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The formation of hydrophilic Np(IV) complexes and their potential application in nuclear fuel reprocessing

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Abstract

A series of organic ligands have been screened for their effectiveness as complexants for Np(IV) in a neptunium rejection stage of an advanced PUREX process. Four of these species, formohydroxamic acid, acetohydroxamic acid, glycolic acid and pyruvic acid, readily form hydrophilic complexes with Np(IV) and can strip the actinide from 30% TBP/OK (30% tributylphosphate in odourless kerosene) into nitric acid. Near infra-red spectroscopy has been used to monitor Np(IV) complexation in nitric acid. Distribution experiments have been undertaken between nitric acid and 30% TBP/OK to examine the effect of ligand and nitric acid concentration on Np(IV) stripping. Finally, it has been shown that the extractability of U(VI) is unaffected by the presence of these ligands and all can be used to selectively strip Np(IV) from a U(VI) product stream in an advanced PUREX process. © 1998 Elsevier Science S.A.

Keywords: Neptunium (IV); Complexation; PUREX process

1. Introduction

1.1. Neptunium control in an advanced reprocessing plant

Irradiated nuclear fuel is reprocessed commercially by the PUREX process, to recycle uranium and plutonium [1,2]. A significant component of spent fuel is neptunium and its effective control in PUREX process streams is important in the efficient production of U and Pu products [3]. In nitric acid, neptunium usually exists 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 (30% tributylphosphate in odourless kerosene), whereas Np(V) is almost inextractable. This can result in Np passing into more than one waste/product streams in commercial reprocessing plants.

Advanced flowsheets under development at British Nuclear Fuels provide different options for neptunium routing. In one such flowsheet, chemical reduction of Pu(IV) to inextractable Pu(III) will also result in the reduction of any Np(VI) and Np(V) present to Np(IV). Thus, Np(IV) will co-extract with the U(VI) solvent product stream after separation from Pu. It is well known that organic ligands complex more readily with Ac(IV) than with Ac(VI) [4]. Assuming a similar behaviour for Np(IV), it is thus envisaged that the introduction of a hydrophilic ligand can result in the selective stripping of Np(IV) from a mixed U(VI)/Np(IV) 30% TBP/OK phase into nitric acid [3].

A wide range of organic ligands were studied as possible Np(IV) stripping agents, all of which had to show the following properties:

- salt-free, thus not adding significantly to the aqueous waste
- readily water-soluble and inextractable into 30% TBP/OK
- reasonably stable in nitric acid
- the Np(IV) complex formed must be readily soluble in the aqueous phase (no precipitation)
- the extractablility of U(VI) into 30% TBP/OK must remain unaffected.

With these criteria in mind, eight different ligands were chosen for an initial scoping study, with the experimental results discussed in this paper.

2. Experimental

Standard techniques were used throughout for the handling of ^{237}Np and ^{238}U solutions. Reagents were either purchased from standard chemical suppliers (Aldrich,

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Fluka and the Cookson Chemical Companies) or prepared ‘in house’ using basic techniques. Neptunium stock solutions were prepared by dissolving $^{237}NpO_2$ in refluxing nitric acid. The resultant mixed Np(V)/Np(VI) solution was reduced to Np(IV) by Fe(II) and the tetravalent actinide was extracted into 30% TBP/OK. Depleted uranium stock solutions were prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ in nitric acid and with subsequent extraction into 30% TBP/OK. Distribution experiments were undertaken by contacting 1:1 volume ratios of a 30% TBP/OK solution of Np(IV) (or combined Np(IV)/U(VI) solution) and a nitric acid solution of selected organic ligand. ^{237}Np concentrations were measured using low energy photon spectroscopy, and uranium concentrations were measured by x-ray fluorescence and acidity measurements by titration with NaOH. Near infra-red spectra were recorded using a Perkin Elmer Lambda 19 spectrophotometer attached by fibre optic cables to an external sample compartment.

3. Results and discussions

3.1. Initial scoping study

Distribution experiments were undertaken for Np(IV) between 30% TBP/OK (organic phase) and various organic ligands in ~0.7 M HNO_3 (aqueous phase) (Fig. 1). Distribution coefficients for Np(IV) ($D_{Np(IV)}$) were calculated as $[Np(IV)]_{organic}/[Np(IV)]_{aqueous}$; the lower the distribution coefficient, the better the stripping properties of the ligand. From these experiments, it was concluded that formohydroxamic acid (FHA) and acetohydroxamic acid (AHA) are the best stripping complexants for Np(IV) and these were selected for further study. A great deal of development work with aceto- and formohydroxamic acids has already been undertaken [5,6]. From these initial studies, it was felt that glycolic and pyruvic acids also showed sufficient promise as Np(IV) stripping agents to warrant continued investigation. All four organic ligands (Fig. 2) can readily deprotonate to form five-membered chelate rings with Np(IV) via two Np–O bonds.

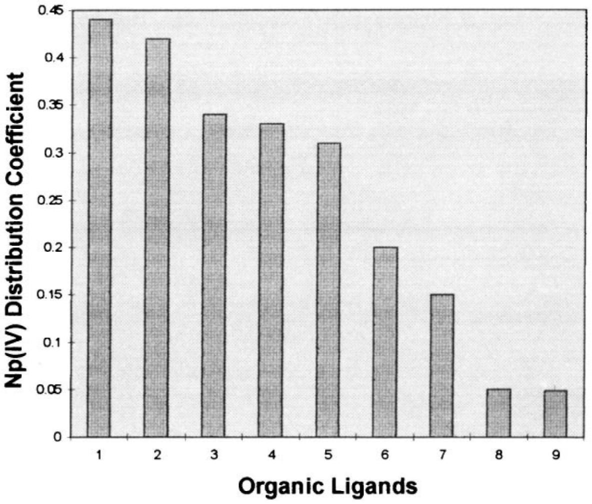

Fig. 1. Np (IV) distribution coefficients in the presence of various organic ligands. Total concentrations: Np(IV)=0.004 M, HNO_3=0.7 M. Organic ligands (0.1 M, aqueous phase only); 1=no ligand, 2=formic acid, 3=carboxymethylamine, 4=acetic acid, 5=butyric acid, 6=pyruvic acid, 7=glycolic acid, 8=formohydroxamic acid and 9=acetohydroxamic acid.

3.2. Near infra-red spectra of organic complexes of Np(IV)

During the course of PUREX process research at Sellafield, near infra-red spectroscopy has been used to monitor Np in solution. This is the standard technique for monitoring the oxidation states of Np [7] and can also be used to monitor the complexation of Np(IV). Tetravalent Np exhibits very distinctive absorbance bands between 640 and 1000 nm. These bands change intensity and shape on the formation of different complexes, e.g. at different HNO_3 concentrations [8,9] and when bound to other inorganic ligands, such as sulphate and iodide [10].

Np(IV) near infra-red band intensities and peak shapes also change on complexation with organic ligands (Fig. 3). In the case of the organic species chosen for further study, distinctive peak shapes can be observed, one characteristic of hydroxamic acid complexation of Np(IV) and one characteristic of glycolic and pyruvic acid complexation of Np(IV). Both spectra are different from those observed in the presence of varying concentrations of HNO_3.

The distinctive peak intensities have been used in titration experiments to monitor the extent of reaction. These experiments indicate that complete complexation of Np(IV) by FHA and AHA in ~0.1 M HNO_3 occurred after the addition of ~2.5× excess ligand and by glycolic and pyruvic acids after the addition of >20× excess ligand.

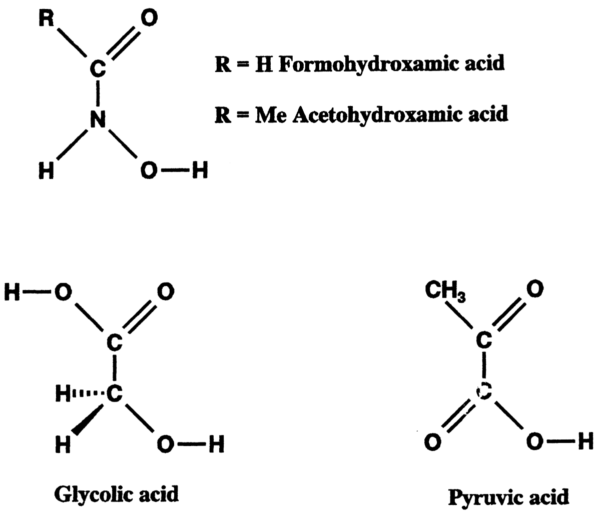

Fig. 2. Structures of selected organic ligands.

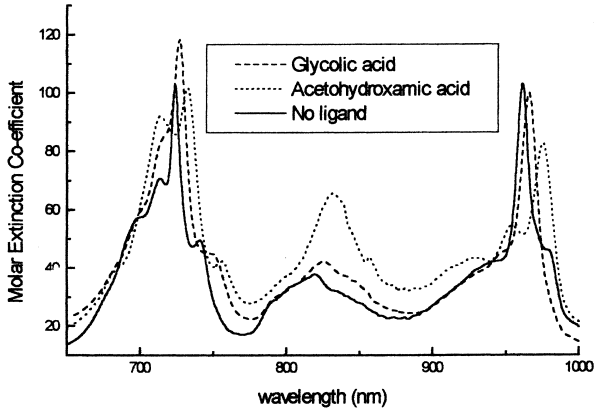

Fig. 3. Near infra-red spectrum of Np(IV) in 0.2 M HNO_3 in the presence of a fivefold excess of AHA and a twentyfold excess of glycolic acid.

Thus, as also indicated in the above distribution experiments, FHA and AHA are stronger complexants and, therefore, more effective stripping agents than glycolic and pyruvic acid. The excess of ligand required for 100% Np(IV) complexation increases with nitric acid concentration, thus, HNO_3 inhibits complexation, as will be discussed more fully in the next section.

Near infra-red spectroscopy was utilised in further distribution experiments, described below, to assess the extent of complex formation in the aqueous phase after equilibrium. It was also used to ensure that no complex was extracted into the organic phase. $Np(NO_3)_4{\cdot}2TBP$ is the normal species extracted into 30% TBP/OK in process conditions and has a distinctive near infra-red spectrum [11]. Extractable Np(IV) complexes yield different spectra, e.g. the Np(IV)–acetylacetone complex is extractable into the organic phase and has different near infra-red peak intensities (Fig. 4). No such spectral changes were observed when the four chosen ligands were used as Np(IV) stripping agents in distribution experiments, indicating that no new organic-soluble complexes were formed.

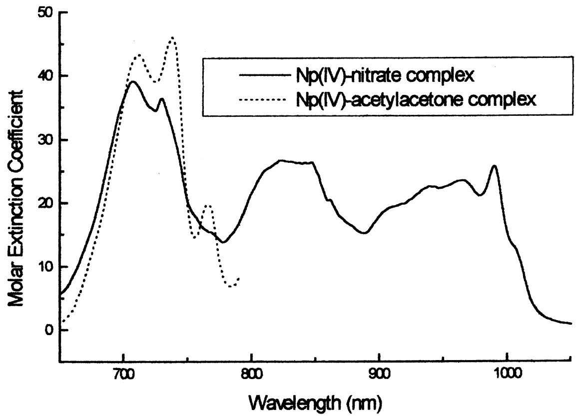

Fig. 4. Near infra-red spectra of Np(IV)–nitrate complex in 30% TBP/OK (i.e. $Np(NO_3)_4{\cdot}2TBP$) and the Np(IV)–acetylacetone complex in 30% TBP/OK.

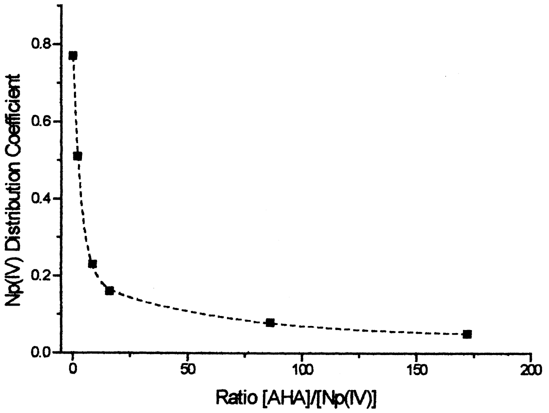

Fig. 5. Effect of increased AHA concentration on Np(IV) distribution between 30% TBP/OK and HNO_3. Total [Np]=0.005 M; equilibrium $[HNO_3]_{aq}=1.2$ M.

3.3. Np(IV) distribution experiments

A series of distribution experiments were undertaken between 30% TBP/OK and an aqueous phase containing various concentrations of organic ligand and nitric acid. The results obtained with variable ligand concentrations for AHA are shown in Fig. 5, and with variable acid concentrations for FHA are shown in Fig. 6. It can clearly be seen that Np(IV) is stripped into the aqueous phase by these hydroxamic acids and that stripping is increased with increased ligand concentration and decreased nitric acid concentration. Therefore, Np(IV) stripping is directly related to complexation with hydroxamic acid and is inhibited by nitric acid. Increased nitric acid concentration leads to an increase in free $[H^+]$, inhibiting deprotonation of the organic ligand and, hence, Np(IV) complex formation. The stripping properties of AHA and FHA were practically identical. Both glycolic and pyruvic acids exhibited similar behaviour, although the two complexants

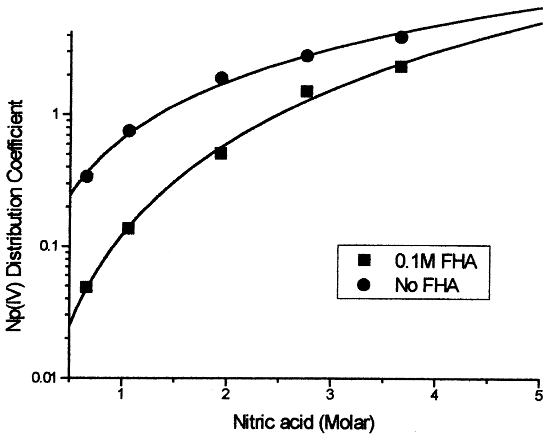

Fig. 6. Effect of increased equilibrium aqueous nitric acid concentration on Np(IV) distribution between 30% TBP/OK and an aqueous phase containing 0.1 M FHA. Total [Np]=0.005 M.

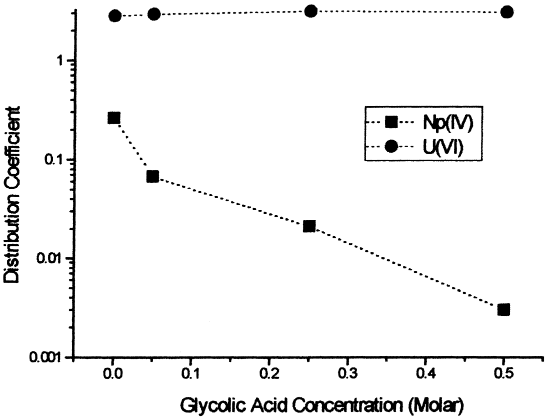

Fig. 7. Np(IV) and U(VI) distribution between 30% TBP/OK and aqueous nitric acid solutions of glycolic acid. Total [Np]~0.005 M; total [U(VI)]=65 g l^{-1}; equilibrium [HNO_3]=0.7 M.

were slightly less efficient in Np(IV) stripping, as indicated previously by initial scoping trials and near infra-red spectroscopy.

3.4. Np(IV) distribution experiments in the presence of U(VI)

To ensure that no significant quantities of U(VI) were back-stripped with Np(IV) in the presence of these organic complexants, a series of Np(IV) distribution experiments were undertaken in the presence of U(VI). In none of the experiments undertaken were any significant quantities of U(VI) back-stripped with Np(IV), for example, distribution experiments in the presence of glycolic acid are shown in Fig. 7. The U(VI) distribution coefficient values were all very similar (±10%) to modelled values based on U(VI) distribution data in the absence of any ligand. Therefore, all of the ligands studied can be used as selective stripping agents for Np(IV) in the presence of U(VI).

4. Conclusion

A range of simple organic compounds have been screened as selective complexants for Np(IV). Simple distribution experiments and a near infra-red spectroscopic investigation demonstrate that four species were found to be effective complexants for Np(IV) and could strip the actinide from 30% TBP/OK. These ligands were formohydroxamic acid, acetohydroxamic acid, glycolic acid and pyruvic acid. Further distribution experiments indicate that increased Np(IV) stripping can be promoted by increasing the ligand concentration and decreasing the nitric acid concentration and that U(VI) extraction was unaffected by the presence of the ligands chosen. Therefore, all four ligands could be used as reagents for the effective stripping of Np(IV) from a U(VI) product stream in an advanced PUREX process.

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