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The Photochemistry of Neptunium in Aqueous Nitric Acid Solutions

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Abstract

Photochemical reactions of Np(IV), (V), and (VI) have been investigated in nitric acid solutions using 254 and 300 nm excitation from standard mercury discharge lamps. Absorption spectrometry was used to monitor the concentrations of the various neptunium species in solution. In the absence of added reagents, all oxidation states of neptunium are converted to the pentavalent state. The effect of adding urea and mild reducing agents such as ethanol and hydrazine on the photolysis has also been examined. Quantum efficiencies for these reactions have been found to vary from 0.001 to 0.1, depending on the acid concentration, wavelength, and reaction conditions.

Introduction

As stated in the previous publication [1], former investigations [2–6] of aqueous neptunium ion photochemistry were noticeably lacking in such important details as quantum efficiency determinations, light intensity measurements, and the effects of different wavelength excitation on the reaction chemistry. These parameters are important in evaluating photochemical separation schemes for practical applications. The investigation leading to the previous paper sought these data for the perchloric acid medium which represented a much simpler system since the perchlorate ion is not subject to direct photolysis. The nitric acid system, however, is the choice in many separation processes, and therefore any photochemical reactions which might be of use must ultimately be studied in this medium.

For these reasons, we have investigated the photochemistry of neptunium in aqueous nitric acid solutions to provide: (1) the general photochemical behavior of neptunium ions in nitric acid media and (2) quantitative values for those parameters which are recognized as important in evaluating the potential of any photochemical process. Absorption spectrophotometry was used to monitor the concentrations of the neptunium species in solution; and since there are no complete spectra available for all the neptunium species expected, reference spectra of these were first obtained and are presented elsewhere [7]. The results of the photochemical study are discussed here.

Experimental

The procedure was essentially identical to that described previously [1]. The reader is referred there for details on solution preparation, molar extinction coefficient determinations, general photochemical studies and quantum efficiency determinations.

Briefly, though, the procedure entailed loading 0.01 *M* neptunium solutions (after first electrolytically adjusting the neptunium valence state) into 15 cm^3 photochemical cells and exposing them to ~1.4 W (absorbed power) 254 nm radiation from a low pressure mercury lamp or ~0.7 W (absorbed power) filtered 300 nm radiation from a high pressure mercury lamp. The progress of the photolysis was monitored spectrophotometrically with a Cary 14 H recording spectrophotometer which was capable of in situ measurements even during the photolysis runs. Quantum efficiencies were determined by dividing the maximum rate of change of a component's concentration by the rate of light absorption within the cell. The rates of concentration change were obtained from the maximum slopes of the lines (cf., figures shown here) before interfering reactions became significant. The rate of light adsorption in the photochemical cell was obtained by chemical actinometry in the cell and assuming that the Np-HNO_3 solutions absorbed all of the 250–350 nm radiation to which they were exposed. The ultraviolett spectra of these solutions justify this assumption.

Results and discussion

Photo-redox reactions of neptunium IV, V, and VI nitrate solutions were followed with and without added reagents. Various well-known dark reactions [8] (not photo-sensitized) often accompanied these light-induced reactions and complicated the overall chemistry of the system. The general reactions can therefore be subdivided into three categories:

(1) Pure HNO_3 solution photo-sensitized reactions

$$2NpO_2^{2+} + NO_2^- + H_2O \overset{h\nu}{\rightleftharpoons} 2NpO_2^+ + NO_3^- + 2H^+ \quad (1)$$

$$2Np^{4+} + NO_3^- + 3H_2O \overset{h\nu}{\rightleftharpoons} 2NpO_2^+ + NO_2^- + 6H^+ \quad (2)$$

$$2Np^{3+} + NO_3^- + 2H^+ \xrightarrow{h\nu} 2Np^{4+} + NO_2^- + H_2O. \quad (3)$$

(2) Photo-redox reactions with added reagents (to be discussed later)

(3) Dark reactions

$$2NpO_2^{2+} + NO_2^- + H_2O \rightleftharpoons 2NpO_2^+ + NO_3^- + 2H^+ \quad (4)$$

$$2NpO_2^+ + 4H^+ \rightleftharpoons Np^{4+} + NpO_2^{2+} + 2H_2O \quad (5)$$

$$2Np^{4+} + NO_3^- + 3H_2O \rightleftharpoons 2NpO_2^+ + NO_2^- + 6H^+ \quad (6)$$

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