

Progress towards Understanding the Interactions between Hydroxamic Acids and Actinide Ions

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BNFL has undertaken a wide-ranging research programme to investigate the fundamental properties of hydroxamic acids and, in particular, their reactions with actinide ions. Most work has focussed on simple hydroxamic acids ($R = H$ and CH_3) although some comparative data with more complex molecules including di-hydroxamates have been obtained. Properties of hydroxamic acids studied to date include, hydrolysis in nitric acid, decomposition to gases, pK_a 's and redox potentials. The redox and co-ordination chemistry of actinides by hydroxamic acids has been investigated using a range of techniques and stability constants for both 4f and 5f hydroxamate complexes have been determined. In conjunction with these fundamental studies, more applied work has been carried out to assess the applications of simple hydroxamic acids under process conditions. A large database of solvent extraction distribution data has been accumulated and, from this, extraction algorithms describing how hydroxamic acids modify actinide extraction in to TBP have been derived. Also the effects of hydroxamic acids on U and Np mass transfer have been studied in single stage centrifugal contactors and this has been modeled theoretically. The third stage of our development work so far has looked at the actual design and testing of novel hydroxamic acid based flowsheets which selectively strip Np(IV) and Pu(IV) from a uranium loaded TBP stream.

KEYWORDS: *hydroxamate, complexation, redox kinetics, hydrolysis, stability constants, solvent extraction*

I Introduction

Hydroxamic acids (XHA) have been identified as useful reagents for the control of Np(IV) and Pu(IV) in Advanced Purex processes which use single cycle flowsheets and centrifugal contactors¹⁻². They are salt free organic compounds with the formula $RCONHOH$ and so can act as di-oxygen chelating ligands with a high affinity for 'hard' cations, such as the actinide ions. They are also redox-active capable of reducing a range of metal ions. This paper will, therefore, briefly review the current state of our research in to the interactions of hydroxamic acids and actinides, ranging from their fundamental chemistry to process applications.

II. Properties of Hydroxamic Acids

1. Hydrolysis and decomposition in nitric acid

In acid solution, hydroxamic acids are hydrolysed to the parent carboxylic acid and hydroxylamine. The kinetics of the hydrolysis of formohydroxamic acid (FHA) and acetohydroxamic acid (AHA) in nitric acid have been determined³.

Hydroxamic acids are salt free reagents containing the elements C, H, O and N only. ¹³C NMR indicated that in 6 M HNO_3 FHA and AHA decomposed to the intermediate carboxylic acids. After reflux in 3 M HNO_3 for 3 hours, FHA decomposed entirely to CO_x whereas after refluxing AHA in 6 M HNO_3 for 3 hours some residual acetic acid was present. Under these conditions, the N fragment –

hydroxylamine – would also have been decomposed to gases and nitrous acid⁴.

If the hydroxamate is bound to a metal ion then the rate of hydrolysis is reduced. If $[M^{x+}] \sim [XHA]$ then pseudo 1st order kinetics are observed but if $[M^{x+}] \ll [XHA]$ the decay of the complex appears S-shaped or exponential. We have developed a semi-quantitative kinetic model that describes the hydrolysis of hydroxamic acids in the presence of (non-oxidising) complexing metal ions⁵. Qualitatively, in excess XHA the concentration of the $\{M-XHA\}$ complex remains constant because any liberated metal ion is immediately recomplexed by any free XHA ligands, this gives the appearance of an induction period. Once free XHA has hydrolysed and $[M^{x+}] \sim [XHA]$, then the pseudo 1st order decay of the complex is observed, as the bound XHA is hydrolysed (excess acid).

2. Onset and Redox potentials

Using cyclic voltammetry we have previously reported onset potentials for both FHA and AHA oxidations³. Using a novel electrochemical quartz crystal microbalance (EQCM), the AHA oxidation was fully characterised and, applying the methods of reference⁵, led to the determination of E^0 for AHA as +0.62 V vs. SCE. This indicates that AHA can thermodynamically reduce Np(VI) and Pu(VI, V, IV) but can not reduce U(VI, V, IV) or Np(V, IV).

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III. Complexation Reactions of Hydroxamic Acids

3. Determination of stability constants for 4f and 5f ions

Potentiometric measurements of FHA and AHA pKa's have been made and these are given in **Table 1**. Using standard potentiometric, spectrophotometric and solvent extraction methods, stability constants for some 4f and 5f ions with hydroxamate ligands have been determined⁷. The majority of the data is for the mono-hydroxamate AHA but some comparative data with example di-hydroxamates, glutarodihydroxamic acid (GDA) and rhodotorulic acid (RDA), is included. Speciation modeling of stability constant data has shown that Nd, Eu and Ho form 1:1, 1:2, 1:3 and 1:4 complexes in solution and that in alkaline solutions Eu and Ho both form a $M^{III}(AHA)_4(OH)$ species. Using this interpretation, Eu speciation data can be shown to agree well with luminescence results. The values for Th(IV) are perhaps low due to interfering hydrolysis reactions. It is, however, evident that hydroxamic acids are strongly binding ligands for f-elements, particularly for tetravalent cations.

4. Complex formation with actinide ions

In solution, hydroxamic acids readily form 1:1 and 2:1 orange-red complexes with uranyl ions, with absorption maxima at ~372 and ~473 nm. If the acidity is reduced the complex becomes increasingly insoluble and precipitates of the uranyl(hydroxamate)₂ complex are formed⁸. Our evidence suggests that in the solid state benzohydroxamic acid adopts a pentagonal bipyramidal structure with one water molecule, whereas in the AHA complex no water molecules are intrinsically bound to the uranyl ion⁹. Solution phase EXAFS shows a common coordination environment for both 1:1 and 1:2 XHA complexes with 5 equatorial U-O distances of ca. 2.4 Å; there was no evidence of dimer or oligomer formation⁹. U(IV) and Np(IV) absorption spectra are slightly changed by complexation with FHA and AHA, with the Np(IV)–hydroxamate spectra resembling those of other Np(IV) complexes such as Np(NO₃)₄·2TBP⁸. Spectrophotometric data also suggests that Np(IV) forms a mixture of 1:1 and 1:2 complexes². It has been shown for U(VI), U(IV) and Np(IV) complexes that as the solution acidity increases, complex formation is suppressed but increased [NO₃⁻] does not affect complex formation¹⁰. Hence, this indicates that hydroxamic acids deprotonate to form anionic bis-oxygen chelate complexes with these ions, as expected. The lack of nitrate ion dependence suggests that the number of nitrate ligands present in the complexes, if any, does not change. Pu(IV) forms a dark red complex with FHA which on standing is reduced to Pu(III). The absorption spectrum is very different to weakly or uncomplexed Pu(IV) ions with the 470 nm peak absent. This implies strong inner sphere coordination (cf. Cl⁻ and EDTA)³.

Preliminary molecular modelling studies of hydroxamate complexes have been undertaken,¹¹ although these results

need experimental verification. The hydroxamic acid was shown to prefer the keto- form, as expected, with the cis isomer having a slightly lower energy. In the complex UO₂(FHA)₂ it was indicated that an unusual bent structure, in which the FHA ligands are at an angle of ca. 33°, was stabilised. This structure can exhibit chair and boat conformations and cis- and trans- isomers. The bending is apparently reduced if water molecules are added to the coordination sphere. The energy changes between bent and flat structures are small and it may be that the flat structure is the energy maximum of a shallow, broad energy well within which 'flapping' of the ligand can occur in solution.

The biological generation of natural hydroxamates (siderophores) and their ability to mobilise Fe(III) and actinides from solid phases have also been investigated¹².

5. The measurement of complexation kinetics

Stopped flow spectrophotometry is being used to study the very fast complexation kinetics of hydroxamic acids with metal ions (Fe³⁺, UO₂²⁺). Preliminary data¹³ indicates that when Fe(III) is in excess (mono- complex formed) the complexation reactions are 1st order with respect to [Fe(III)] and [XHA]. The rates are slower in acid than in water. The rates of complexation of FHA and AHA are similar in water but in 1 M HNO₃, the rate with AHA is slower due to its greater size. The kinetics when AHA is in excess and the relationship with [H⁺] are complicated by the equilibria of the 1:1 – 1:3 M:L complexes. Uranyl ion complexation is apparently even more rapid than Fe(III).

IV. Redox Chemistry of Hydroxamic Acids

1. Reaction with An(VI)

Stopped flow spectrophotometry has been used to investigate the kinetics of the very rapid reaction between Np(VI) and FHA. The rate equation is 1st order with respect to both Np(VI) and FHA, with a rate constant $k = 1.17 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at [H⁺] = 2.0 M. The order with respect to [HNO₃] and the activation energy have not yet been determined. Indications are that FHA is one of the fastest reducing agents yet reported for Np(VI)¹⁴.

The addition of AHA to Pu(VI) solution in 0.5 M acid led to the complete reduction of Pu(VI) to Pu(V), Pu(IV) and ultimately, after 6 days, Pu(III)¹⁵. Kinetic data is not yet available for these reactions.

2. Reaction with Pu(IV)

FHA and AHA initially complex Pu(IV), but on standing reduction to Pu(III) is observed. There is an initial induction period, during which no reduction occurs because the Pu(IV) remains bound in stable complexes with FHA. However, [FHA] is decreasing due to hydrolysis and, at the end of the induction period, Pu(IV) in some "active" state is available for a fast reduction, probably by hydroxylamine. The kinetics of reduction are, to a first approximation, controlled by the hydrolysis kinetics of free FHA¹⁶.

V. Purex Process Applications

1. Solvent extraction behaviour

Much distribution data for AHA and FHA with Np(IV) have been accumulated and a lesser amount for U(IV) and Pu(IV) have also been obtained^{2,17}. These data are used to construct extraction algorithms which describe the solvent extraction behaviour of Np(IV) in the presence of these species. These algorithms are then used in process simulations. The trends observed for all 3 actinides with both AHA and FHA are similar. Briefly, increasing hydroxamic acid and decreasing nitric acid concentrations decreases the distribution coefficient. Increasing U(VI) loading of the solvent phase decreases the distribution coefficient, as expected but uranium extraction is unaffected. The efficiency of hydroxamic acid stripping appears to follow the expected trends of actinide complex formation, i.e. U(IV) < Np(IV) < Pu(IV).

2. Mass transfer studies

U(VI) and Np(IV) mass transfer studies were undertaken in a 1 cm rotor diameter single stage centrifugal contactor in the presence of FHA/AHA. These trials confirmed that Np(IV) could be selectively stripped from a U(VI) solvent stream and that the rapid kinetics of An(IV)-XHA complexation are compatible with residence times in centrifugal contactors¹⁸⁻¹⁹.

3. Advanced Purex process

AHA and FHA are being developed as aqueous phase complexants for Np(IV) and Pu(IV) in Advanced Purex flowsheets for LWR and/or FBR fuel reprocessing¹⁻². Processes are based on single cycle solvent extraction flowsheets with centrifugal contactors. For instance, in a Np Rejection flowsheet², after U/Pu separation, the solvent phase containing Np(IV) and U(VI) is contacted with an aqueous nitric acid phase, at a low acidity, containing the hydroxamic acid. Np(IV) is complexed by the hydroxamate and stripped to the aqueous phase whilst U(VI) is not complexed and remains solvated in the TBP phase.

To date, a number of counter-current solvent extraction trials of this Np Rejection process have been carried out in multi-stage centrifugal contactor rigs at the Khlopin Radium Institute, St. Petersburg (KRI) and at BNFL Sellafield¹⁹⁻²⁰. A trial at Sellafield using AHA obtained a Np DF on the solvent product of at least 270. This DF was limited by analytical limits of detection and so may actually be higher (DFs >10³ were obtained in different trials at the KRI). Further trials will test whether this is a true figure for the flowsheet tested and will test flowsheet variations, which should produce higher DFs. Dynamic simulations of start-up and run-down produced good agreement with observed concentrations and reasonable agreement with Np concentration profiles at steady state were also achieved. Some improvements to the model's Np extraction algorithms and mass transfer routines were identified²⁰.

VI. Conclusions

Much data on the fundamental chemistry and process applications of hydroxamic acids have been obtained to date. Further work is in progress to extend our fundamental understanding of hydroxamic acids (including redox and complexation kinetics; electrochemistry²¹; coordination and solution speciation studies) and to validate flowsheets (improved extraction algorithms; counter-current trials).

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Table 1 Stability constants for hydroxamic acid complexes

Ion	Ligand	Log β_1	Log β_2	Log β_3	Log β_4	Log β_5
H ⁺	AHA	9.49				
H ⁺	FHA	8.9				
H ⁺	GDA	9.81	18.60			
H ⁺	RDA	9.38	18.35			
Nd ³⁺	AHA	6.29	12.24	18.05	21.87	13.41
Eu ³⁺	AHA ^a	6.46	12.95	19.32	22.92	14.44
Gd ³⁺	AHA	6.17				
Ho ³⁺	AHA	7.16	13.63	19.46	23.22	15.26
Th ⁴⁺	AHA	9.46	18.73			
U ⁴⁺	AHA	12.25	22.24	30.11	34.36	36.80
UO ₂ ²⁺	AHA	7.94	14.11			
UO ₂ ²⁺	GDA	14.68	25.61			
UO ₂ ²⁺	RDA	15.63	26.14			
Np ⁴⁺	AHA	12.83	22.96	31.00	36.17	39.33
NpO ₂ ⁺	AHA	4.83	8.09			
Pu ³⁺	AHA	5.77	11.66	14.83	15.84	
Pu ⁴⁺	AHA	13.9	24.1	32.7	38.8	
Am ³⁺	AHA	5.85	11.17	15.48	16.59	

^a At pH = 4.20. Slightly lower values were obtained at pH = 5.15 perhaps due to changes in the form of Eu (e.g. hydrolysis) or AHA (e.g. increased conversion to Na salt).