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The Solvent Extraction of Np(III) by Means of Bis(2-ethyhexyl)-hydrogenphosphate in an Octane Solution and the Absorption Spectrum of the Organic Phase

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Tervalent neptunium in an $HClO_4$ solution was extracted by means of bis(2-ethylhexyl)hydrogenphosphate, HDEHP, in an octane solution. The oxidation state of neptunium in the organic phase was determined by spectrophotometry. The intense peak in the absorption spectrum of tervalent neptunium was found at 348 nm, this peak was attributed to the $f \rightarrow d$ transition. The oxidation rate of the Np(III)–HDEHP complex in an oxygen-free octane solution was about 10%/h.

It has been well known that the tervalent neptunium ion in an acidic solution is fairly stable in an oxygen-free atmosphere. However, during a chemical operation like solvent extraction or ion exchange, it is difficult to maintain the neptunium ion in a tervalent state. Consequently, the study of the aqueous chemistry of Np(III) has been made mainly by means of the spectrophotometric technique. Shiloh and Marcus[1] found the characteristic absorption peaks of 384 nm and 387 nm in the chloride and bromide solution of Np(III) respectively. They determined the stability constants of the chloride and bromide complexes by measuring the increases in their characteristic peaks as the concentrations of the chloride and bromide ions increased.

Inoue *et al.*[2] recently investigated the effect of the neptunium concentration on the fraction of tervalent neptunium produced by hydrogen reduction. They concluded that neptunium was quantitatively reduced to the tervalent state at concentrations higher than 10^{-3} M (1 M=1 mol dm^{-3}), while the tracer concentrations of neptunium were quantitatively reduced to the tervalent state in the presence of more than 10^{-3} M Sn(II).

It has not been reported up to the present, however, that tervalent neptunium could be evidently extracted to the organic phase in the solvent extraction, which has been one of the most effective methods of investigating aqueous chemistry. In order to extract the tervalent neptunium, and in order to determine the oxidation state of the extracted neptunium by spectrophotometry, we made a specially designed reduction and extraction apparatus with reference to other authors'.[2,3] The apparatus was constituted of two parts: the spectrophotometric cell in which the extracted tervalent neptunium was introduced, and the reduction and extraction part.

HDEHP was used as the extractant, and octane, as the solvent, in this work.

Experimental

The ^{237}Np was obtained from the Radiochemical Centre, Amersham, and was purified by the method of Moore,[4] while the final stock solution was 10 M HNO_3. The concentration of ^{237}Np in the stock solution was determined by the α-counting method using a surface barrier Si-detector and the EDTA titration method. The results of the two methods agreed well within the limits of experimental error.

HDEHP was purified by the way of McDowell *et al.*[5] and was stocked as the copper salt. The desired quantities of the copper salt were weighed and then dissolved in octane. After the copper had been removed by shaking with an acid solution, the concentration of HDEHP in the octane solution was determined by the titration of the NaOH solution. The results of the titration method agreed well with the results of the gravimetry, within the limits of experimental error.

For the measurement of the absorption spectrum, a Hitachi 330 recording spectrophotometer was used.

The experimental apparatus used in this work is shown in Fig. 1. It was made of quartz, and at the top of it, a polyethylene plug was placed, through which Teflon tubes passed. At the end of the Teflon tubes, freshly prepared platinum-black-coils were fixed.

Three milliliters of the 2 M HDEHP/octane solution was placed in the spectrophotometric cell, while the same volume of a 0.3 M $HClO_4$ solution containing 20 mg of ^{237}Np (2.7×10^{-2} M) was placed in the other part.

The hydrogen gas, which had been deoxidized by passing through a pyrogallol–KOH solution, was bubbled into the $Np/HClO_4$ solution, and the neptunium was reduced to the tervalent state by the hydrogen gas catalyzed by the platinum-black-coil. A part of the deoxidized hydrogen gas was passed through the octane solution and then bubbled into the HDEHP/octane solution.

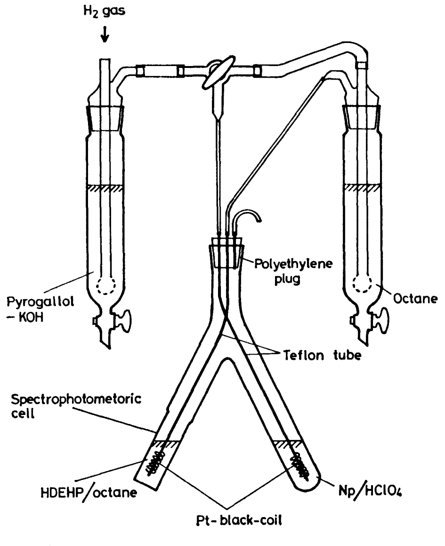

Fig. 1. Experimental apparatus.

The neptunium in the $HClO_4$ solution was completely reduced to the tervalent state about after three hours bubbling, as was recognized by the change in color. Then the apparatus was tilted and the HDEHP/octane solution in the spectrophotometric cell was introduced into the other part. The apparatus was shaken about ten minutes while the hydrogen gas was bubbling. After the two phases had separated, the organic phase was introduced to the spectrophotometric cell and the absorption spectrum was immediately measured. The Teflon tube and the platinum-black-coil were placed in the upper side so as not to disturb the measurement of the absorption spectra. The spectrophotometry of the organic phase was carried out every hour after the extraction in order to investigate the stability of the Np(III)–HDEHP complex in an octane solution. The absorption spectrum of the Np(IV)–HDEHP complex in an octane solution was measured after the oxidation had been completely concluded.

The absorption spectra of Np(III) and Np(IV) in 0.3 M $HClO_4$ solution were also measured.

An aliquot part of the organic phase was placed in the polyethylene test tube, and the concentration of the ^{237}Np was determined by γ-ray spectrometry. For the γ-ray spectrometry, a Tracor Northern TN-4000 pulse-height analyzer and a pure-Ge detector were used. The peak at 86.49 keV, the characteristic peak of ^{237}Np, was used to determine the concentration of neptunium. ^{233}Pa, the daughter of ^{237}Np, also has a weak peak at 86.59 keV. These two peaks could not be separated, so the contribution of the peak at 86.59 keV to the peak at 86.49 keV was eliminated by the γ-ray spectrometry of pure ^{233}Pa.

Results and Discussion

The absorption spectrum of the Np(IV)–HDEHP complex in an octane solution shown in Fig. 2 is very similar to the spectrum of Np(IV) in a 0.3 M $HClO_4$ solution except in the region of 900 nm. The characteristic peaks of the former are 427, 508, 735, 812, 896, 968, and 1167 nm, and the former shifts toward a lower energy compared with the latter. This shift may be caused by the nephelauxetic effect.[6]

On the other hand, the absorption spectrum of the Np(III)–HDEHP complex (shown in Fig. 3) is not so similar to the spectrum of Np(III) in the 0.3 M $HClO_4$ solution. This shows that the $f \rightarrow f$ transition was affected by the environment, *e.g.*, the ligand or the crystal field. The characteristic peaks of the former are 348, 557, 630, 760, 782, 835, 931, 987, and 1345 nm. Among these, the peak of 348 nm is clearly distinguished from the other peaks, which are attributed to the $f \rightarrow f$ transition in the visible and near-infrared regions. The molar extinction coefficient, ε_m, of this peak is about 1500, while the half-width toward the lower energy, $\sigma(-)$, is 1500 cm^{-1}. This peak is attributed to the $f \rightarrow d$ transition or the electron-transfer-from-ligand transition. Usually, the former band is relatively more intense and narrow than the latter.[7] However, it is difficult to discriminate between them. Poturaj-Gutniak and Taube[8] identified the absorption peak as the $f \rightarrow d$ transition by $\varepsilon_m > 3000$, and $\sigma(-) < 2000$ cm^{-1}, and as electron-transfer by $\varepsilon_m < 3000$, and $\sigma(-) > 2000$ cm^{-1}.

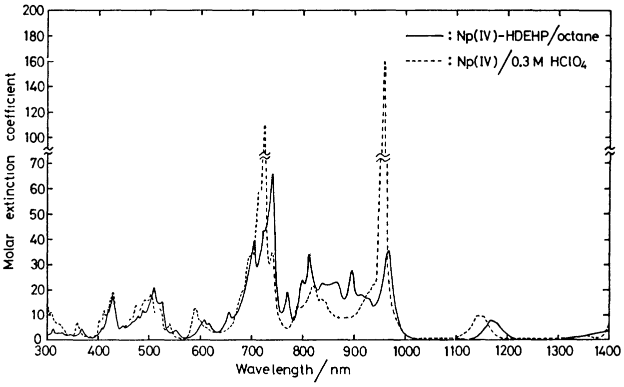

Fig. 2. Absorption spectra of Np(IV) in $HClO_4$ solution and Np(IV)–HDEHP complex in octane solution.

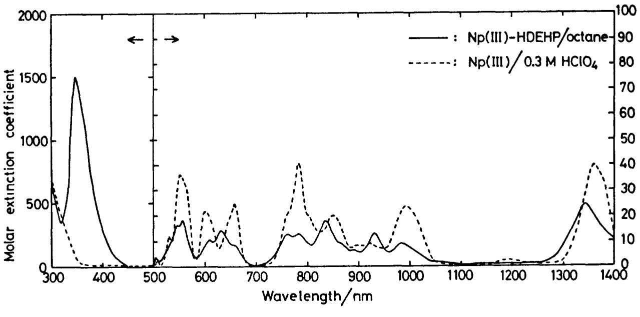

Fig. 3. Absorption spectra of Np(III) in $HClO_4$ solution and Np(III)–HDEHP complex in octane solution.

The characteristic peaks of Np(III) in concentrated LiCl and LiBr solution found by Shiloh and Marcus[1] are $\varepsilon_m = 1170$ and $\sigma(-) = 2400$ cm^{-1} at 384 nm (26000 cm^{-1}) in LiCl and $\varepsilon_m = 830$ and $\sigma(-) = 2400$ cm^{-1} at 387 nm (25800 cm^{-1}) in LiBr. These bands are attributed to the $f \rightarrow d$ transition.

The peak at 348 nm (28700 cm^{-1}) found in this work seemed to have the same cause as the peaks found by Shiloh and Marcus described above. The shifts of these peaks effected by the ligands are small. Generally, the shift of the $f \rightarrow d$ transition with a ligand is much less than that observed in the case of the electron-transfer band.[7] For example, the shift of the electron-transfer is 7000—9000 cm^{-1}; on the other hand, that of the $f \rightarrow d$ transfition is about 1000 cm^{-1} in tervalent actinoide hexahalides.[9] Therefore, the peak at 348 nm is ascribed to the $f \rightarrow d$ transition.

The Np(III)–HDEHP complex in an octane solution is unstable and is oxidized to the quadrivalent state, even in an oxygen-free atmosphere. The oxidation rate was found to be about 10%/h by the spectrophotometry that was carried out every hour after the extraction.

The color of the Np(III)–HDEHP complex in an octane solution is golden yellow, while that of the Np(IV)–HDEHP complex is slightly greenish yellow. It is difficult to distinguish between them by color, especially at a low concentration of neptunium.

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