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Neptunium(IV) and uranium(VI) complexation by hydroxamic acids

Iain May[a,*], Robin J. Taylor[a], Iain S. Denniss[a], Geoff Brown[a], Andrew L. Wallwork[a], Nick J. Hill[b], Jeremy M. Rawson[c], Robert Less[c]

[a] *Research and Technology, British Nuclear Fuels plc, Sellafield, Seascale, Cumbria CA20 9NG, UK*
[b] *Applied Technology, British Nuclear Fuels plc, Risley, Cheshire WA3 6AS, UK*
[c] *Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, UK*

Abstract

Hydroxamic acids complex more readily with Ac(IV) than Ac(VI). Formohydroxamic acid (FHA) is a hydrophilic organic ligand which can readily complex with Np(IV), as indicated by near infrared spectroscopy. Distribution experiments have also shown that FHA can strip Np(IV) from 30% TBP/OK into aqueous nitric acid. In contrast U(VI) does not complex as strongly with FHA and the reaction is greatly inhibited by nitric acid, as observed by UV-Vis spectroscopy. After stripping Np(IV) it has also been proven, by ^{13}C NMR spectroscopy, that FHA can be decomposed to gaseous products in concentrated nitric acid leaving no organic waste products in solution. This experimental evidence proves that FHA can be used to selectively strip Np(IV) from a 30% TBP/OK solution of Np(IV) and U(VI) into aqueous nitric acid and is thus a viable new reagent for inclusion in an advanced PUREX process.

Keywords: Neptunium(IV); Uranium(VI); Formohydroxamic acid; Complexation; Purex process

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1. Introduction

1.1. Neptunium control in an advanced reprocessing plant

Irradiated nuclear fuel is reprocessed commercially by the PUREX process to recover uranium and plutonium [1,2]. A major component of spent fuel is neptunium and its effective control in the PUREX process is important in the efficient production of U and Pu products [3]. In nitric acid neptunium exists mainly in three oxidation states, (IV), (V) and (VI), all of which can co-exist. Both Np(IV) and Np(VI) can be readily extracted into 30% TBP/OK, whereas Np(V) is almost inextractable. This results in Np passing into more than one waste/product streams in reprocessing plants.

Advanced flowsheets under development at British Nuclear Fuels provide different options for Np routing one of which envisages that Np will exist as Np(IV) in the U(VI) solvent product stream after partition from Pu. It is well known that organic ligands complex more readily with Ac(IV) than with Ac(VI) [4]. It is thus envisaged that the introduction of a hydrophilic ligand will result in the selective stripping of Np(IV) from a mixed U(VI)/Np(IV) 30%TBP/OK phase into nitric acid.

1.2. The coordination chemistry of hydroxamic acids with actinides

Initial scoping studies concluded that hydroxamic acids (RC(=O)NHOH) are one class of compound that could selectively complex and strip Np(IV). These organic acids readily deprotonate to form five-membered chelate ligands with metal ions [5] and have been shown to complex strongly with Th(IV) [6] and Pu(IV) [7]. It was also noted that the stability constant for the Pu(IV)–benzohydroxamate complex was significantly larger than that for the U(VI)–benzohydroxamate complex [8,9]. Finally, an aliphatic hydroxamic acid has been tested as a selective extractant for Np(IV) and Pu(IV) from U(VI) in an amine-based extraction system [10].

After an initial screening of the simple hydroxamic acids it was decided that formohydroxamic acid, HC(=O)NHOH, (FHA) would be the best candidate as a Np(IV) stripping agent due to several important factors: (1) the small organic backbone would ensure insolubliity in the organic phase (30% TBP/OK); (2) although FHA is

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[*] Corresponding author. Tel.: +44 1946 774747; fax: +44 1946 775698; e-mail: imay@bnfl.demon.uk

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unstable in nitric acid only insignificant quantities of ligand would be destroyed in the proposed phase contact timescales envisaged in an advanced reprocessing plant; (3) the decomposition products of FHA in nitric acid are NO_x gases and CO_2, thus there would be no increase in liquid waste.

2. Experimental

Standard techniques were used throughout for the handling of ^{237}Np and depleted U solutions. Reagents were either purchased from standard chemical suppliers (Aldrich, Fluka and the Cookson Chemical Companies) or prepared ‘in house’ using standard techniques. Neptunium stock solutions were prepared by dissolving $Np^{237}O_2$ in refluxing nitric acid and Np^{237} concentrations measured using low energy photon spectroscopy. Near infrared spectra were recorded using a Perkin-Elmer Lambda 19 spectrophotometer attached by fibre optic cables to an external sample compartment and ^{13}C NMR spectra using a Bruker AC250 spectrometer.

3. Results and discussions

3.1. The decomposition of formohydroxamic acid

In order to confirm that FHA decomposed in nitric acid to produce only gaseous products a ^{13}C NMR spectrum of FHA in H_2O was recorded showing a peak for FHA at 162 ppm and also trace formic acid (169 ppm). On dissolution in 6 M HNO_3 the initial spectra showed there to be a great increase in the quantity of formic acid present (the first decomposition product along with hydroxylamine). After 12 h no peak attributable to FHA or formic acid was present and there was no carbon-based material left in solution. Thus, all the carbon-based material had been converted to gaseous products.

3.2. The complexation of Np(IV) by formohydroxamic acid

The next stage of the experimental programme was to confirm that FHA would complex with Np(IV). The standard method of examining aqueous solutions of neptunium is near infrared spectroscopy which can distinguish between the different oxidation states [11]. Np(IV) exhibits very distinctive absorbance bands between 640 and 1000 nm (Fig. 1). These bands change intensity and shape on the formation of different complexes, e.g. at higher HNO_3 concentration [12,13] and when bound to other inorganic ligands such as sulphate and iodide [14]. In the presence of FHA, distinct peaks at 714, 732, 851 and 975 nm can be observed. In low acidities near complete complexation is observed after the addition of 2.5× molar excess ligand. This indicates that a 1:1 or 2:1 FHA:Np(IV) complex is readily formed in low HNO_3 concentration. On increasing nitric acid concentration near infrared spectroscopy indicates that complex formation is inhibited, i.e. more FHA is required to induce near total complexation with Np(IV).

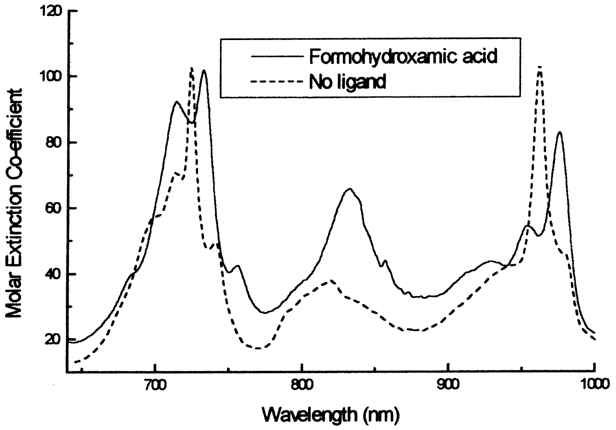

Fig. 1. Near infrared spectrum of Np(IV) in 0.2 M HNO_3 in the presence and absence of 5× excess FHA.

3.3. Distribution experiments for Np(IV) in the presence of formohydroxamic acid

Thirty percent TBP/OK solutions of Np(IV) (organic phase) were contacted with formohydroxamic acid in nitric acid (aqueous phase) in 1:1 volume ratios for a sufficient period to allow Np(IV) to reach equilibrium distribution between phases. The equilibrium concentration of Np(IV) was then measured in each phase using both radiometric methods and spectrophotometrically. Distribution coefficients for Np(IV) $[D_{Np(IV)}]$ were calculated as $[Np(IV)]_{org}/[Np(IV)]_{aq}$ and typical results are shown in Figs. 2 and 3. It can clearly be seen that Np(IV) is stripped

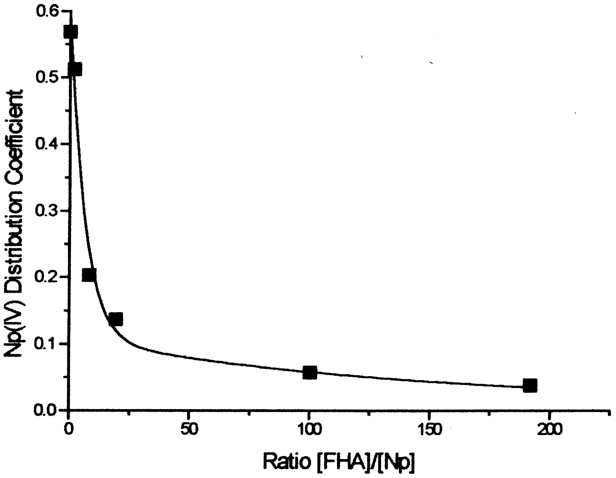

Fig. 2. The effect of increased FHA concentration on Np(IV) distribution between 30% TBP/OK and 1 M HNO_3. Total [Np] ~0.005 M.

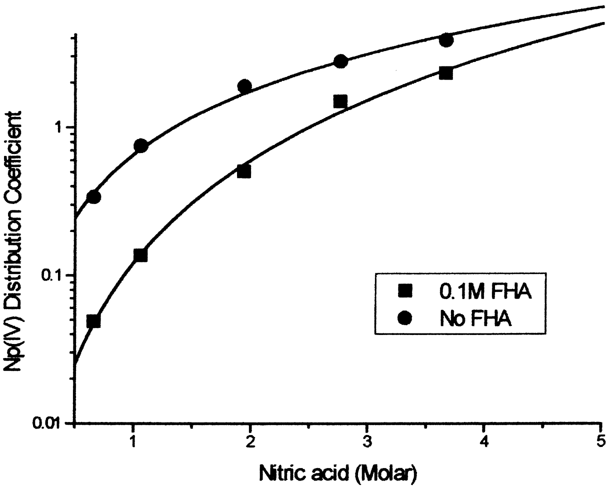

Fig. 3. The effect of increased nitric acid concentration on Np(IV) distribution between 30% TBP/OK and an aqueous phase containing 0.1 M FHA. Total [Np] ~0.005 M.

into the aqueous phase by FHA and that stripping is increased with increased ligand concentration (Fig. 2) and decreased nitric acid concentration (Fig. 3). Therefore, Np(IV) stripping is directly related to complexation with formohydroxamic acid and is inhibited by nitric acid. After phase separation aqueous phase spectra were run to ensure no oxidation to Np(V) or Np(VI), with no characteristic absorbance bands for these two species observed, at 980 or 1223 nm, respectively, [11]. Organic phase spectra were also run to ensure no FHA–Np(IV) organic soluble species were present. Only the characteristic absorbance bands for $Np(NO_3)_4{\cdot}2TBP$ at 706 and 729 nm [15] were visible—previous experimental programmes had shown that Np(IV) peak shapes and intensities do change in 30% TBP/OK in the presence of soluble organic ligands [16].

All the distribution data obtained were statistically analysed and used to further develop the BNFL computer model of a single-cycle flowsheet. It will be used to predict the behaviour of Np(IV) in the presence of FHA in solvent extraction processes using intensified centrifugal contactors in conjunction with further experimental research and development.

3.4. The complexation of U(VI) with hydroxamic acids

The complexation of UO_2^{2+} with hydroxamic acids has been studied extensively with one or two hydroxamate groups shown to bind to the metal centre [17–20]. During the course of this research programme it has been shown that the uranyl ion reacts with benzohydroxamic acid to form a 2:1 ligand:metal complex (as indicated by UV-Vis, IR, NMR and mass spectroscopies) [21]. An analogous reaction occurs between 1 M FHA and an aqueous solution of $UO_2(NO_3)_2$ (50 g l^{-1}) yielding an instant deep red solution, probably $UO_2(FHA^*)^+$ (FHA*=deprotonated FHA) and, after 24 h, a red/orange precipitate ($UO_2(FHA^*)_2$). In nitric acid this complex formation is inhibited and in 1 M HNO_3 no precipitation is observed even after 3 weeks.

By monitoring the characteristic absorbance peaks (at 373 and 473 nm) for the FHA–U(VI) complex (Fig. 4) it can be shown that >95% complexation is only observed for >40× excess ligand (cf 2.5× excess for the Np(IV)–FHA complex). Also, again by monitoring the FHA–U(VI) absorbance peak at 480 nm it can be seen that in nitric acid solutions the complex formation is greatly inhibited (Fig. 5).

From this data it would appear that in 0.1–1.0 M HNO_3 (i.e. predicted process conditions) FHA will much more readily complex with Np(IV) than with U(VI). This has been confirmed in preliminary distribution experiments which have shown that Np can be selectively stripped from a mixed Np/U solvent phase (30% TBP/OK) into aqueous nitric acid solutions [16].

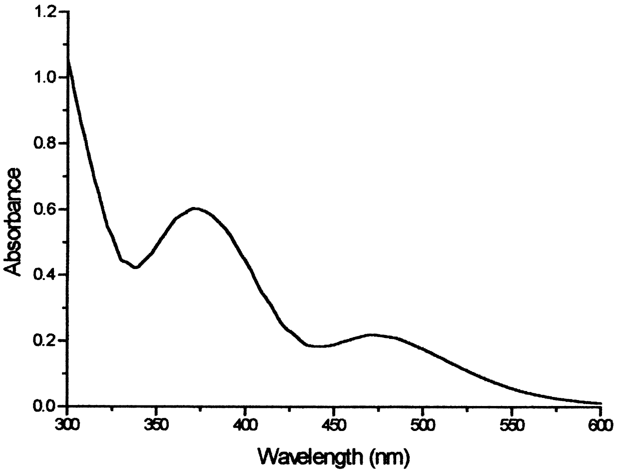

Fig. 4. UV-Vis spectrum of U(VI)–FHA complex in H_2O (2 g l^{-1} U, ~10× excess FHA).

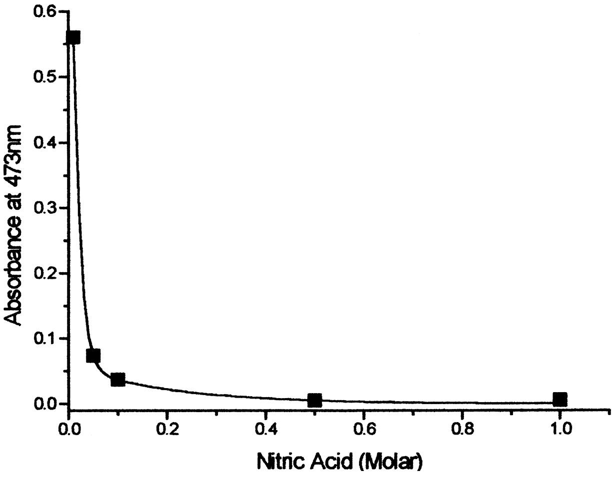

Fig. 5. Effect of nitric acid on the U(VI)–FHA complex peak at 473 nm (2.5g l^{-1} U, ~25× excess FHA).

4. Conclusions

Hydroxamic acids are very strong complexing agents for Ac(IV). It has been shown that formohydroxamic acid can readily complex Np(IV) and an aqueous solution of formohydroxamic acid can strip Np(IV) from 30% TBP/OK. Although U(VI) can bind to formohydroxamic acid, complexation is much less pronounced and is strongly inhibited in nitric acid. This will enable the use of formohydroxamic acid as a selective salt free stripping agent for Np(IV) from a 30% TBP/OK solution of U(VI) in an advanced PUREX process for nuclear fuel reprocessing.

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