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Hydrolysis Reactions of Neptunium (V)

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Abstract

Hydrolysis of Np(V) in 1.0 *M* $NaClO_4$ was investigated by radiometric pH-titration of $^{237}NpO_2^+$ under CO_2-free Ar atmosphere. From the resulting solubility curve the first and second hydrolysis constant β_1 and β_2 as well as the solubility product *Ksp* were evaluated: $\log \beta_1 = 2.3$, $\log \beta_2 = 4.89$ and $\log Ksp = -8.81$.

Introduction

As for the migration behaviour of actinides in neutral aqueous media like groundwater systems, neptunium is an element of particular interest because of its rather long half life and relatively large abundance in nuclear waste. Several authors investigated the hydrolysis of Np(V), which is a stable oxidation state under natural conditions, and determined the first hydrolysis constant and the solubility product [1 – 5]. Although in some cases negatively charged hydrolysis products were supposed [4, 6], no formation constants of such species are known up to now. We have investigated the hydrolytic behaviour of Np(V) in the pH range of 6 – 13 by radiometric pH-titration, which resulted in reliable pH dependent solubility data and hence a good basis for evaluation of hydrolysis constants.

Experimental

Freshly prepared and washed $^{237}NpO_2OH$ (ca. 1 g) was dissolved in 35 ml 1 *M* $HClO_4$ and transfered into a thermostated titration cell (200 ml, 25 ± 0.2 °C) containing 150 ml 1 *M* $NaClO_4$ solution. After bubbling Ar (99.999%) through this solution for about 10 hours, several drops of CO_2-free 6.6 *M* NaOH (Baker Co.) were added until the pH remained stable at about pH 13. This solution was allowed to stand for two days under Ar atmosphere in order to attain solubility equilibrium. The pH was then measured by a combination glass electrode (type ROSS, Orion Co.) with 3 *M* NaCl as junction electrolyte. The Np concentration was determined radiometrically after phase separation by filtration, using three kinds of filters (220 nm pore size, Millipore Co.; 30 nm pore size, Nuclepore Co.; ca. 1 nm pore size (5 kD), Sartorius Co.). By adding small amounts of $HClO_4$, the pH of solution was changed stepwise down to pH 6.8 and the equilibrium concentration of Np was determined at each pH. The whole experiment was carried out under CO_2-free conditions in order to avoid the influence of carbonate complexation.

Results and discussion

The pH dependent solubility curves are shown in Fig. 1. Independent of the filter pore size used for phase separation, in the higher pH range (pH > 11) the solubility curves demonstrate clearly the formation of anionic species which causes an increase of the Np solubility. While the data from the filtration with 220 nm are similar to that with 30 nm, use of 5 kD (ca. 1 nm) pore size leads to somewhat lower Np concentrations in the pH region of 10 – 12.5. The reason may be the adsorption of neutral NpO_2OH species on the filter surface during the relatively long filtration time required for this filter (about 1 hour). For this reason, the hydrolysis constants are calculated from the experimental data after 220 nm and 30 nm filtration.

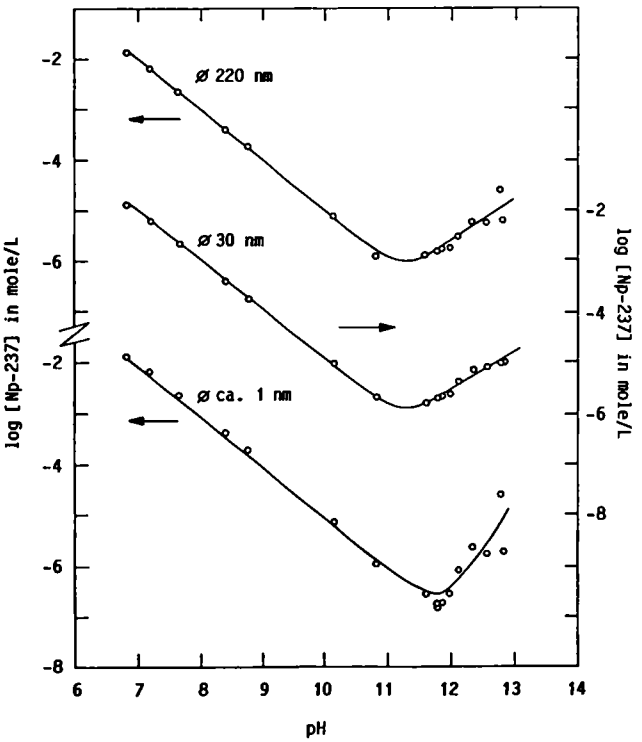

Fig. 1. Solubility of NpO_2OH as a function of pH: concentrations of Np-237 in solution after phase separation with three different filter pore sizes

The total Np(V) concentration in solution is given by

$$[Np(V)] = [NpO_2^+] + [NpO_2OH] + [NpO_2(OH)_2^-] + [NpO_2(OH)_3^{2-}] \quad (1)$$

or

$$[\mathrm{Np(V)}] = \frac{Ksp}{[\mathrm{OH^-}]} \cdot \sum_{i=0}^{3} \beta_i \cdot [\mathrm{OH^-}]^i \qquad (2)$$

with

$$\beta_i = \frac{[\mathrm{NpO_2(OH)_i^{1-i}}]}{[\mathrm{NpO_2^+}] \cdot [\mathrm{OH^-}]^i} \qquad (3)$$

and

$$Ksp = [\mathrm{NpO_2^+}] \cdot [\mathrm{OH^-}] \qquad (4)$$

Fitting the experimental data to Eq. 2, using a linear least-square computer program, the following values are obtained:

$$\log Ksp = -8.81 \pm 0.05$$
$$\log \beta_1 = 2.3 \pm 0.62$$
$$\log \beta_2 = 4.89 \pm 0.05$$

There is no evidence for anionic species other than $NpO_2(OH)_2^-$; β_3 is found to be insignificant.

In Table 1, the present results are compared with literature values. Except the data from SEVOSTYANOVA [4], all solubility products Ksp are in good agreement with one another. Considerable discrepancies are observed for the first hydrolysis constant β_1. The data given by KRAUS [1, 2] and SEVOSTYANOVA [4] can only be accepted as a rough estimation, because their evaluation neglected the influence of anionic Np species. MOSKVIN [3] calculated β_1 from Ksp and only one solubility value at pH 8.6 assuming that Np(V) is totally hydrolyzed as NpO_2OH at this pH. MAYA [5] derived β_1 from a carbonate complexation experiment with Np(V) but he considered NpO_2OH as the only hydrolyzed species.

Table 1. Comparison of the hydrolysis constants of Np(V) with literature values

Method	Conditions	$\log Ksp$ [1]	$\log \beta_1$ [2]	$\log \beta_2$ [2]	Ref.
Solubility	$\mu = 0.1$ [3] 25°C	−8.85	4.93	–	1
Titration	$\mu = 0.1$ 25°C	−9.2	–	–	2
Solubility	$\mu = 0.2$ 20°C	−9.0	3.92	–	3
Potentiometry	$\mu = 0.02$	−9.73	5.1	–	4
Solubility	$\mu = 1.0$ 25°C	–	4.68	–	5
pH-Titration	$\mu = 1.0$ 25°C	−8.81	2.33	4.89	this work

1 $Ksp = [\mathrm{NpO_2^+}] \cdot [\mathrm{OH^-}]$
2 $\beta_i = [\mathrm{NpO_2(OH)_i^{1-i}}] \cdot [\mathrm{NpO_2^+}]^{-1} \cdot [\mathrm{OH^-}]^{-i}$
3 μ - ionic strength

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