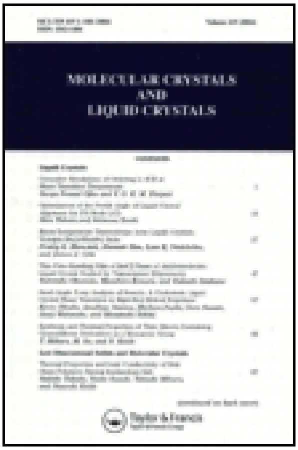

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NMR Relaxation Studies of Slow Motions of HDA Hydrocarbons Chains Inside Lamellar Structures

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NMR Relaxation Studies of Slow Motions of HDA Hydrocarbons Chains Inside Lamellar Structures

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Measurements of ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) for the nanocomposite materials formed by the intercalation of hexadecylamine (HAD) in metal oxides (TiO_2, V_2O_5, CrO_3 and MoO_3), are reported. The ^1H NMR relaxation results reflects the complexity of the chain segments motions in these systems. The proton (and the carbon) mobility depends on the position in the HDA hydrocarbon chain to the restriction imposed by the anchoring of the head group. The nonexponential behavior of the proton magnetization is clearly a result of the anisotropic motion of the HDA chains. For most of the protons, the rate of motion is not fast enough to fulfill the condition for the nuclear spin-lattice relaxation (NSR) maximum in the laboratory frame but they fulfill the condition for the NSR in the rotating frame. The $T_{1\rho}^{-1}$ maximum at around 280 K reflects the relative lower mobility of the protons of the HDA chain inside the low-dimensional space of the metal oxide. The description of the segmental motion of long chains require the use of an asymmetric distribution of correlation times to describe relaxation in flexible polymer chains.

Keywords: foam; hexadecylamine; intercalation compound; nanostructure; NMR

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INTRODUCTION

Interest in organic – inorganic compounds derived from titanium and vanadium oxides has increased in recent years, mainly for their structural diversity and their potential applications in solid-state lithium batteries, catalysis and electrochromic devices [1–3]. One of the new materials recently proposed is obtained from the reaction of hydrogen peroxide inside a metal oxide (TiO_2, V_2O_5) containing intercalated alkylamine [4,5]. In these hybrid composite materials, the long-chain alkyl are intercalated inside thin planar metal oxide walls, forming a lamellar nanostructure. The interest in the study of these organic-inorganic materials arises not only for their potential in technological applications, but also for providing a convenient macroscopic model system to study fundamental scientific issues concerning molecular dynamics in low dimensional spaces. In the present work, we report a proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) investigation of the conformational and dynamical properties of hexadecylamine (HDA) intercalated in metal oxides (TiO_2, V_2O_5, CrO_3, and MoO_3). NMR is a well-known experimental technique for the selective study of molecular motions in nanostructured materials since it is sensitive to the effects that such motions have on the linewidth and spin-relaxation times [6].

EXPERIMENTAL

The samples are prepared from the direct decomposition and reaction of hydrogen peroxide inside a metal oxide/HDA. In the synthesis process, the HDA is dissolved in boiling acetone, the metal oxide (TiO_2, V_2O_5, CrO_3, or MoO_3) is added in the hot solution and, finally, 50 mL of H_2O_2 is added at once. The foam generated after the H_2O_2 addition is dried at room temperature. Scanning electron microscopy and X-ray diffraction revealed the lamellar structure of the resulting material, with basal distance of around 50 Å [4,5]. In this materials, the HDA hydrocarbon chains are packed inside the matrix with the chains perpendicular to the metal oxide walls. Proton (^{1}H) NMR line shapes and spin-lattice relaxation experiments were carried out in powder samples from 170 to 370 K using a pulsed NMR spectrometer operating at 36 MHz. The high-resolution ^{13}C NMR measurements were performed at a magnetic field of 9.4 T (100.6 MHz) on a Varian Unity Inova spectrometer, using a 7 mm Magic Angle Spinning (MAS) probe. Samples were spun up to 5.5 KHz in silicon nitride rotors. Spectra were measured with a single pulse excitation and also by ^{1}H-^{13}C cross-polarization (CP) technique. The CP experiment was carried out using a $\pi/2$ ^{1}H pulse of 3.5 μs, contact time of 1ms, recycle delay of 30 s and

^{1}H decoupling of 80 KHz. In single pulse experiments a $\pi/2$ pulse of 3.5 μs was used with recycle delay of 30 s and ^{1}H decoupling of 80 KHz. Also, the delayed ^{1}H decoupling technique (DD) was used to suppress non-quaternary carbon signals, using a delay time of 30 μs between the end of the excitation pulse and the beginning of the decoupling irradiation [7]. The reference for ^{13}C chemical shift was tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Figure 1 shows the proton (^{1}H) NMR spectra recorded between 173 K and 293 K in the sample HDA:MoO_3. The experimental lineshape at

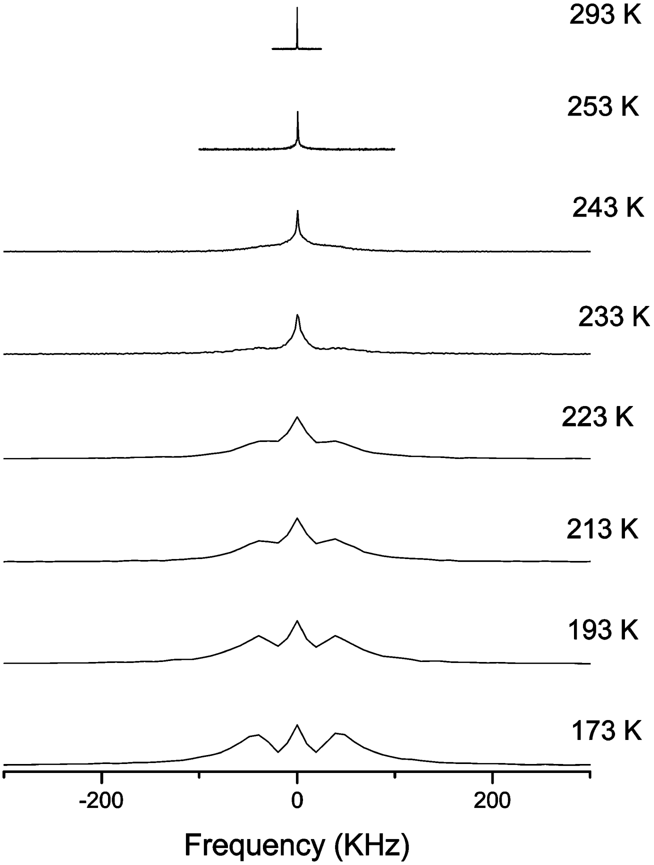

FIGURE 1 ^{1}H NMR spectra of hexadecylamine intercalated in molybdenum oxide, HDA:MoO_3, recorded between 173 K and 293 K.

low temperature was simulated with a narrow line of lorentzian shape flanked by a pair of peaks, of Gaussian shape, separated by $\sim$75 kHz (18 Gauss). The side peaks conform a Pake doublet [8] attributed to paired protons in CH_2 with a proton–proton separation of 1.7 Å. Protons of the CH_3 group in the HDA molecule (H−H distance 1.78 Å) can also contribute to the outer peaks of the Pake doublet. The central line is attributed to the central component of the ^1H spectrum belonging to the CH_3 group. Neighboring group interactions are responsible for the broadening of the low temperature ^1H NMR spectrum. Above $\sim$200 K, the mobility of the protons averages out the inter- and the intra- molecular dipolar interactions, and the ^1H line narrows. From the analysis of the line narrowing data we obtain activation energies of 0.15 eV for the proton motion. This result is consistent with the average value reported for CH_2 and CH_3 groups in aliphatic and alkyl chains, $E = 0.13$–0.16 eV [9].

The proton spin-lattice relaxation time T_1 of the samples HDA:TiO_2, HDA:MoO_3, HDA:V_2O_3 and HAD:Cr_2O_3 was measured in the temperature range 150–330 K. The source of the proton relaxation in these systems is the random fluctuations of the $^1H-^1H$ dipole interaction caused by the HDA chain motions inside the lamellar structure of the metal oxide. The ^1H magnetization recovery curve towards equilibrium was found to be non-exponential for the HDA:MoO_3 and HDA:V_2O_3 compounds and was adequately fitted by a sum of two exponential functions associated with two different characteristic relaxation times, $T_1 \approx 127$ ms and 500 ms for HDA:MoO_3, 90 ms and 13 ms for HDA:V_2O_3 at 170 K. For the other compounds, the magnetization recovery was adequately fitted with a single exponential, yielding $T_1 \approx 250$ ms for HDA:TiO_2 and $T_1 \approx 3$ ms for the HDA:Cr_2O_3 compound. The small value of the ^1H relaxation time for the last compound is attributed to the strong dipolar coupling of the proton spin with the electronic spin of the Cr^{3+} paramagnetic ion.

The relaxation times in the HDA:TiO_2, HDA:MoO_3, HDA:V_2O_3 and HAD:Cr_2O_3 compounds were found to be constant from 150 to 240 K. Above 240 K the relaxation time decreases slightly with increasing temperature, until a weak minimum is attained between 250 K and 280 K. The position of the relaxation time minimum indicates the temperature at which the motional correlation time τ is comparable to the reciprocal of the ^1H Larmor frequency in the laboratory frame ($\tau \sim 1/\omega_o \approx 10^{-9}$ s). The weak ^1H spin-lattice relaxation minimum observed in our samples indicate that few protons have rate motion of the order of ω_o. It is a reasonable conjecture that the protons of the terminal CH_3 group in the HDA chain are undergoing such fast motions.

The ^{1}H NMR relaxation results reflect the complexity of the chain segments motions in these systems. The proton (and the carbon) mobility depends on the position in the HDA hydrocarbon chain. The protons of the terminal CH_3 group, for example, have higher mobility than those protons of the CH_2 groups of the HDA chain head due to the restriction imposed by the anchoring of the head group. The non-exponential behavior of the proton magnetization is clearly a result of the anisotropic motion of the HDA chains. Anisotropic chain segments motions has also been reported for micellar systems where the polar head group is anchored. In this system, the motional correlation time is largest for the carbon close to the polar head and decreases towards the terminal methyl group [10]. For most of the protons, the rate of motion is not fast enough to fulfill the condition for the nuclear spin-lattice relaxation (NSR) maximum in the laboratory frame, $\omega_0\tau \approx 1$ in the temperature region investigated.

However, for measurements of the relaxation time carried out in the rotating frame ($T_{1\rho}$), the Larmor frequency is shifted from the MHz regime to the kHz regime, and the NSR rate maximum can be detected at lower temperatures. The relaxation time $T_{1\rho}$ is the time characterizing the recovery of the longitudinal magnetization equilibrium in the rotating frame, i.e., it is the relaxation time when the magnetization is locked along the RF magnetic field H_1 (typically 5–20 G). This relaxation time is sensitive to low motions (10–50 kHz). In this case, the position of a $T_{1\rho}$ minimum (or equivalently, a relaxation rate maximum) indicates the temperature at which the correlation time of the proton motions (τ_c) is comparable to the reciprocal of the ^{1}H frequency in the lock field H_1 (i.e., $\tau_c \sim (2\gamma H_1)^{-1} \approx 10^{-5}$ s, where γ is the proton gyromagnetic ratio). Measurements of the proton spin-lattice relaxation in the rotating frame ($T_{1\rho}$) were undertaken between 173 K and 350 K using a lock field $H_1 \approx 18$ G in the sample HDA:MoO_3 (Fig. 2). The ${T_{1\rho}}^{-1}$ maximum at around 280 K reflects the relative lower mobility of the protons of the HDA chain inside the low dimensional space of the molybdenum oxide.

The description of the segmental motion of long chains in terms of just one correlation time or in terms of a symmetric distribution of correlation times may be unrealistic. A model extensively used in polymer literature is that of Schaefer, which proposed a broad asymmetric distribution of correlation times to describe the ^{13}C relaxation in flexible polymer chains [11]. Lycknert *et al.* reported a C-13 spin-lattice (T_1) and spin-spin (T_2) relaxation time measurements of glycolipid in SDS micelles [12]. The authors characterized the motional restriction via an order parameter and, under the assumption of isotropic overall tumbling, they estimated a correlation time of 1.68 ns from the T_1/T_2

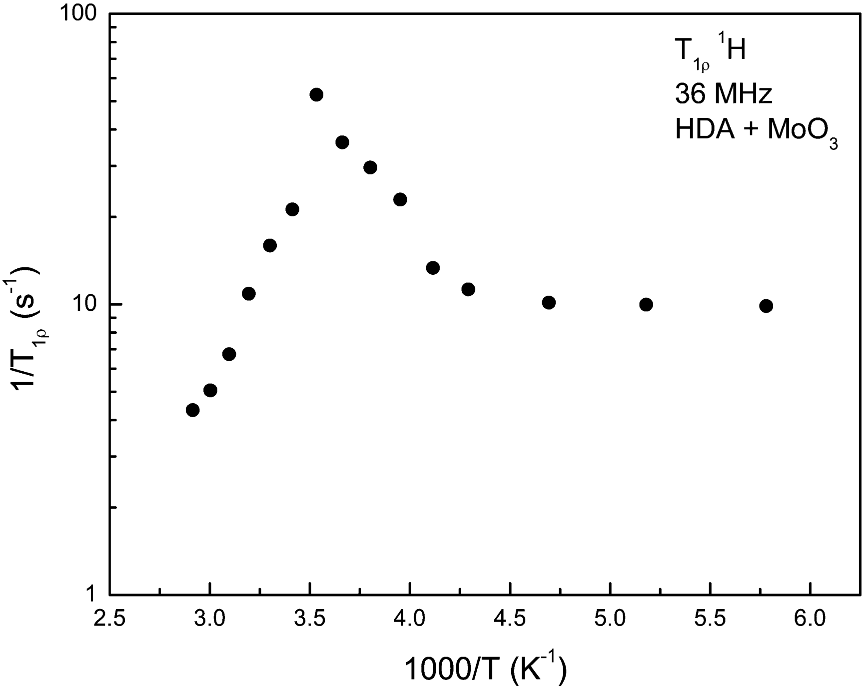

FIGURE 2 Temperature dependence of the ^{1}H spin-lattice relaxation rates in the rotating frame ($T_{1\rho}{}^{-1}$) in HDA:MoO$_3$, measured at the frequency $\omega_1 \approx 76\,\mathrm{kHz}$.

ratio at 305 K [11]. This value is of the same order of magnitude than those found in the samples HDA:TiO$_2$, HDA: MoO$_3$ and HDA:V$_2$O$_3$ for the few protons of the terminal CH$_3$ group in the HDA chain. The results of spin-lattice relaxation in the rotating frame indicate however that most of the protons of the HDA chain have a relative lower mobility. Further systematic investigations, including NMR measurements and simulations with asymmetric distribution of correlation times are in progress to confirm our description.

On the other hand, the ^{13}C high-resolution NMR spectra for the samples HDA:MoO$_3$ and HDA:TiO$_2$ are shown in Figures 3 and 4 respectively. A possible attribution of these lines with the different carbons in the HDA molecule is shown in the figures and in Table 1, where the isotropic chemical shift for each line is indicated. For each compound, spectra were taken in three different conditions: direct polarization, CP and direct polarization with DD by 150 μs. The different intensity response of the NMR lines in these experiments supports

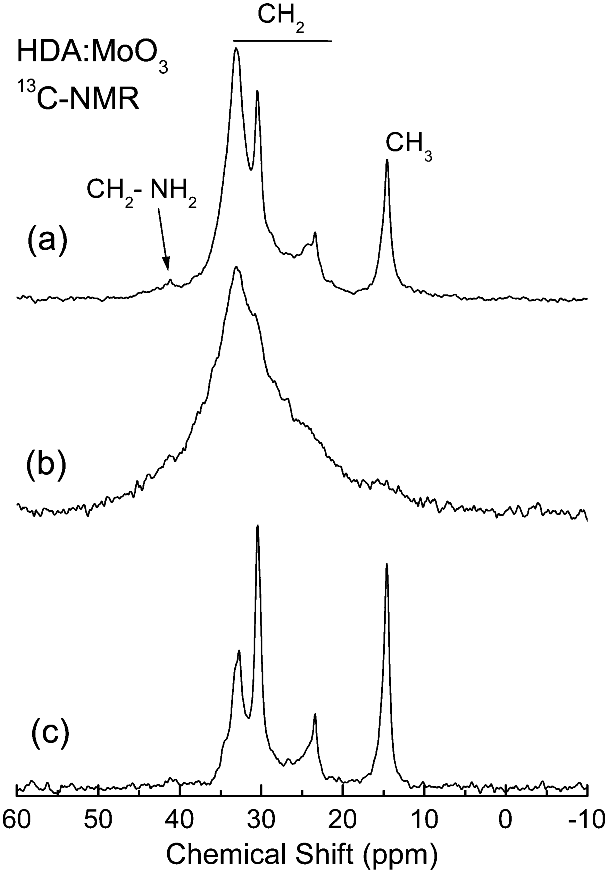

FIGURE 3 ^{13}C high-resolution NMR spectra of hexadecylamine intercalated in molybdenum oxide (HDA:MoO_3). (a) direct polarization. (b) cross-polarization. (c) direct polarization with ^1H decoupling delayed by 150 µs.

the line attributions. It can be seen in Figures 3b and 4b that the stronger NMR signals in CP spectra correspond to CH_2 carbons and not to CH_3, due to the fact that the latter groups undergo rapid reorientations reducing the effective dipolar coupling of the methyl carbon. Conversely, a significant attenuation of the CH_2 lines can be observed in the DD spectra (Figs. 3c and 4c), due to the faster time decay of these carbons with stronger dipolar couplings with H. The lines at 33 ppm and 30 ppm correspond to several, almost equivalent, CH_2 carbons in the backbone of the hexadecylamine molecule. On the other hand, the signal around 40 ppm corresponds to the carbon bonded to

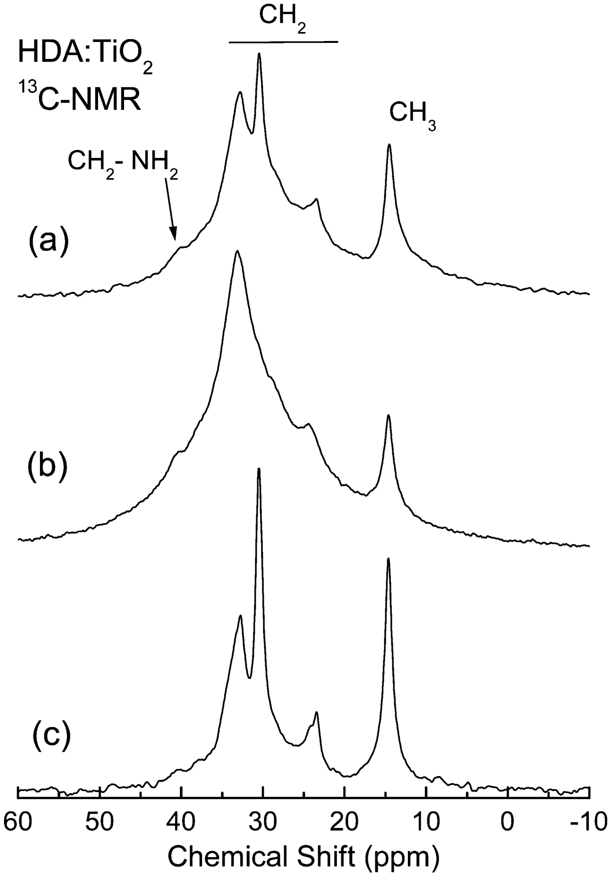

FIGURE 4 ^{13}C high-resolution NMR spectra of hexadecylamine intercalated in titanium oxide (HDA:TiO$_2$). (a) direct polarization. (b) cross-polarization. (c) direct polarization with ^{1}H decoupling delayed by 150 μs.

the amine group. It can be noted that this signal is broader in the MoO$_3$ compound with respect to the TiO$_2$, and in both cases this line is broader than the other signals from individual carbons (for example those at 24.4 and 23.4 ppm). The broadening is caused by the indirect quadrupolar coupling with the bonded ^{14}N species ($I = 1$), which have electric quadrupolar coupling with the local electric field gradient [13]. The difference in the line broadening in these two compounds indicates that in the molybdenum complex the electric field gradient at the N site, and consequently the quadrupolar coupling, is higher than in the Ti compound. This observation reveals the differences in the

TABLE 1 ^{13}C Isotropic Chemical Shifts for the Magnetically Non-Equivalent Carbons Observed NMR Spectrum of Molybdenum and Titanium Complexes and their Attribution with Carbon Groups in the HDA Molecule

	HAD:MoO_3 (δ ppm)	HDA:TiO_2 (δ ppm)
CH_3	14,6	14,6
CH_2	23,4	23,3
CH_2	24,4	24,4
CH_2	30,5	30,5
CH_2	32,9	32,8
CH_2–NH_2	41,2	40,1

atomic environments around the anchorage site of the HDA molecule on the substrate. On the other hand, the comparison of the data in Table 1 show that in both complexes the chemical shift values for each magnetically non-equivalent site of the molecule are identical except for the carbon bonded to the amine group. From this fact it is possible to conclude that the geometry of the HDA molecule is identical in both in the Ti and Mo complexes, and the only difference concerns to the amino group, which should be attributed to the local properties of the substrate. Therefore, the high-resolution NMR results are fully compatible with the picture of HDA molecules arranged perpendicularly to the substrate and anchored only at the amino group.

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