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^{31}P NMR STUDY OF THE COMPLEXATION OF TBP WITH LANTHANIDES AND ACTINIDES IN SOLUTION AND IN A CLAY MATRIX

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ABSTRACT

The goal of these studies has been to apply the techniques of NMR to gain insight into the behavior of tributyl phosphate/lanthanide complexes in the interlayer or on edge sites of clays. Initial work in this laboratory yielded details of the complexation of the two lanthanide salts $Eu(NO_3)_3$ and $Pr(NO_3)_3$ with TBP in a hexane solution. This information on complexation in solution is crucial to interpretation of the results of NMR studies of the complexes exchanged into the clays. The solution ^{31}P-chemical shift values were improved by repeating the studies on the lanthanide salts dissolved directly into neat TBP. NMR studies of these neat solutions of the $Eu(NO_3)_3 \bullet 3TBP$-complex and the $Pr(NO_3)_3 \bullet 3TBP$-complex show that the ^{31}P chemical shift remains relatively constant for TBP:lanthanide ratios below 3:1. At higher ratios, the chemical shift approaches that of free TBP, indicating rapid exchange of TBP between the free and complexed state. Exchange of these complexes into the clay hectorite yielded discrete ^{31}P-NMR signals for the Eu•TBP complex at -190 ppm and free TBP at -6 ppm. Adsorption of the Pr•TBP complex yielded broad signals at 76 ppm for the complex and -6 ppm for free TBP. There was no evidence of exhange between the incorporated complex and the free TBP.

RESULTS

The results of the work are given below for the major stated goals.

- Solution ^{31}P NMR studies of $Eu(NO_3)_3$, $Pr(NO_3)_3$ and $UO_2(NO_3)_2$ complexation with TBP

Although solution ^{31}P-NMR values had been obtained for the complexation of the lanthanide and actinide salts with TBP in the co-solvent hexane, the values fluctuated among replicate extractions. We found that stable values of the ^{31}P-chemical shift were obtained by direct dissolution of the salt into TBP. The ^{31}P-NMR spectra of Eu•TBP solutions prepared at the stated ratios are shown in Figure 1. The chemical shift values are given in Table I.

As TBP in excess of 3:1 is added, the chemical shift moves downfield. This behavior is expected for a situation in which rapid exchange is occurring between the complexed and uncomplexed state. In an exchanging system, the observed chemical shift is the weighted average of the shifts of the bound and free species[1]. The following equation relates the chemical shifts of solutions of differing composition, σ_n and σ_i. In this case, n and i are molar ratios TBP:Eu.

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$$\sigma_n = \sigma_i\left(\frac{i}{n}\right) + \sigma_{TBP}\left(\frac{n-i}{n}\right)$$

The observed shift of solution n can be calculated given the shift of solution i. To predict σ of the 3:1 solution, σ of the 15:1 solution was substituted into equation 1. The experimental ^{31}P-chemical shifts of TBP and the 15:1 solution are 0.30 and -34.57 ppm, respectively. The unbound and bound values for TBP are 15-3 and 3 since one Eu complexes with three TBP molecules. The calculated value is -172.16ppm. Equation 1 is used to predict the chemical shifts of samples with varying TBP:Eu ratios, n. In this case, the calculated value of the 3:1 shift is used. A comparison of the calculated values and the experimental values are shown in Figure 2.

- Solid state ^{31}P NMR studies of TBP/lanthanide and actinide complexes in clays

The behavior of TBP and Eu in the clay hectorite is studied by ^{31}P-MAS of the solid samples. The observed ^{31}P chemical shift values (σ) and the d-spacing determined by powder X-ray diffractometry are tabulated in Table II. The spectra obtained from these samples are shown in Figure 3.

The most dramatic change in σ is displayed by the Eu•TBP which is directly adsorbed into the clay, samples III-VII. These samples show broad peaks in the range -180.7 to -194.8 ppm. This represents a significant upfield shift relative to TBP in hectorite alone at -0.7 ppm (sample I).

In contrast, TBP that is adsorbed into Eu-exchanged hectorite, samples VIII-X, shows only downfield signal in the range -6.0 to -27 ppm. This is indicative of TBP that is distant from Eu. This Eu-hectorite was prepared under conditions of low ionic strength at pH=5. These conditions favor cation exchange into the interlayer for the system uranyl exchanged into a Wyoming montmorillonite. The d-spacings of 18.17 and 17.94 Å found in samples IX and X indicate that the TBP did adsorb into the interlayer. The smaller amount of TBP used in sample VIII was insufficient to expand the interlayer spacing. The d-spacing of 12.36 Å differs little from the spacings of 12.32 Å and 12.48 Å in Eu-hectorite and Ca-hectorite, respectively. These studies indicate that TBP is adsorbed into the clay but does not form a complex with Eu in the process. It seems plausible that in these samples Eu is on the edge sites while TBP moves into the interlayer.

We see no indication that TBP is in proximity to Eu in the samples prepared by exchanging Eu into a TBP-adsorbed hectorite, sample II.

The spectra to this point indicate that the complex displays a signal in the region of -196 ppm. We wish to look for evidence of exchange of free TBP with the complex. Hectorite was adsorbed with solutions of TBP:Eu in the ratios 3:1, 5:1 and 7:1. Results of the ^{31}P-NMR are detailed in Table II, samples V, VI and VII. The spectra are shown in Figure 4. These samples show signal attributed to the Eu•TBP complex in the region -189.1 to -194.8 ppm and to uncomplexed TBP in the region -2.3 to -6.0 ppm.

Spectra of Pr•TBP complex adsorbed into hectorite show a chemical shift of 75.6 ppm for the complex and -6 ppm for the free TBP. The shift for the complex is somewhat downfield of the solution complex value of 62.98 ppm. The Eu•TBP -complexes displayed the same behavior. These spectra are shown in Figure 5.

REFERENCES

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PRESENTATIONS OF THIS WORK

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PUBLICATION IN PREPARATION

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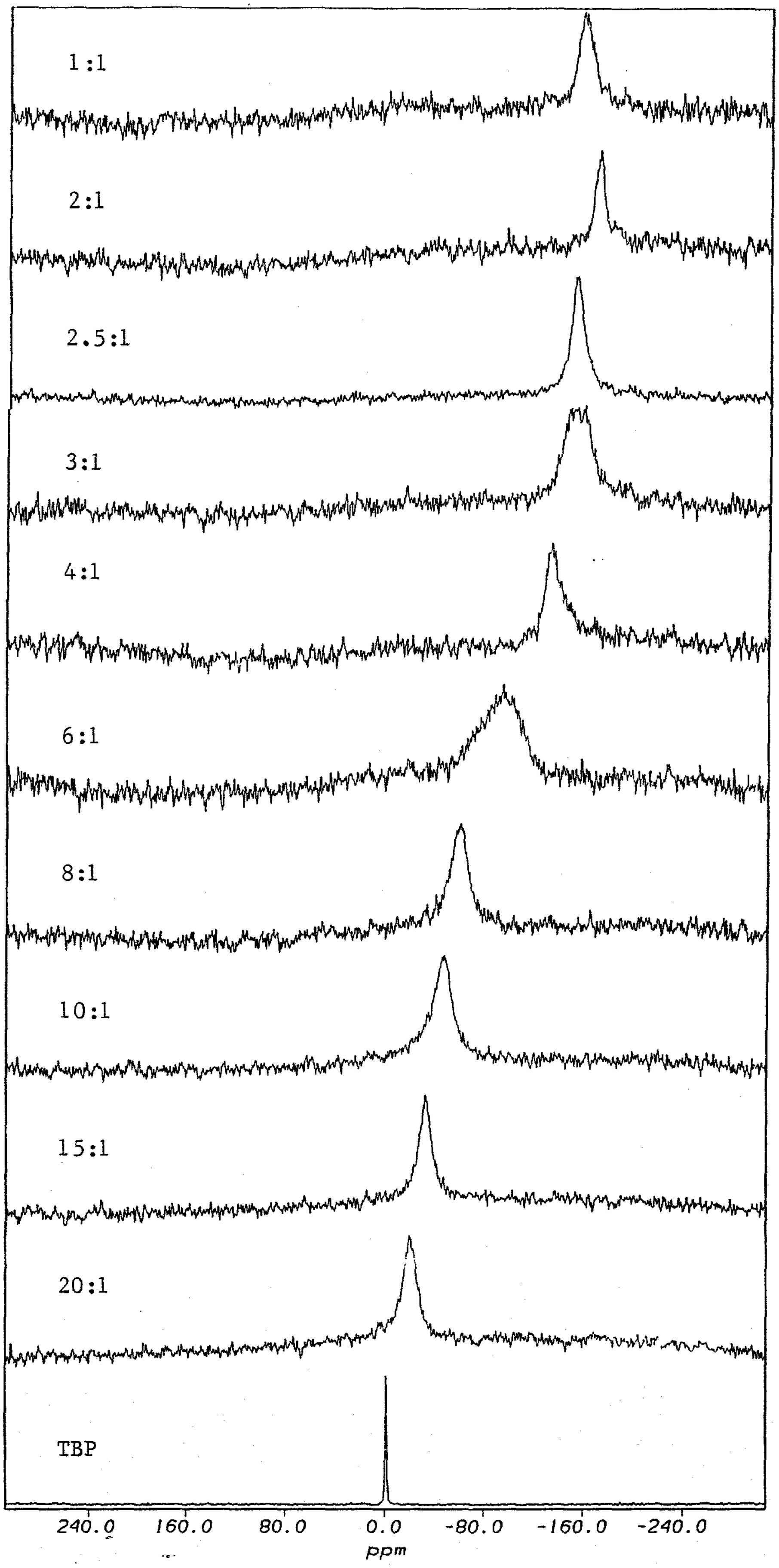

FIGURE 1. ^{31}P spectra of solutions prepared by direct dissolution of $Eu(NO_3)_3 \cdot 6H_2O$ in TBP. The molar TBP:Eu ratios are indicated.

Table I ^{31}P chemical shift of solutions prepared at different TBP:Eu ratios

TBP:Eu ratio	^{31}P chemical shift, ppm
1:1	-158.1
2:1	-172.9
2.5:1	-156.0
3:1	-150.9
4:1	-132.8
6:1	-99.1
8:1	-61.1
10:1	-48.1
15:1	-34.6
20:1	-23.4
TBP	0.3

Table II ^{31}P chemical shift, *d*-spacing values for hectorite exchanged with europium, TBP or Eu-TBP

Sample number	Sample	Chemical shift ppm	d-spacing Å
	TBP (solution)	-0.3	
I	TBP·Hectorite	-0.7	18.4
II	TBP·Hect + Eu(IS = 0.003)	-5.0	18.1
III	Hectorite + 3:1 TBP·Eu	-2.3 -180.7	
IV	Hectorite + 3:1 TBP·Eu	-191	18.2
V	Duplicate of Sample IV	-6.1 -189.1	17.9
VI	Hectorite + 5:1 TBP:Eu	-4.0 -189.3	
VII	Hectorite + 7:1 TBP:Eu	-6.0 -194.8	
VIII	Eu·Hectorite + TBP (The intended TBP to Eu ratio was 2:1)	-27	12.4
IX	Eu·Hectorite + TBP (excess)	-20	18.4
X	Duplicate of sample IX	-6.2	17.9
XI	Eu·Hectorite	No Signal	12.3
XII	Ca·Hectorite	—	12.5

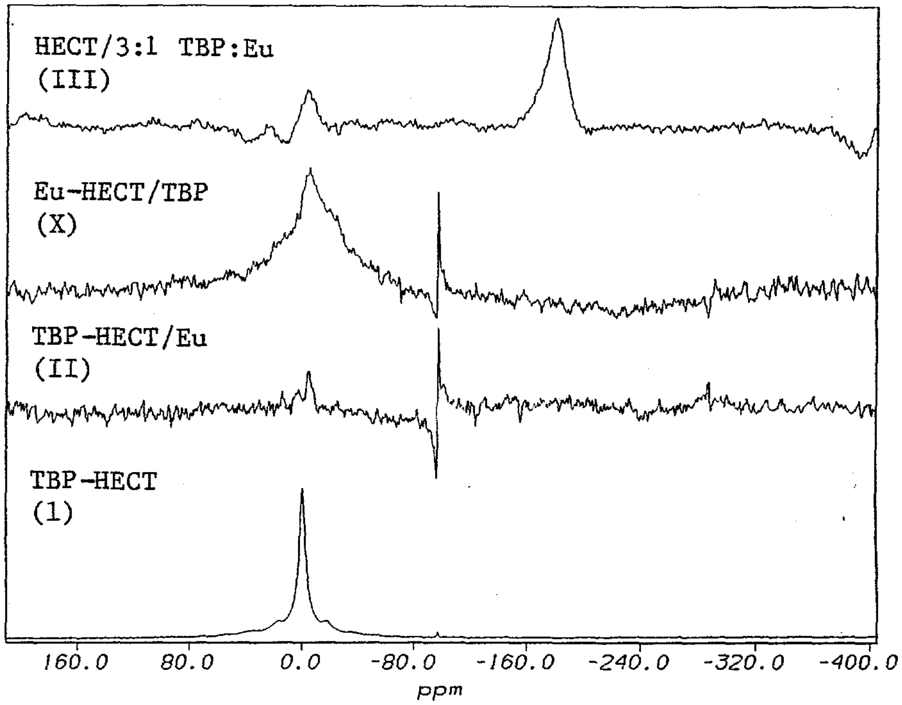

FIGURE 3. ^{31}P-MAS spectra of hectorite adsorbed with Eu and/or TBP as described in Table II.

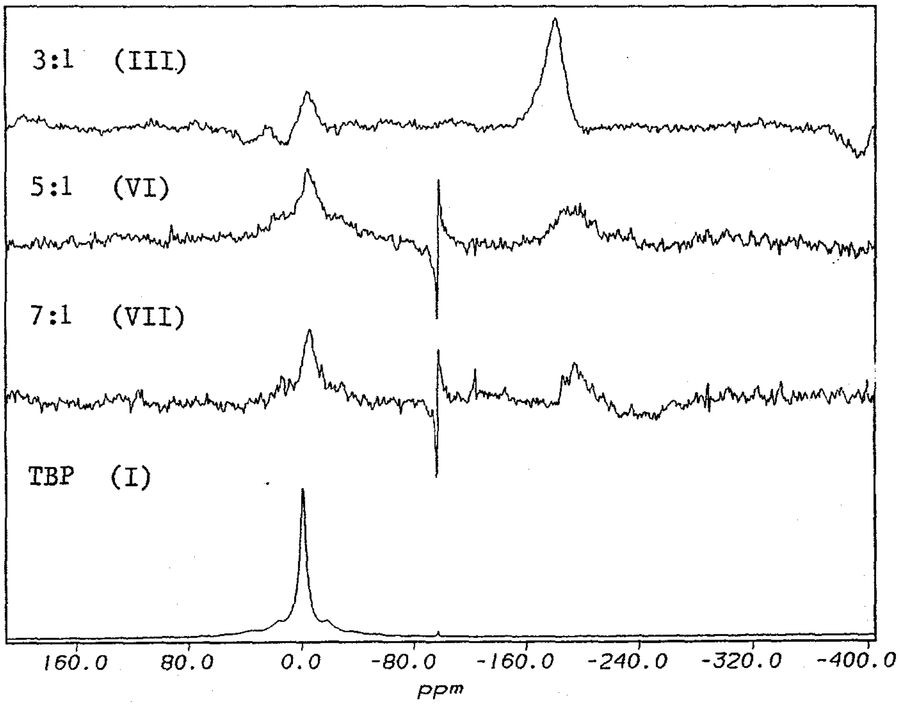

FIGURE 4. ^{31}P-MAS spectra of hectorite adsorbed with TBP:Eu soltions prepared with the given ratios.

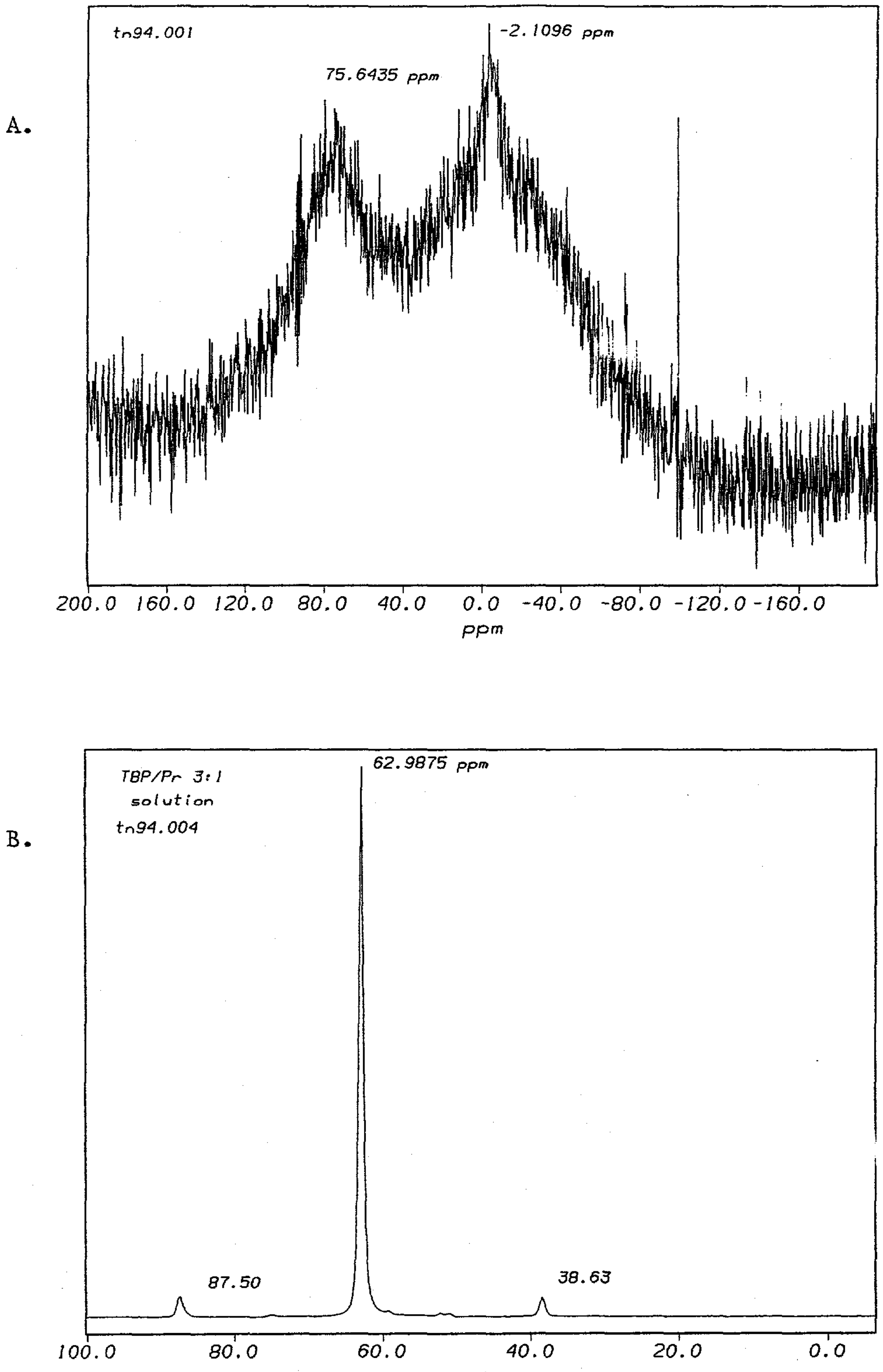

FIGURE 5. ^{31}P-MAS spectrum (A) of hectorite adsorbed with a 3:1 molar solution of TBP and Pr(NO$_3$)$_3$. The solution spectrum of this 3:1 TBP:Pr is shown in B.