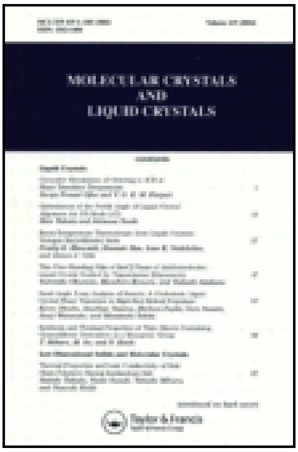

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Lanthanide Relaxation and Shift Properties as NMR Probes for the Location of Tributylphosphate in Clays

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LANTHANIDE RELAXATION AND SHIFT PROPERTIES AS NMR PROBES FOR THE LOCATION OF TRIBUTYLPHOSPHATE IN CLAYS

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Abstract The interaction of Eu^{3+} and tributylphosphate in the montmorillonite clay SAZ1 has been investigated by NMR spectroscopy. The ^{13}C-NMR spectrum of TBP sorbed onto SAZ1 partially exchanged with Eu^{3+} shows two sets of four peaks differing by 2-3ppm. Longitudinal relaxation times for ^{13}C -TBP sorbed to SAZ1 and Eu^{3+}-SAZ1 (as D_2O slurries) are .9s and .4s, respectively. The T_1's determined by ^{13}C-CPMAS on the solid samples are .24s and .28s, respectively. Linewidths of the CPMAS spectra of ^{13}C-TBP sorbed to SAZ1 and Eu^{3+}-SAZ1 are 204 Hz and 305 Hz.

Keywords: tributylphosphate, CPMAS of tributylphosphate, europium shift effects, clays, montmorillonite, NMR

INTRODUCTION

Clays are of interest in the environmental arena because of their exchange of metal cations and sorption of organic molecules. An understanding of the mutual interaction of these two processes is vital to the design of models applicable to environmental restoration. The sensitivity of NMR to molecular environment and motion makes NMR a prime technique for elucidating the environment of sorbed organic molecules and exchanged cations in the solid state. Over the last ten years CPMAS has been applied to the study of silicates, aluminosilicates[1,2] and zeolites[1].

An evaluation of hazardous waste at the Hanford nuclear facility[3] lists tri-n-butyl phosphate(TBP) as a major component of organic waste released over the 20 year period 1952 to 1972. Radioacitve waste includes Cs^{137}, Pu^{239}, Eu^{151}, Eu^{152} and Eu^{154}-contaminated TBP.

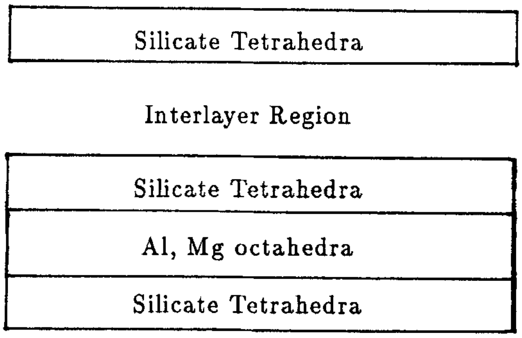

FIGURE 1 Schematic representation of the structure of the 2:1 phyllosilicate, montmorillonite.

We have undertaken studies to detail the interaction of clays with these metal cation/organic mixtures. Clays of the smectite group are important stratigraphic components of units beneath the Hanford facility. A schematic structure of the smectite, montmorillonite, is shown in Figure 1. Most exchangeable cations are situated in the interlayer region between tetrahedral silicate layers. These cations balance the net negative charge resulting from ion substitution such as Mg^{2+} substitution for Al^{3+} in the octahedral layer[4]. Organic molecules enter this interlayer region, swelling the clay.

The goal of the work presented here is to gain information on the location of tributylphospate in ion-exchanged clays by probing distance-dependent NMR interactions in the solid state. The exchanged cation in these studies is the lanthanide Eu^{3+} . This lanthanide acts as an NMR shift agent which induces chemical shift changes in neighboring nuclei as a function of distance and orientation to the observed nucleus.

EXPERIMENTAL

The clay used in this study is the well characterized montmorillonite SAZ1 which has Ca^{2+} as the dominant interlayer cation. The clay is washed with sodium citrate buffer to remove surface iron, dialyzed against NaCl(aq), rinsed with deionized H_2O and dried at room temperature. To prepare Eu^{3+} -

exchanged SAZ1 (Eu^{3+}-SAZ1), the washed clay (SAZ1) is stirred for 24hr in .1N $Eu(NO_3)_3.(H_2O)_6$ in H_2O, rinsed exhaustively with deionized H_2O and dried at room temperature. Tributylphosphate(TBP) is incorporated by stirring the clay in 15% TBP/dodecane for 24 hrs., rinsing with hexane and drying at room temperature.

NMR studies are carried out both on D_2O slurries of the clays and on solid samples. Clay slurries are prepared by mixing .2 gm clay with 1 mL D_2O. ^{13}C-NMR studies of slurries are carried out on a Varian GEMINI-200MHz spectrometer at 25° C. The T_1 experiments use a $180° -\tau- 90°$ inversion-recovery sequence. Chemical shift values are reported relative to TMS.

Solids experiments are carried out on a Bruker CXP-200 using a Doty CPMAS probe. The B_1 fields were 13 Gauss for proton and 52 Gauss for carbon. The proton-enhanced ^{13}C T_1 is determined as described by Torchia[5].

TBP enriched with ^{13}C is synthesized from 1-^{13}C-butanol(MSD) and phosphorous oxychloride(Aldrich). To a solution of .68 mL butanol(7.43 mmol), .6 mL benzene and .59 mL pyridine(7.43 mmol), .21 mL $POCl_3$ (2.3 mmol) is added dropwise. After stirring for 2.5 hr, the organic phase is washed with .6 mL H_2O then dried over sodium sulfate. Purity is verified by NMR.

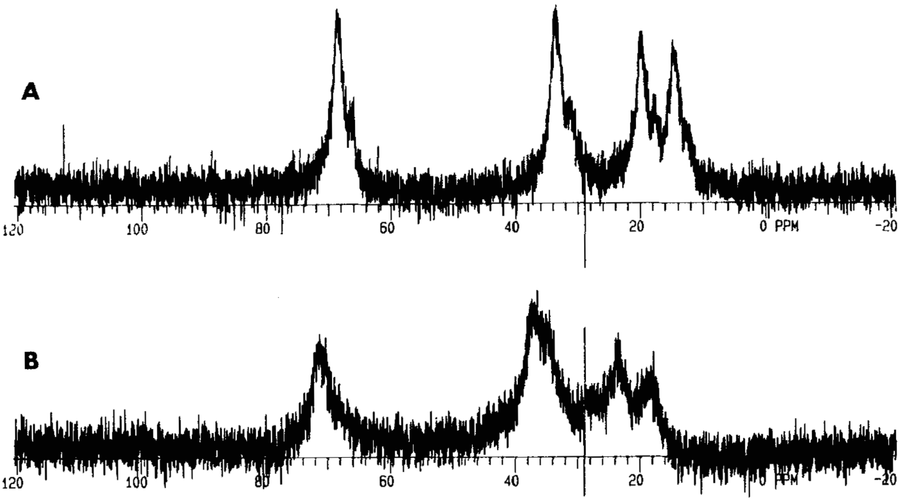

FIGURE 2 ^{13}C-NMR spectra of TBP sorbed to Eu^{3+}-SAZ1 prepared with .1N Eu^{3+} (A) and .2N Eu^{3+} (B). Samples are D_2O slurries.

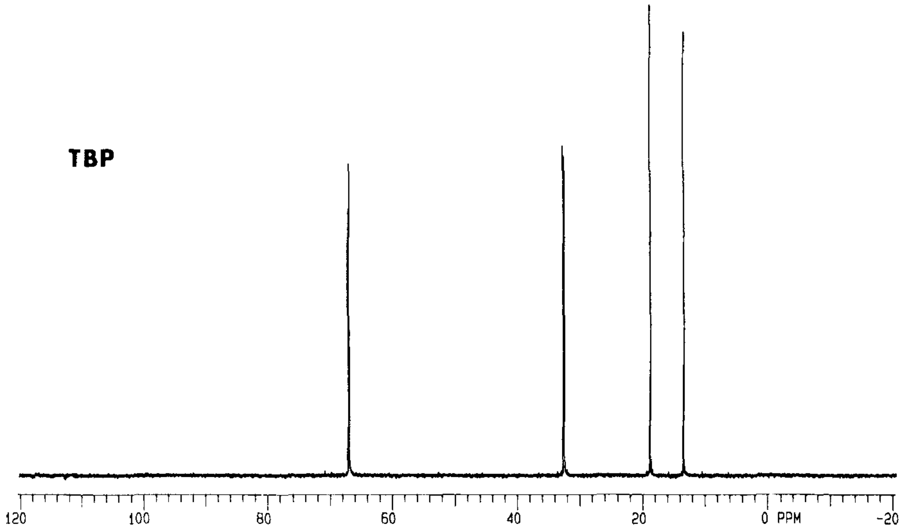

FIGURE 3 ^{13}C-NMR spectrum of tributylphosphate in d_6-benzene.

RESULTS

Shown in Figure 2A is the ^{13}C-NMR spectrum (D_2O slurry) of TBP sorbed to Eu-SAZ1 prepared from a .1N solution of Eu^{3+}. This spectrum displays two sets of four lines indicating the presence of TBP in two different environments. The downfield set of lines is the more intense. As shown in Figure 2B, the spectrum of TBP in Eu^{3+}-SAZ1 prepared from a more concentrated Eu^{3+} solution (.2N) displays one set of peaks shifted downfield relative to the lines of spectrum A. These spectra indicate that Eu^{3+} causes a 2-3 ppm downfield shift in the TBP ^{13}C spectrum. The NMR spectrum of TBP in d_6-benzene is shown in Figure 3.

Relaxation studies were carried out on samples prepared with ^{13}C-enriched TBP. The ^{13}C longitudinal relaxation times (T_1) obtained on slurries of TBP sorbed to SAZ1 and Eu^{3+}-SAZ1 are .9s and .4s, respectively. The paramagnetic contribution by Eu^{3+} to the longitudinal relaxation time is expected to be small[6,7]. The interlayer spacing in SAZ1 with Ca^{2+} , Na^{+} or Eu^{3+} as the interlayer cation should be similar since these ions have comparable ionic

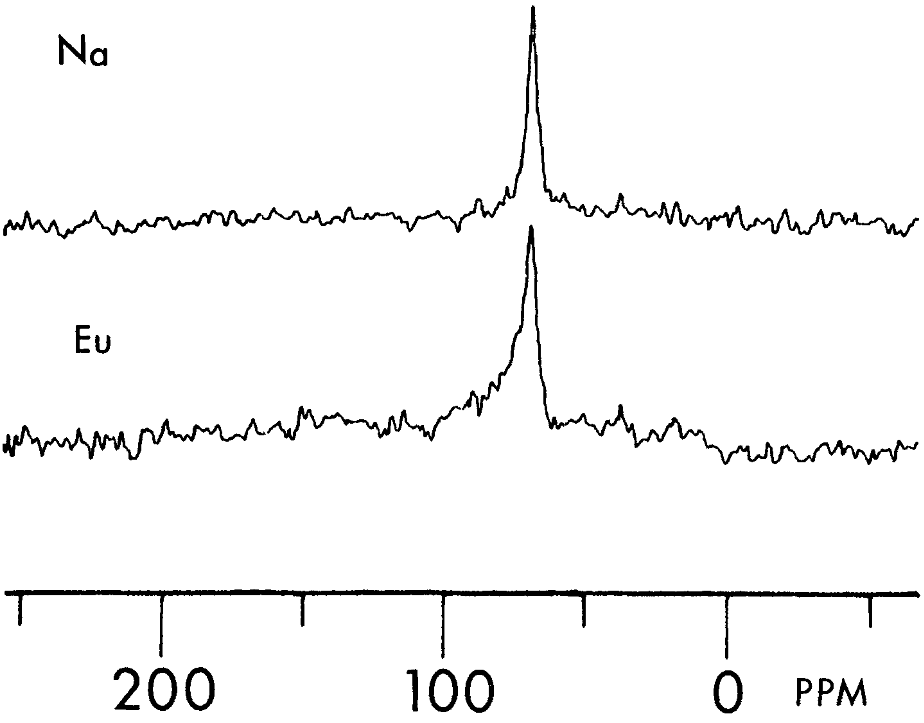

FIGURE 4 ^{13}C-CPMAS spectra of ^{13}C-TBP sorbed into SAZ1 and Eu^{3+}-SAZ1.

radii, .99Å , .95Å and .95 Å , respectively. Significant differences in the NMR linewidths were observed for ^{13}C-TBP in SAZ1 and Eu^{3+}-SAZ1 studied as the D_2O slurries. The ^{13}C-linewidth is 2.9ppm for TBP in SAZ1 and 19ppm for TBP in Eu^{3+}-SAZ1. The increased linewidth in Eu^{3+}-SAZ1 may be attributed to TBP molecules at different distances from Eu^{3+}.

The CPMAS spectrum of solid SAZ1 sorbed with ^{13}C-TBP shows a sharp peak at 68 ppm with a linewidth of 204Hz. The spectrum obtained from the Eu^{3+}-exchanged clay displays a slightly broader peak (305Hz) at 68ppm. The most striking difference between the two spectra is a shoulder extending out to 91 ppm on the later. The signal in this broadened downfield region is attributed to TBP near the Eu^{3+} ion. The T_1 values of ^{13}C-TBP in the solid SAZ1 and Eu^{3+}-SAZ1 samples are .24s and .28s. This decrease in T_1 for

^{13}C-TBP in the SAZ1 solid sample compared to the slurry sample reflects a decreased mobility in the solid sample. Chemical shifts for the spectra shown are collected in Table 1.

TABLE I ^{13}C-Chemical Shift Values from TBP Spectra.

SAMPLE	C-1	C-2	C-3	C-4
TBP/benzene	67.1	32.8	19.0	13.6
Eu^{3+}SAZ1(.1M)	68.2,66.1	34.0,31.0	20.0,17.5	14.5,12.5
Eu^{3+}SAZ1(.2M)	71.4	37.0	23.8	18.5
Eu^{3+}SAZ1 CPMAS	68.0,91br			
SAZ1 CPMAS	68.0			

ACKNOWLEDGMENTS

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