEC, to interlayer surfaces. On the same basis, a Δ -value of 0.86 nm corresponds to an interlayer volume of $0.32 \text{ cm}^3 \text{ g}^{-1}$, in excellent agreement with the space requirement of TDTMA ions at full interlayer surface coverage.

Mixing dry TDTMA-Mt with solid phenanthrene (in a 3:1 ratio) gave rise to a complex with a $d(001)$ spacing of 3.37 nm (Fig. 1b), similar to what Ogawa *et al.* (1992) had found for anthracene. The intense peak near 1.7 nm was therefore identifiable with the second-order basal reflection, and not due to 'unreacted' TDTMA-Mt as Ogawa *et al.* (1992) seemed to imply. The large increase in basal spacing and the rational series of higher-order reflections are good evidence for the formation of an intercalation complex with long-range regularity. That the reaction was apparently complete after 10 minutes of mixing would indicate rapid diffusion of phenanthrene into the interlayer space. As a result, the interlayer volume increases from 0.32 to 0.90 cm^3 . Although an increase in volume must occur when phenanthrene enters the interlayer space, the magnitude of the increase (0.58 cm^3) is about twice that required to accommodate the guest molecules.

The intercalation of phenanthrene has, therefore, induced a re-orientation of the alkyl chains of TDTMA ions in the interlayer space. Instead of lying parallel, the chains are probably inclined at a high angle to the silicate layers. This is the preferred orientation in alkylammonium-exchanged vermiculite (Theng, 1974; Lagaly, 1993) but, unlike the situation in vermiculite, the carbon zig-zag chains of TDTMA in the KpF-phenanthrene

complex do not appear to adopt an all-*trans* conformation. The IR spectra (not shown) also indicate a shift of the C-H out-of-plane bending vibration of phenanthrene from 731 cm^{-1} for the pure compound to 740 cm^{-1} for the intercalated species. The extent of the shift is similar to what Ogawa *et al.* (1992) have reported for naphthalene intercalated into dodecyltrimethylammonium-montmorillonite. Both XRD and IR spectroscopy suggest an intimate mixing of phenanthrene and TDTMA ions in the interlayer space. This suggestion is fully supported by the NMR data discussed below.

NMR spectroscopy

Chemical shifts. Figure 2 shows the ^{13}C CP/MAS NMR spectrum of TDTMA-bromide. The signal assignments are based on data for hexadecyltrimethylammonium bromide (Canet *et al.*, 1987). The signal at 63.7 ppm is assigned to C-1, at 55.3 ppm to methyl groups bonded to N, at 35.2 ppm to C-12, at 33.1 ppm to C-4-C-11, at 30.0 ppm to C-3, at 25.0 ppm to C-2, at 24.3 ppm to C-13, and at 17.2 ppm to C-14. The NMR spectrum of phenanthrene is shown in Fig. 3. On the basis of solution-NMR data (Johnson & Jankowski, 1972; Stothers, 1972), the signal at 132 ppm is assigned to the four non-protonated C atoms, and that at $126\text{--}128 \text{ ppm}$ to the ten CH groups.

The signals for TDTMA ions in montmorillonite are distinctly broader than those for their counterpart in the bromide salt (Fig. 4). This is consistent with a more disordered structure in the TDTMA-Mt complex. However, the chemical shift at 32.8 ppm , assigned to $-(\text{CH}_2)_n-$ for TDTMA in the complex, is close to the corresponding value for TDTMA-bromide. This suggests that the polymethylene chains of TDTMA in the interlayer complex are essentially extended in an all-*trans* zig-zag conformation as in the solid TDTMA-bromide.

Intercalation of phenanthrene into TDTMA-Mt shifts the $-(\text{CH}_2)_n-$ signal of TDTMA from 32.8 to 29.9 ppm (Fig. 5). The displacement of -2.9 ppm may largely be ascribed to a change from an all-*trans* to a disordered conformation as Earl & VanderHart (1979) have observed for amorphous polyethylene. The displacement may also be influenced by the diamagnetic nature of the aromatic rings in phenanthrene resulting in the shielding of TDTMA ^{13}C -nuclei.

The signals due to C-1 at 63.7 ppm and to N-methyl carbon at 55.3 ppm for TDTMA-bromide

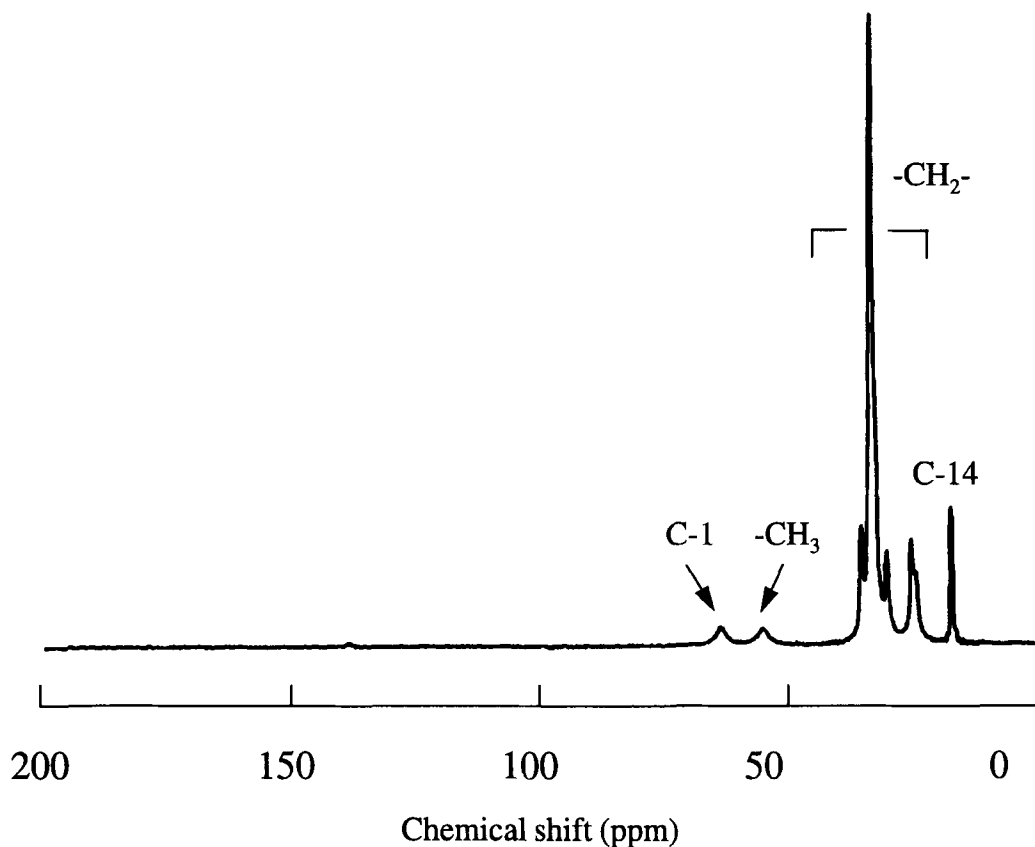


FIG. 2. ^{13}C NMR spectrum of solid TDTMA-bromide.

(Fig. 2) are shifted to 68.7 and 54.0 ppm, respectively, for TDTMA-Mt (Fig. 4). These displacements are ascribable to changes in the electrostatic interactions between the cationic 'heads' of TDTMA and the negatively charged sites on the clay. In the TDTMA-Mt-phenanthrene intercalate the C-1 and N-methyl carbon bands for TDTMA are further displaced to 65.8 and 53.0 ppm, respectively (Fig. 5). This is tentatively attributed to electrostatic interactions between the TDTMA cation and the polarizable π orbitals of phenanthrene in the interlayer space. A displacement in chemical shift between +1.3 and -2.9 ppm has also been observed for toluene interacting with Na ions in a zeolite (Pfeifer, 1976). In addition, the band for intercalated phenanthrene is broadened relative to that of the pure compound. Although electrostatic interactions may partly be responsible, the anisotropic magnetic susceptibility of the clay

layers can also contribute to line broadening even when the sample is spun at the 'magic angle' (Schwerk *et al.*, 1996).

Spin relaxation time constants. Proton spin relaxation time constants, $T_1(\text{H})$ and $T_{1\rho}(\text{H})$, are generally long for rigid crystalline solids, and short for mobile disordered substances adsorbed on solid surfaces or for materials containing paramagnetic species (Pfeifer, 1976; Lechert & Basler, 1989). Of greater importance, in the current context, is that proton spin information diffuses over distances of nanometres during periods of milliseconds. As already remarked on, it is not the protons themselves that move but the information that is transmitted through flip-flop transitions involving neighbouring spins. Since mixing of spin information between protons in two adjacent molecules results in a single averaged value for any selected spin relaxation time constant (Zumbulyadis, 1983;

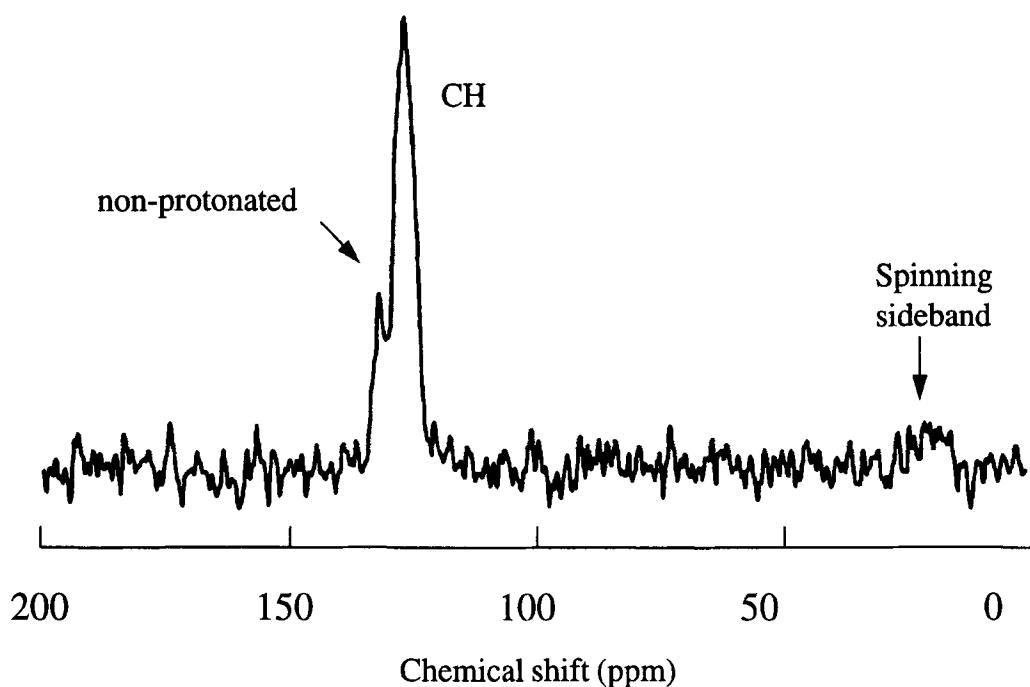


FIG. 3. ^{13}C NMR spectrum of solid phenanthrene.

Tekely *et al.*, 1989), spin diffusion can be used to test for intimacy of mixing.

Table 2 shows that this averaging process occurs for both $T_1(\text{H})$ and $T_{1\rho}(\text{H})$ in the TDTMA-Mt-phenanthrene intercalation complex. Notably, the $T_1(\text{H})$ value for phenanthrene is more than four orders of magnitude shorter than for the pure compound. Equally striking is the close similarity of the proton spin relaxation time constants between TDTMA and phenanthrene in the complex. This

observation is unlikely to arise from coincidence given the magnitude of the changes relative to the pure compounds. The data have led us to conclude that TDTMA and phenanthrene are intimately associated in the clay interlayers.

Cross-polarization time constants (T_{CH}) provide information about the rigidity of a molecule or a portion of it. Since the cross-polarization process involves a static dipole-dipole interaction, a relatively short time constant is indicative of a

TABLE 2. Nuclear spin relaxation time constants and estimated standard errors (in brackets). Time constants were measured via ^{13}C NMR signals assigned to polymethylene in tetradecyltrimethylammonium (TDTMA) or CH carbon in phenanthrene.

Sample	NMR signal	T_1 (H)(s)	$T_{1\rho}$ (H) (ms)	T_{CH} (ms)
TDTMA-bromide	polymethylene	0.57 (0.01)	5.05 (0.11)	0.036
TDTMA-Mt	polymethylene	0.008 (0.001)	0.36 (0.07)	0.032
TDTMA-Mt-phenanthrene	polymethylene in TDTMA	0.017 (0.002)	0.50 (0.05)	0.080
	CH carbon in phenanthrene	0.016 (0.002)	0.54 (0.05)	0.040
Phenanthrene	CH carbon	>300	>10	0.084

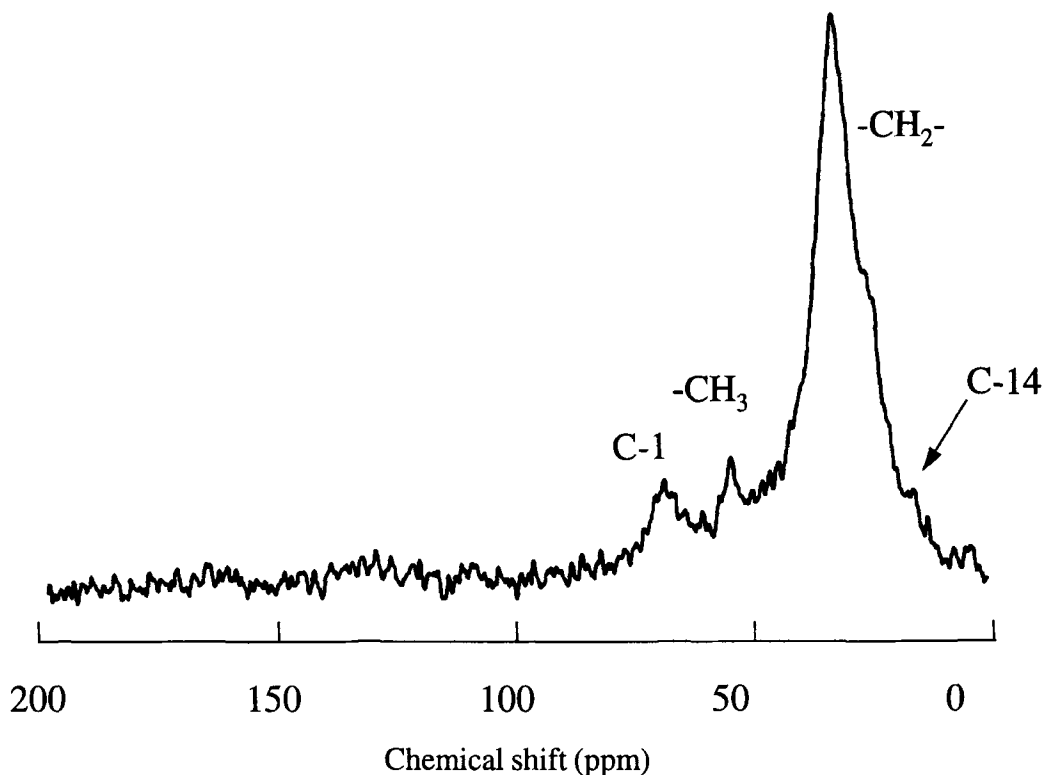


FIG. 4. ^{13}C NMR spectrum of TDTMA-montmorillonite.

rigid system and/or an abundance of nearby protons. The T_{CH} values for solid TDTMA-bromide and TDTMA-Mt (Table 2) indicate that the methylene groups in the alkylammonium ion are relatively rigid. By the same token, the large increase in T_{CH} for TDTMA following intercalation of phenanthrene may be explained in terms of a decrease in chain rigidity. As discussed above with reference to chemical shifts, interaction with phenanthrene has apparently loosened the rigid all-*trans* zig-zag conformation of the polymethylene chains in TDTMA.

The cross-polarization time constant for CH carbon in pure phenanthrene is longer than for CH_2 carbon in pure TDTMA-bromide, in keeping with the greater abundance of protons in the latter case. However, the opposite is true when phenanthrene and TDTMA are intercalated into montmorillonite (Table 2). This reversal in the order of T_{CH} values for the clay complex is probably because phenanthrene now satisfies both criteria for efficient cross-polarization, namely, (a) rigidity

in that the molecule cannot freely tumble in the interlayer space, and (b) an abundance of protons as spin polarization can diffuse from the TDTMA chains.

We should point out that the values of T_{CH} in Table 2 are confined to those measured for the strongest signals. Additional estimates for signals at 64 and 55 ppm in the spectrum of TDTMA-bromide, which are respectively assigned to CH_2 and methyl carbon bonded to nitrogen (Fig. 2), indicate that cross-polarization is relatively efficient for the methylene groups ($T_{\text{CH}} < 50 \mu\text{s}$) but that rotation of methyl groups around C-N bonds interferes with the cross-polarization process ($T_{\text{CH}} = 108 \mu\text{s}$). That the signal for N-methyl carbon is weaker than expected for three carbon atoms cannot be explained in terms of T_{CH} because the contact time used (1.0 ms) was much greater than T_{CH} . The deficit in signal strength can rather be ascribed to efficient ^{13}C rotating-frame relaxation, a complication ignored in the simplified version of eqn. (1). However, this signal appears

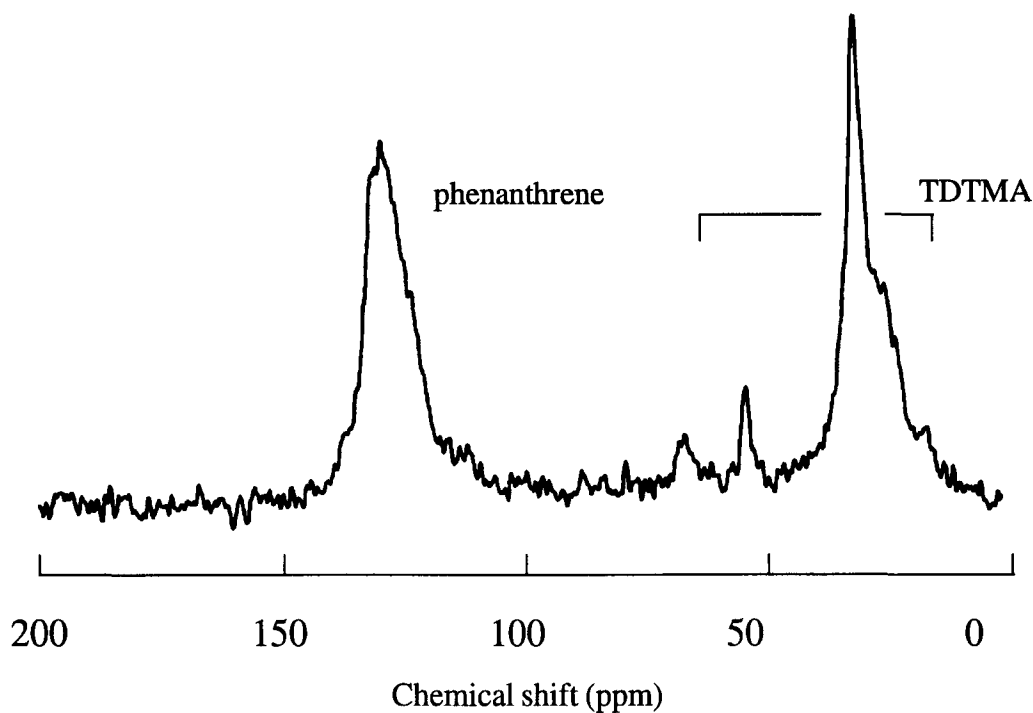


FIG. 5. ^{13}C NMR spectrum of TDTMA-montmorillonite-phenanthrene intercalate.

at full strength in the spectrum of the TDTMA-Mt-phenanthrene intercalation complex (Fig. 5), presumably because of changes in molecular dynamics of TDTMA.

Pure phenanthrene shows a signal at 132 ppm due to non-protonated carbon (Fig. 3) with a T_{CH} of 0.52 ms. This signal could not be resolved from the broad band assigned to phenanthrene in the spectrum of the complex (Fig. 5). Since the value of T_{CH} is marginally greater than $T_{1\rho}(\text{H})$ for the complex this signal would also be severely suppressed.

CONCLUSIONS

Large amounts (20–30% w/w) of phenanthrene can be intercalated into montmorillonite (Mt) saturated with tetradecyltrimethylammonium (TDTMA) ions by a solid-solid reaction. This offers the potential of using alkylammonium-smectites as agents for the containment and entrapment of PAHs in contaminated sites near disused gas works. We have unpublished data to indicate that once intercalated,

phenanthrene is no longer biodegradable. This would suggest intimate mixing between guest and host organic species presumably involving hydrophobic interactions (Ogawa *et al.*, 1992).

In line with this suggestion, XRD shows that intercalation of phenanthrene alters the orientation of the TDTMA chains in the interlayer space. Instead of lying parallel to the silicate layer the chains now extend away from it, increasing the basal spacing from 1.8 to 3.4 nm. Measurements of chemical shifts and spin relaxation time constants using ^{13}C NMR spectroscopy indicate that in the complex with phenanthrene, the alkyl chains of TDTMA are not held in a rigid all-*trans* zig-zag conformation (as in TDTMA-Mt) but are more disordered and closely associated with the phenanthrene.

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