147. Radiochemical Studies on the Solvent Extraction of Inorganic Ions with Dodecylbenzenesulfonic Acid, (III)

Extraction of Neptunium (IV), (V) and (VI)

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The solvent extraction behavior of Np(IV), (V) and (VI) were surveyed in the systems dodecylbenzenesulfonic acid-dilute hydrochloric, nitric and perchloric acid, together with the behavior of U(VI), thorium, protactinium, zirconium, hafnium and niobium for comparison. The behavior found for Np(IV), (V) and (VI) was assigned to that for quadrivalent, univalent and bivalent cationic species respectively, and in this respect resembled that for thorium, niobium and uranium. Therefore, it was deduced that the ionic species Np⁴⁺, NpO₂⁺ and NpO₂²⁺ should exist for neptunium in dilute acid solutions. The similarity between Np(IV) and thorium; Np(VI) and U(VI) had been confirmed. Np(V), however, was found to behave differently from protactinium.

The characteristic behavior of inorganic extraction with dodecylbenzenesulfonic acid has been presented in this series of papers and it has been shown to be suitable for identification of the valency or ionic charge of cation in solution. This characteristic for DBSA** extraction was widely ascertained in an extension of the initial study of the partition behavior of typical uni-, bi-, and tri-valent cations, and is applied in the present study to get some information on the chemistry of neptunium in aqueous solution.

**EXPERIMENTAL**

1. Sources of materials

The preparation of dodecylbenzenesulfonic acid solution in a 1:1 mixture of ethyl acetate and diethyl ether has been reported in a previous publication.

Hydrochloric, nitric and perchloric acid solutions of various concentrations were prepared by diluting commercial concentrated acids of analytical grade. The acidity was adjusted to the desired concentration by the use of volumetric analysis.

Oxidizing and reducing agents used viz., potassium chlorate, silver peroxide, potassium bromate, hydroxylamine hydrochloride, potassium iodide and hydroquinone, were all C. P. grade.

2. Radioisotopes used

Neptunium and protactinium tracers, ⁰³⁹Np and ⁰³³Pa, were carrier free, and were prepared from uranyl nitrate and thorium nitrate respectively, after irradiation in the usual way. Three oxidation states of neptunium in various mineral acids were prepared; in each case the suitable oxidizing or reducing agent was used. In hydrochloric acid medium, Np(IV) was obtained after reduction with hydroxylamine hydrochloride, or was prepared with thenoyltrifluoroacetone extraction after reduction with granulated zinc. In nitric acid medium, however, Np(IV) was obtained by reduction with 0.1 M potassium iodide and 0.1 M hydroquinone. Np(V) was obtained by evaporating the perchloric acid solution of neptunium and removing Np(VI) with tri-n-butyl phosphate from 0.5 N perchloric acid solution. Np(VI) in hydrochloric acid was obtained by warming on a water bath with potassium chlorate. In nitric or perchloric acid media, Np(VI) was oxidized with potassium bromate or silver peroxide, respectively.

⁰⁹⁵Zr-Nb, ¹⁸¹Hf and ⁰⁹⁷Nb were imported.

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** Dodecylbenzenesulfonic acid
from Oak Ridge National Laboratory, U.S.A., and were used as received. \(^{95}\)Zr-Nb was measured for the hard \(\beta\) rays of \(^{95}\)Zr cutting off the soft \(\beta\) rays of \(^{95}\)Nb. \(^{233}\)U tracer was separated by counter current techniques from thorium dioxide which had been irradiated for a long period. Some results of uranium was carried out using \(^{239}\)U as tracer.

Radiochemical purity of radioisotopes was checked by \(\gamma\) spectrometry, decay data or \(\beta\) ray absorption.

3. Determination of \(K_d\) values

Distribution ratios, \(K_d\), were determined radiometrically, as stated in the previous papers. The scrubbing techniques were used in the determination of \(K_d\) values for \(\text{Np}(\text{IV})\), \(\text{Th}\), \(\text{Pa}\), \(\text{U}(\text{VI})\), \(\text{Zr}\), \(\text{Hf}\), \(\text{Nb}\), \(\text{Co}\) and \(\text{Ba}\) in the system of \(0.1\) N acid.

![Graphs showing acid dependence curves for various elements](image)

**RESULTS**

1. Acid dependence behavior

The \(K_d\) values for \(\text{Np}(\text{IV})\), \(\text{V}\) and \(\text{VI}\) were determined in the systems 3% DBSA-hydrochloric, nitric and perchloric acid varying the acidity from 0.01 to 2.0 N; data

![Graph showing acid dependence curves for various elements](image)
for Np(IV) were obtained in hydrochloric and nitric acid solutions only because of a difficulty of preparing perchloric acid solution of Np (V) tracer. The results obtained are given in Fig. 1 together with the acid dependence curves for thorium, zirconium, hafnium, protactinium, niobium, cobalt(II) and uranium for comparison, where some of them were quoted from preceding reports\(^2\).

The acid dependence behavior of Np (V) was attributed to that of quadrivalent cationic species, because the slope of the acid dependence curves for Np(IV) was \(-4\) in the acidity range from 0.1 to 1.0 N, and the magnitude of \(K_d\) values were thought to be that of quadrivalent cations. Thorium gave a similar behavior. The similarity between Np(IV) and thorium had been shown in other extraction systems such as di-(2-ethyl hexyl) phosphoric acid\(^5\). From these results it can be said that Np(IV) exists as Np\(^{4+}\) in dilute acid media similar to thorium; both being members of the actinide elements. On the other hand, Zr(IV) and Hf(IV) showed the behavior of bivalent cationic species, and therefore, they may exist as ZrO\(^{2+}\) and HfO\(^{2+}\) in solution.

The existence of Np\(^{4+}\) ion in perchloric acid solution had already been reported by Sullivan and Hindman\(^8\) from the results of thenoyltrifluoroacetone extraction under special conditions, e.g. the electrolytic preparation of Np(IV), and keeping Np(IV) solution under an atmosphere of nitrogen to prevent aerial oxidation to the quinquevalent state. In this study, however, the existence of Np\(^{4+}\) in hydrochloric and nitric acids were ascertained by a very simple solvent extracting method using DBSA.

In the case of Np(IV) the characteristics of quadrivalent cationic species were more clearly shown in hydrochloric acid than in nitric acid system.

In hydrochloric or perchloric acid system the acid dependence behavior for Np(V) was clearly assigned to that of univalent species, so that was the behavior of niobium. In other words, their acid dependence curves showed a slope of \(-1\) in the acidity range from 0.1 to 1.0 N, and the \(K_d\) values at 0.01 N were rather low and were around 0.01. In nitric acid system, the behavior of Np(V) was possibly thought to be that of univalent species in spite of its little higher \(K_d\) values than that of usual univalent species. From these results Np(V) was supposed to exist as theionic species NpO\(^{2+}\) in dilute acid solution. As mentioned above a similarity was found between the acid dependence behavior of Np(V) and niobium, whereas a dissimilarity was shown between the behavior of Np(V) and protactinium, where the latter behaved as bivalent cationic species rather than univalent. The dissimilarity had been also obtained in the other solvent extraction systems such as thenoyltrifluoroacetone or di-(2-ethyl hexyl) phosphoric acid\(^9\). Concerning the ionic species of protactinium, protactinyl ion PaO\(^{2+}\), had been reported by some other investigators\(^10\) as cited in the previous paper\(^2\). At this stage, it appears rather difficult to explain the similarity between the behavior of protactinium and that of bivalent species.

In hydrochloric, nitric and perchloric acid system, Np(IV) and U(IV) showed the acid dependence behavior of bivalent cationic species; the slope of the curves were \(-2\) in the acidity range of 0.1 to 1.0 N. In aqueous solution U(IV) is known to exist as bivalent species, viz. uranyl ion UO\(^{2+}\), as also noticed in the previous paper\(^1\). Therefore, their ionic species in solution are supposed to be NpO\(^{2+}\) and UO\(^{2+}\) respectively. The acid dependence curves for cobalt(II) and barium, which are quoted from the previous papers\(^1\), are also given in Fig. 1 for comparison. Difference of aqueous phase studied did not cause so large difference in the extraction curve obtained. However, the clearness of the shape of the Np(IV) curves in nitric and perchloric acid systems rather than in hydrochloric acid seems to show the higher stability of the most oxidized form of neptunium, Np(IV), in the former two acids rather than in hydrochloric acid.

2. Solvent dependence behavior

Similar to the method followed in case of acid dependence behavior, \(K_d\) values for the same elements were determined in DBSA-
0.1 N hydrochloric, nitric and perchloric acid system, changing the DBSA concentration from 3.0 to 0.3%. The results obtained are shown in Fig. 2. Most of elements studied gave the solvent dependence curve having slope of 2 in log-log scale. Some exceptional behavior were found in the behavior in perchloric acid system. A solvent dependence curve for Np(IV) in nitric acid could not be obtained because of fluctuating K_d values.

This fact proves that DBSA plays an important role in extraction of these cations.

To sum up, the ionic charges of Np(IV), (V) and (VI) were shown to be +4, +1 and +2, and the chemical species in dilute acid solutions are supposed to be Np^{4+}, NpO_2^+ and NpO_2^{2+} respectively. A dissimilarity was recognized between Np(V) and Pa(V).

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REFERENCES

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(9) K. KIMURA, Y. YOKOYAMA, H. SANO, H. MABUCHI: Japan Analyst, 6, 637 (1957).

K_d values obtained without DBSA i.e. with the ethyl acetate diethyl ether mixture alone were lower than those usually obtained with DBSA. Results are given in Table 1.

<table>
<thead>
<tr>
<th>Aqueous media</th>
<th>HCl</th>
<th>HNO_3</th>
<th>HClO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(IV)</td>
<td>0.0111</td>
<td>0.0241</td>
<td>-</td>
</tr>
<tr>
<td>Th</td>
<td>0.000057</td>
<td>0.0386</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>0.00222</td>
<td>0.000104</td>
<td>-</td>
</tr>
<tr>
<td>Hf</td>
<td>0.00125</td>
<td>0.0196</td>
<td>-</td>
</tr>
<tr>
<td>Np(V)</td>
<td>0.00914</td>
<td>0.000716</td>
<td>0.000507</td>
</tr>
<tr>
<td>Pa</td>
<td>0.00135</td>
<td>0.000554</td>
<td>0.000312</td>
</tr>
<tr>
<td>Nb</td>
<td>0.00095</td>
<td>0.00183</td>
<td>0.000678</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>0.00117</td>
<td>0.00133</td>
<td>0.00011</td>
</tr>
<tr>
<td>U</td>
<td>0.0918</td>
<td>0.00889</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

Fig. 2 Solvent dependences

Table 1 K_d values of "blank"