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IN ION EXCHANGE RESINS AND IN A SOLVENT EXTRACTANT

by

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ABSTRACT

A Mössbauer effect has been observed for Np(IV) ions sorbed on a cation exchange resin from HNO_3 and HCl solutions and for $[\text{NpCl}_6]^{-2}$ and $[\text{Np}(\text{NO}_3)_6]^{-2}$ complexes sorbed on an anion exchange resin. Mössbauer spectra have also been recorded for $[\text{NpCl}_6]^{-2}$ and $[\text{Np}(\text{NO}_3)_6]^{-2}$ complexes extracted into a tri-n-octylamine-benzene solution. The isomer shifts and quadrupole splittings for the sorbed and extracted species have been found to agree, but the quadrupole splittings were found to differ from those observed for the parent compound in the crystalline state. The Mössbauer spectra for all noncrystalline systems at 4.2°K were found to be dominated by magnetic hyperfine splitting.

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INTRODUCTION

Of the methods currently used for the separation of the actinide elements, those based on ion exchange and solvent extraction techniques are by far the most important. In the application of these techniques, a question often arises as to the nature of the individual species sorbed on the ion exchange resin or the species present in the extracted phase. In solvent extraction systems, much use has been made of spectrophotometric measurements in the identification of the extracted species [1]. Unfortunately, since ion exchange resins are opaque to most spectroscopic investigations, experimental information at the molecular level for sorbed species has been limited. During recent years, however, the Mössbauer effect, which utilizes penetrating gamma radiation, has been applied to the study of complexes of elements such as iron and tin sorbed on ion exchange resins [2-4].

It seemed important to assess the possibility of using Mössbauer spectroscopy to identify and characterize actinide elements in such noncrystalline systems as ion exchange resins and solvent extractants. Practically every actinide nuclide would seem to lend itself to Mössbauer spectroscopy because each has a low-lying γ -transition to the ground state and a favorable lifetime of the first excited state. On close examination, however, most of the nuclides are in fact unsuitable, either because the

parent nuclide is too short-lived or because it can be obtained only with difficulty or in very small quantities. Only ^{237}Np , among the selection of possible Mössbauer nuclides of the actinides, has so far been investigated in any detail [5,6]. The properties of the 59.54-keV γ -transition are highly favorable for Mössbauer spectroscopy, and studies [5,6] have shown that chemical properties of neptunium are correlated with experimental Mössbauer spectroscopic parameters.

This paper describes a Mössbauer spectroscopic study of tetravalent ^{237}Np species sorbed on anion and cation exchange resins and liquid extracts of tetravalent ^{237}Np . It is hoped that this study will demonstrate the utility in applying Mössbauer spectroscopy to investigations of neptunium and other actinide elements in noncrystalline systems.

EXPERIMENTAL

PREPARATION OF RESIN SAMPLES

The ion exchange resins used were 200 to 400 mesh "Dowex"* 50W-X8, a cation resin of the sulfonated styrene-divinylbenzene type, and "Dowex" 1-X8, a strongly basic anion resin of the quaternary ammonium type. The neptunium species were introduced into the resin by adding 1 g of the wet resin to 25 ml of the appropriate neptunium solution contained in a 50-ml Erlenmeyer flask and stirring for two hours. The resin was removed from

* Registered Trademark of Dow Chemical Co.

the solution by passing the mixture through a fritted glass filtering crucible. Excess solution was removed by washing with a small amount of distilled water. The resin was dried by passing a stream of nitrogen through the resin contained on the filtering crucible.

The dried resin was loaded into a Mössbauer sample holder to a depth sufficient to produce an absorber thickness of about 30 to 50 mg/cm² of ²³⁷Np.

PREPARATION OF NEPTUNIUM SOLUTIONS

Solutions of ²³⁷Np(IV) were prepared from a stock solution containing 20 mg/ml of ²³⁷Np in 1.5M HNO₃. The neptunium stock solution was spectrophotometrically found to be Np(V). Valence was adjusted to the tetravalent state by increasing the nitric acid concentration of a small aliquot (10 to 20 ml) of the stock solution to approximately 4M. The solution was then made 0.05M in hydrazine by the addition of hydrazine hydrate. The solution was then heated to 50 ±5°C, and 1M ascorbic acid was added in an amount stoichiometrically required to reduce the oxidized neptunium species to the tetravalent state and leave a 0.03M excess of ascorbic acid in solution. The HNO₃ concentration in the solution was then adjusted to correspond to the values reported later in this paper.

Hydrochloric acid solutions of ^{237}Np were prepared from the HNO_3 solutions of tetravalent neptunium by precipitating the ^{237}Np as the hydroxide and redissolving the precipitate in concentrated HCl . All subsequent HCl solutions of tetravalent ^{237}Np were prepared from this stock solution.

Tri-n-octylamine (TOA) extracts of tetravalent neptunium were prepared by extraction with 20 vol % TOA in benzene from 8M HNO_3 or concentrated HCl .

PREPARATION OF SOLID COMPOUNDS

Tetraethylammonium hexanitratoneptunate(IV) was prepared in a manner described previously [7]. Cesium hexanitratoneptunate(IV) was prepared by adding a stoichiometric quantity of cesium nitrate to an 8M HNO_3 solution of tetravalent neptunium. The fine needle-like crystalline precipitate formed immediately; the precipitate was allowed to digest at 25°C for 24 hours, was then suction-filtered on fritted glass, and was washed thoroughly with 8M HNO_3 . The compound was dried for two days under vacuum at 25°C over solid NaOH . The neptunium content of the compound was found to be 26.8%, which agrees with the theoretical value of 27% for $\text{Cs}_2[\text{Np}(\text{NO}_3)_6]$.

MÖSSBAUER SPECTRA

Velocity spectra were obtained with a loudspeaker type constant-acceleration Mössbauer spectrometer. All measurements were made with source and absorber at 4.2°K. The source was an alloy of ^{241}Am (3%) in thorium metal, which emits a single line with a very weak secondary line at -2.0 cm/sec from the strong line. The Mössbauer spectrometer [8], cryogenic system [9], and Am-Th source [10] have been described previously.

RESULTS AND DISCUSSION

The Mössbauer spectra at 4.2°K for four different tetravalent ^{237}Np systems obtained from 8M HNO_3 are shown in Figure 1. The isomer shifts and hyperfine parameters derived from these spectra are presented in Table 1.

The principal features of the spectra are the same for each of the four systems studied. Their features, the spans of the hyperfine patterns, and the number of lines are characteristic of magnetic hyperfine splitting [5]. This phenomenon has been noted previously for other neptunium compounds and has been attributed to slow paramagnetic relaxation rates at 4.2°K [11,12]. The isomer shifts for each sample, within experimental error, are the same and are indicative of the Np(IV) state. For example, similar isomer shift values have been reported for such tetravalent compounds as NpCl_4 (-0.34 cm/sec) [8] and NpBr_4 (-0.23 cm/sec) [13], converted to the NpAl_2 reference.

Spectrophotometric studies by Ryan and coworkers [7,14] have shown that tetravalent neptunium is sorbed on anion exchange resins and extracted into trioctylamine solutions from 8M HNO₃ as the hexanitrate anion, [Np(NO₃)₆]⁻². The presence of the same type of neptunium complex in each of the four systems shown in Figure 1 would explain the observed agreement between their Mössbauer spectra. However, while agreement is observed for most of the major spectral features, slight differences in quadrupole splitting do occur.

The spectra for Np(IV) sorbed on anion exchange resin and Np(IV) in a 20% TOA-benzene extract exhibit the same quadrupole splitting (+ 0.42 cm/sec), but this value differs from the quadrupole splitting observed for the solid neptunium hexanitrate compounds. The conclusion that can be drawn from these Mössbauer data is that all features of the coordination environment of the Np(IV) ion in the resin and TOA-benzene extract are the same. The quadrupole splitting in Cs₂[Np(NO₃)₆] (-0.33 cm/sec) and (Et₄N)₂[Np(NO₃)₆] (+0.06 cm/sec) indicates that the symmetry of the six nitrate groups coordinated to a Np(IV) ion in a solid crystalline compound is slightly different than that found in noncrystalline resin and solvent-extract systems.

Although the quadrupole splittings for (Et₄N)₂[Np(NO₃)₆] and Cs₂[Np(NO₃)₆] differ, the anion exchange resin and TOA-benzene systems exhibit the same quadrupole splitting. This implies that the resin and solvent systems are not imposing any unique structural requirements on the coordination environment of the Np(IV) ion.

The Mössbauer spectra at 4.2°K for tetravalent neptunium systems obtained from 12M HCl are shown in Figure 2. The isomer shifts obtained from these spectra are presented in Table 2 and are representative of tetravalent neptunium. Previous studies [15] suggest that Np(IV) is loaded on the anion exchange resin and extracted with TOA as the $[\text{NpCl}_6]^{-2}$ complex anion.

As observed in the Np(IV)-nitrate systems, magnetic hyperfine splitting is the dominant feature in the spectra for the Np(IV)-chloride systems. Magnetic splitting also has been observed [16] at 4.2°K for $(\text{Et}_4\text{N})_2[\text{NpCl}_6]$, $(\text{Me}_4\text{N})_2[\text{NpCl}_6]$, and $\text{Cs}_2[\text{NpCl}_6]$. The broad, partially unresolved spectra of Np(IV) sorbed on anion exchange resin, and Np(IV) in a TOA-benzene extract apparently are due to an intermediate relaxation rate.

Even though the Mössbauer spectra for the Np(IV)-chloride and Np(IV)-nitrate systems are complex and simplifying features are absent, the spectra may be used to give qualitative information about the state of the neptunium ion. Indeed, since the complexity of each spectrum is unique to a particular Np(IV) system, the spectra can be used as "fingerprints" for neptunium ion identification purposes.

In addition to studying anionic complexes, we also devoted some attention to the study of Np(IV) ions sorbed on cation exchange resins. Several spectra are shown in Figure 3, and isomer shifts extracted from the spectra are shown in Table 3.

All of the spectra exhibit broad unresolved lines. This broadening, which is similar to that observed for some of the anionic complexes of neptunium, is apparently due to an intermediate relaxation rate. Isomer shift values can be extracted from these spectra if one assumes that the centroid of the spectrum corresponds to the midpoint between the two outermost peaks. The isomer shifts reported in Table 3 were calculated in this manner. It was not possible to extract hyperfine splitting parameters from these partially resolved spectra. The spectra may be representative of a common Np(IV) species because all the spectra shown in Figure 3 are identical. Drying the samples under vacuum and over P₂O₅ produced no observable change in the spectral pattern, although the intensity of all peaks did increase by 25%.

Previous studies [17] on the cation exchange behavior of actinide elements suggest that cationic species of the type $[\text{Np}(\text{NO}_3)_n]^{+4-n}$ may be sorbed on the resin as the HNO₃ concentration increases. The spectra in Figure 3 show no evidence for the sorption of such species as the HNO₃ concentration is increased from 0.3 to 4.0M. Additional evidence that supports the absence of coordinated nitrate groups in the sorbed neptunium cations is obtained from the spectrum for Np(IV) loaded onto a cation exchange resin from 1M HCl. This spectrum, shown in Figure 3, is identical to the spectra obtained from HNO₃ solution. Because the spectra for the hexanitrate and hexachloro complexes were found to be very different, one would also expect to observe differences between

the spectra of cationic complexes containing chloride and nitrate groups. The agreement between the spectra for the cationic systems obtained from HNO_3 and HCl solutions suggests that Np(IV) is sorbed on the cation exchange resin free of coordinated NO_3^- and Cl^- groups.

Even though the spectral pattern for tetravalent neptunium sorbed on a cation exchange resin is completely different from that observed for anionic hexanitrate systems, the isomer shifts are the same within experimental error. Thus, the Np(IV) ion in the resin may be hexacoordinated with the coordination environment composed of acidic oxygen groups. The acidic oxygens could be supplied by the sulfonic acid residues of the cation exchange resin. As additional support for this suggestion, resin samples dried over P_2O_5 produced spectra identical to those obtained for wet resin. The water molecule plays only a minor role in the coordination sphere of the Np(IV) ions sorbed on the resin, assuming that the drying process removed a major fraction of the water associated with the resin.

From the results obtained in this study, it may be concluded that Mössbauer spectroscopy can be a useful and powerful tool for investigating neptunium in such noncrystalline systems as ion exchange resins and solvent extractants.

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TABLE 1. Mössbauer parameter of tetravalent neptunium obtained from 8M HNO₃

Sample	Isomer Shift (NpAl ₂ ref.), cm/sec	eqQ/4 for Np Ground State, cm/sec	Magnetic splitting $g_0 \mu_n H_{eff}$, cm/sec
Np(IV) on "Dowex" 1-X8	-0.28 ±0.05	+0.42 ±0.05	6.59 ±0.05
Np(IV) in 20% TOA-benzene extract	-0.28 ±0.05	+0.42 ±0.05	6.59 ±0.05
Cs ₂ [Np(NO ₃) ₆]	-0.40 ±0.05	-0.33 ±0.05	6.06 ±0.05
(Et ₄ N) ₂ [Np(NO ₃) ₆]	-0.33 ±0.05	+0.06 ±0.05	6.35 ±0.05

TABLE 2. Mössbauer parameters of tetravalent neptunium obtained from 12M HCl

Sample	Isomer Shift (NpAl ₂ ref.), cm/sec
Np(IV) on "Dowex" 1-X8	-0.64 ±0.09
Np(IV) in 20% TOA-benzene extract	-0.64 ±0.09

TABLE 3. Mössbauer parameters of tetravalent neptunium on "Dowex" 50W-X8 cation exchange resin

Sample	Isomer Shift (NpAl ₂ ref.), cm/sec
Np(IV) from 0.3M HNO ₃	-0.23 ±0.10
Np(IV) from 1.0M HNO ₃	-0.19 ±0.10
Np(IV) from 4.0M HNO ₃	-0.25 ±0.10
Np(IV) from 1.0M HCl	-0.23 ±0.10

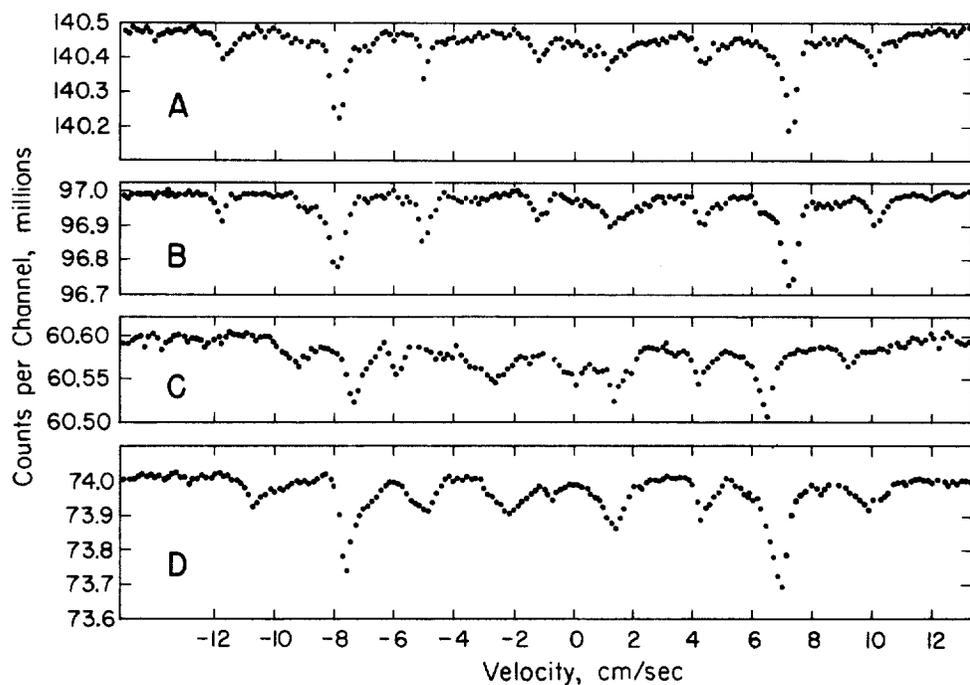


Figure 1. Mössbauer spectra of neptunium(IV) samples obtained from 8M HNO₃ solution. A. Np(IV) on "Dowex" 1-X8 resin; B. Np(IV) in a 20% tri-n-octylamine - benzene extract; C. Cs₂[Np(NO₃)₆]; D. (Et₄N)₂[Np(NO₃)₆].

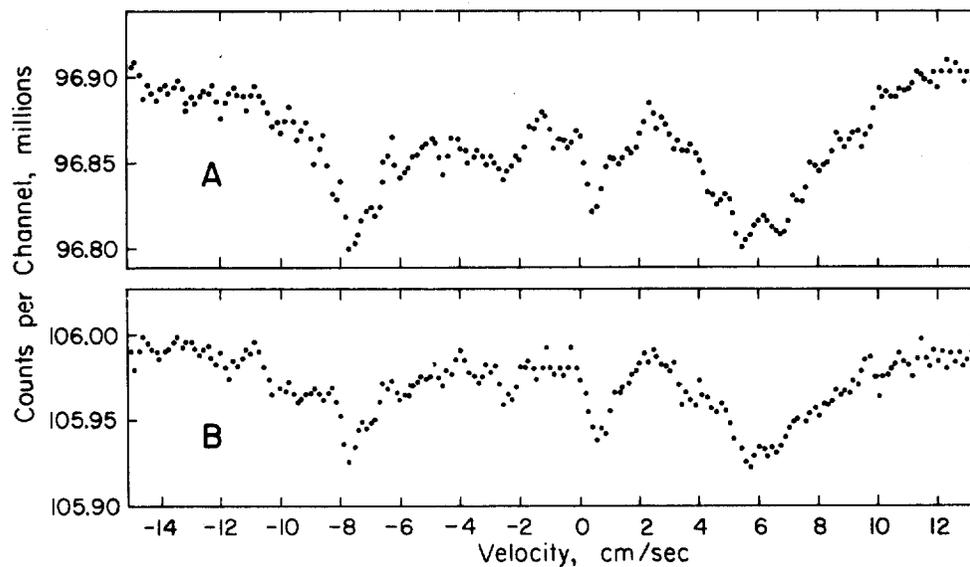


Figure 2. Mössbauer spectra of neptunium(IV) samples obtained from 12M HCl solution. A. Np(IV) on "Dowex" 1-X8 resin; B. Np(IV) in a 20% tri-n-octylamine - benzene extract.

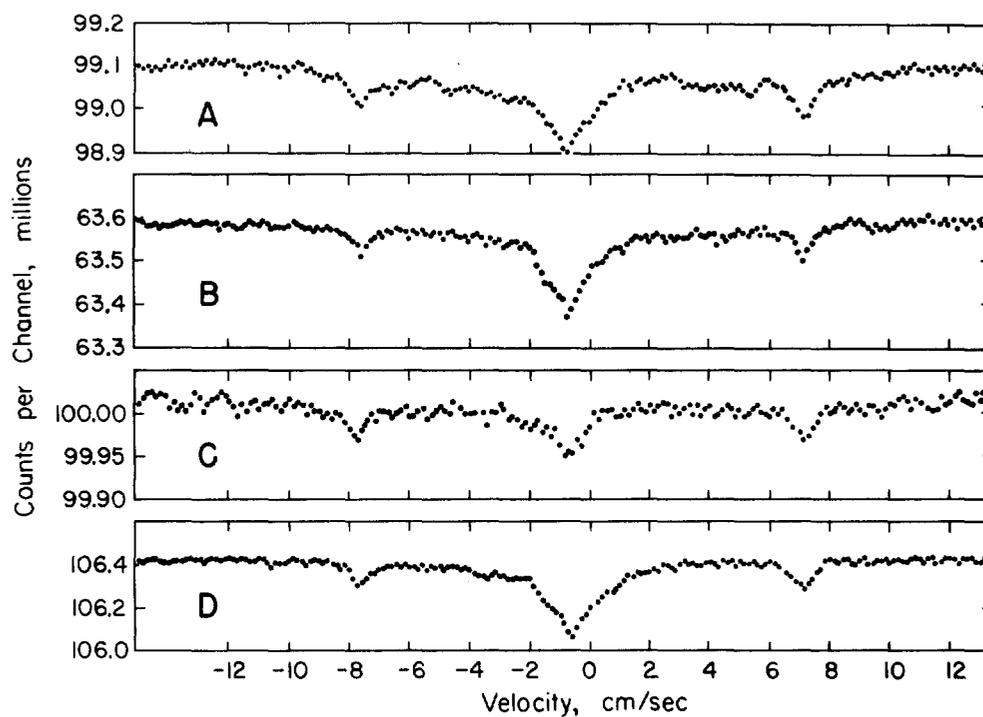


Figure 3. Mössbauer spectra of neptunium(IV) on "Dowex" 50W-X8 cation exchange resin. A. Np(IV) from 0.3M HNO₃; B. Np(IV) from 1.0M HNO₃; C. Np(IV) from 4.0M HNO₃; D. Np(IV) from 1.0M HCl.