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Neptunium Binding Kinetics with Arsenazo(III)

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Neptunium Binding Kinetics with Arsenazo(III)

Fuel Cycle Research & Development

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Idaho National Laboratory
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SUMMARY

This document has been prepared to meet FCR&D level 2 milestone M2FT-14IN0304021, "Report on the results of actinide binding kinetics with aqueous phase complexants" This work was carried out under the auspices of the Thermodynamics and Kinetics of Advanced Separations Systems FCR&D work package.

The report details kinetics experiments that were performed to measure rates of aqueous phase complexation for pentavalent neptunium with the chromotropic dye Arsenazo III (AAIII). The studies performed were designed to determine how pH, ionic strength and AAIII concentration may affect the rate of the reaction. A brief comparison with hexavalent neptunium is also made. It was identified that as pH was increased the rate of reaction also increased, however increasing the ionic strength and concentration of AAIII had the opposite effect. Interestingly, the rate of reaction of Np(VI) with AAIII was found to be slower than that of the Np(V) reaction.

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TABLES

ACRONYMS

AAIII	Arsenazo III
CL-AAIII	Chlorophosphonazo III
COEX	Co Decontamination Process
CPC	Controlled Potential Coulometry
FCR&D	Fuel Cycle Research and Development
INL	Idaho National Laboratory
TALSPEAK	Trivalent Actinide Lanthanide Separation by Phosphorus-reagent Extraction from Aqueous Komplexes
US DOE	United States Department of Energy
UV/Vis	Ultra Violet-visible
XO	Xylenol Orange

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

1. Introduction

At the heart of every liquid-liquid distribution for metal ion separation is selective complex formation in aqueous and organic media. Although thermodynamics drives the complex formation, these parameters give no information about the mechanism by which these reactions take place. To determine such information, the kinetics of these reactions have to be studied. For example, the complex separation of An(III) from Ln(III) performed using solvent-extraction relies upon the subtle differences in the chemistry of 4*f* and 5*f* elements. Currently there are two main approaches used to perform such separations; accessing the higher oxidation states of the actinide elements, for example making Am(VI), or using complexants with soft donor atoms in a liquid-liquid partitioning process.[1-8] While there have been multiple studies over many decades on processes such as TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus-reagent Extraction from Aqueous Komplexes)[2, 9-11] questions still remain as to the mechanisms by which these separations take place. In addition, the TALSPEAK separation in its original formulation suffered from poor phase transfer kinetics, which have been attributed to the rate of the Ln-DTPA complex dissociation in the aqueous phase.[11,12] This is somewhat unsurprising due to the strength of these complexes in aqueous solution. With COEX[13] type systems being considered as one reference technology for used fuel separations investigations into the behavior of oxidized transuranics is becoming paramount. By studying the chemistry of neptunium researchers have a more stable window into what might occur with Am(V) and Am(VI) in such systems. In addition, with the ability to study U(VI), Np(VI) and Pu(VI), predictive trends may become apparent across the actinide series.

There have been relatively few absolute kinetic studies for extraction ligand complexations with lanthanides, and even fewer reported for the actinides. In the latter studies, use of the dye Arsenazo III (2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bis(benzenearsonic acid, abbreviated AAIII) is common, as this dye forms highly colored complexes with actinide ions in acidic aqueous solution. Despite its usefulness, a survey of the literature has shown that AAIII ligand binding kinetics have only been reported for the tetravalent aquo actinide ions Th(IV), U(IV), and Np(IV), pentavalent Np(V) and hexavalent U(VI). In perchloric acid solution, values for the second-order rate constants for the reaction

$$\mathrm{X(IV)} + \mathrm{AAIII} \rightarrow \mathrm{X(AAIII)} \qquad (1)$$

have been determined (see Table 1) using standard stopped-flow absorbance spectroscopy type techniques.

Table 1. Summary of literature kinetic and thermodynamic parameters for AAIII complexation with actinide ions.

Species	k at 298K (M^{-1} s^{-1})	E_a (kJ mol^{-1})	ΔS^* (J /K-mol)	Acidity	Ref.
Th(IV)	(2.90 ± 0.12) x 10^6			2.0 M $HClO_4$	14
U(IV)	(4.33 ± 0.23) x 10^5	36.8 ± 2.1	-7.5	2.0 M $HClO_4$	14
U(VI)	(2.14 ± 0.08) x 105	30.1 ± 6.0	-42.2 ± 20.2	2.0 M $HClO_4$	15
U(VI)	2.1 x 10^5			pH 0.2 – 2.0	16
U(VI)	1.69 x 10^7			pH 4.6, 0.1M ionic strength acetate buffer	17
U(VI)	1.09 x 10^6			0.10 M acid	17
Np(IV)	(3.29 ± 0.19) x 10^5	34.3 ± 4.6	33.0	2.0 M $HClO_4$	14
Np(V)	(9.6 ± 1.6) x 10^5	60 ± 50		pH 4.6, 0.1M ionic strength acetate buffer	17

Additional work reported upon the reaction of AAIII with Np(V) (NpO_2^+) and U(VI) (UO_2^{2+}) under various conditions showed that these ion complexations by AAIII were strongly dependent upon the acid concentration and total ionic strength. The solution buffer used was also important, for example, in 5.0 mM acetate (Ac) buffer Np(V) represents more than 98% of the total Np, while U(VI) is distributed as 35% UO_2^{2+}, 37% UO_2Ac^+, 19% $(UO_2(Ac)_2$, and 7% other hydrolysis products.[17] The measured kinetics varied considerably, and in some cases (particularly Np(V)) had very large error. Mechanistically, these and other studies involving ligands such as methanediphosphonic acid (MDPA), 1-hydroxy-ethane-1,1-diphosphonic acid (HEDPA), and chlorophosphonazo III (2,7-bis(4-chlorophosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid-Cl III (Cl-AAIII) showed that measured activation parameters were generally consistent with an associative mechanism for complex formation.[18]

In addition to the complexation rate constants for AAIII reaction with actinides, some reverse decomplexation rate constants for the reaction:

$$Np(V)(AAIII) \rightarrow Np(V) + AAIII \qquad (2)$$

have also been obtained using this same approach. These rate constants are determined from intercept values of the second-order plots, and the calculated kinetic and thermodynamic parameters are given in Table 2. For this particular study, Cl-AAIII was used. In the decay there were two pathways noted, one that was dependent upon the acid concentration used (0.1 to 1.0 M $HClO_4$) and the other that was independent.

Table 2. Summary of literature kinetic and thermodynamic parameters for Cl-AAIII complexation with Np(V) at 1.0 M ionic strength. $\Delta H_a^*/\Delta S_a^*$ and $\Delta H_a^*/\Delta S_a^*$ refer to the acid-dependent and acid-independent pathways, respectively.[18]

Species	k_{-1a} at 298K (s^{-1})	k_{-1} at 298K (s^{-1})	ΔH_a^* (kJ mol^{-1})	ΔS_a^* (J mol^{-1} K^{-1})	ΔH_2^* (kJ mol^{-1})	ΔS_2^* (J mol^{-1} K^{-1})	I (M)
Np(V)	22.53 ± 2.67	11.22 ± 4.56	38.8 ± 0.6	-96 ± 18	70.0 ± 0.1	17 ± 1	1.0

It is worthy of note that these investigations were performed some 15-16 years ago. As such much work is needed to train new scientists in understanding the chemical kinetics of actinide reactions in solution. This study represents an initial effort to confirm some of the previously studied systems through a systematic investigation of Np(V) binding kinetics with AAIII using stopped-flow spectrophotometry and UV-visible absorption spectroscopy. Further, these investigations were expanded to incorporate one Np(VI) condition to begin exploring the differences in behavior of these two actinyl cations in solution.

2. Approach

2.1 Stopped flow procedure

The complexation kinetics of Np(V) and Np(VI) binding to AAIII were followed using an OLIS DB620 UV-vis NIR system with stopped flow attachment. The reaction was followed at a single wavelength monitoring the ingrowth of the complexed neptunium species at 650 nm with a photomultiplier detector arrangement. The solutions mixed in these experiments were [Np + $NaNO_3$+$NaC_2H_3O_2$] + [AAIII + $NaNO_3$+$NaC_2H_3O_2$]. At least five replicate measurements were made for each set of experimental conditions, and all of the experiments were performed at room temperature (21.0 ± 1.0 °C).

The limiting reagent in these experiments was the AAIII complexant. In most experiments, apart from where the concentration of AAIII was changed, this concentration was kept constant at 1.0×10^{-5} M.

2.2 Solution preparation

All chemicals used were of reagent grade or higher purity. The neptunium used in these studies was from INL stocks. Stock solutions of the sodium nitrate, AAIII and sodium acetate buffer were prepared by weight using 18 MΩ de-ionized water.

Samples for the stopped flow experiments were prepared by mixing the appropriate quantities of stock solution of the sodium nitrate, AAIII and sodium acetate solutions in volumetric flasks. The neptunium solutions were prepared by adding the required volume of Np(V or VI) to a solution of $NaNO_3$+$NaC_2H_3O_2$ to bring it to 10 mL total volume. The concentration of Np was varied from $1.0\text{x}10^{-5}$ M to $1.0\text{x}10^{-4}$ M. The pH of the aqueous solutions were adjusted to the correct pH using HNO_3 or NaOH accordingly. The absorbance versus time data were analyzed individually using the integrated first order rate law (Equation 3) to obtain the k_{obs} (s^{-1}) these values were then plotted as a function of [Np(V,VI)] to determine the second order rate constant.

$$A = (A_{ini}-A_{fin})e^{-kt} + A_{fin} \qquad (3)$$

Neptunium in the desired oxidation state was prepared immediately prior to the experiments by bulk electrolysis using a Digi-IVY DY2322 potentiostat. A three electrode H-cell consisting of a Pt gauze working electrode, Ag/AgCl reference electrode and Pt wire counter electrode was utilized for the bulk electrolysis. To obtain Np(V), the cell was held at a potential of 0.8 V, while for Np(VI) the cell was held at 1.2 V. The oxidation state of Np was confirmed by UV-vis spectrophotometry (Figure 1).

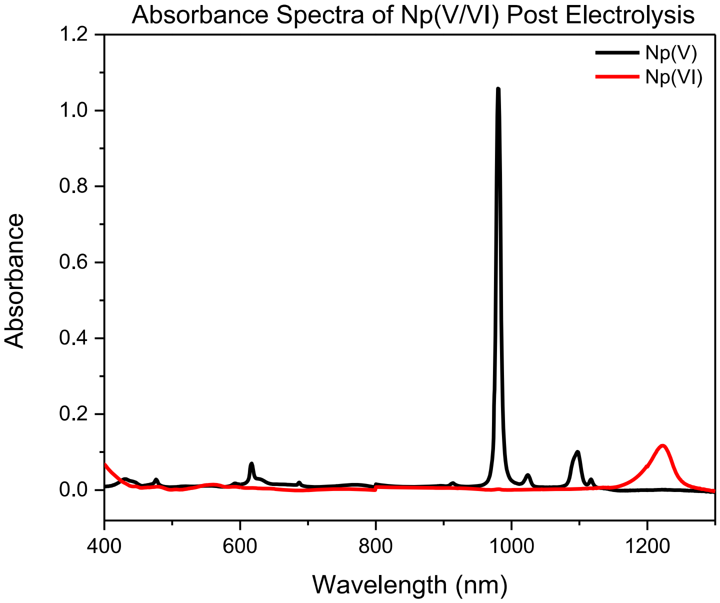


Figure 1. UV-vis spectra of 4.2 mM Np(V) and Np(VI) in nitrate media.

The neptunium concentration of the stock solution was determined using Controlled Potential Coulometry (CPC).[19] By cycling the neptunium oxidation state from V to VI and applying Faraday's Law (Equation 4) the charge passed can be used to calculate the absolute concentration of the Np in solution using the expression

$$N = \frac{Q}{nF} \tag{4}$$

where N is the moles of analyte, Q is the total charge passed, n is the number of electrons transferred per ion of analyte and F is Faradays constant. Using this method the concentration of the Np stock was calculated at 82 mM (Figure 2).

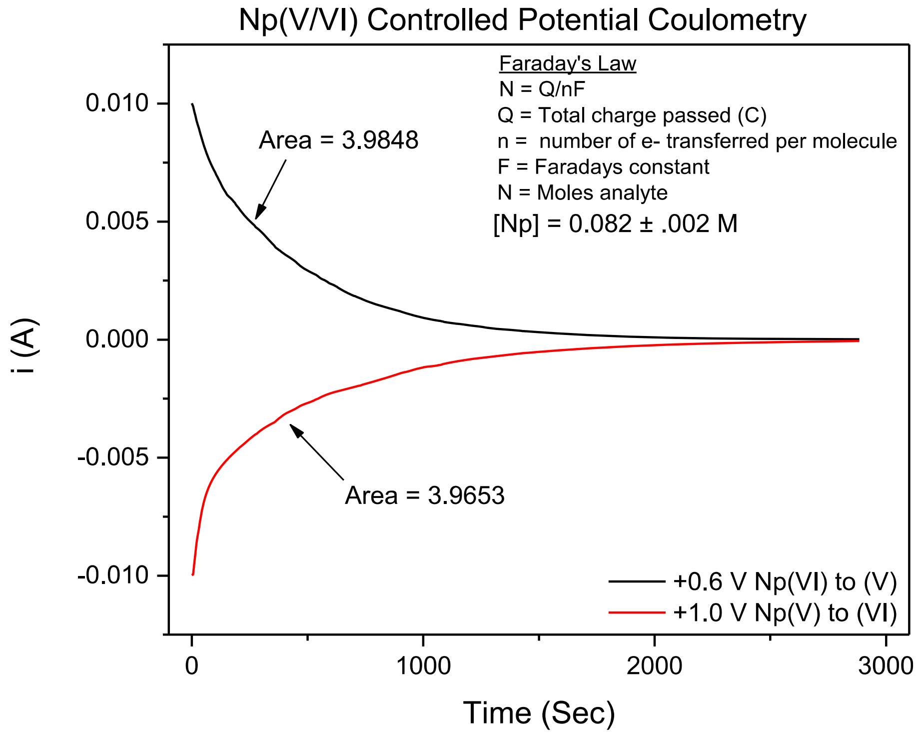


Figure 2. Graphical representation of the experimental determination of [Np] using Faraday's law.

3. Summary of Results

Previous studies with the lanthanides performed under the Thermodynamics and Kinetics work package had used Xylenol Orange (XO) as the indicator dye,[21] however initial experiments performed towards this body of work found weak or no complexation of XO with the neptunyl ions (V or VI) at the pH region of interest. As such the arsenazo III (Figure 3) was chosen as a suitable alternative for this work.

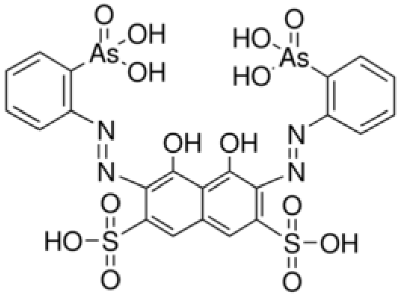


Figure 3. Chemical structure of chromotropic dye ArsenazoIII (AAIII).

Prior to performing the stopped flow experiments the spectral characteristics of free AAIII and the Np(V)-AAIII in solution were measured. Figure 4 shows the UV-vis spectra of both species which were consistent with those previously reported by Fugate et al.[18] An absorption band at 650 nm due to the formation of the Np(V)-AAIII complex is evident. The uncomplexed AAIII has a broad absorption centered around a λ_{max} at 541 nm. Similar features were found for the Np(VI)-AAIII complex, as such the complexation reactions for both species were followed by monitoring the increase in absorption at 650 nm. A typical kinetic trace obtained is shown in Figure 5.

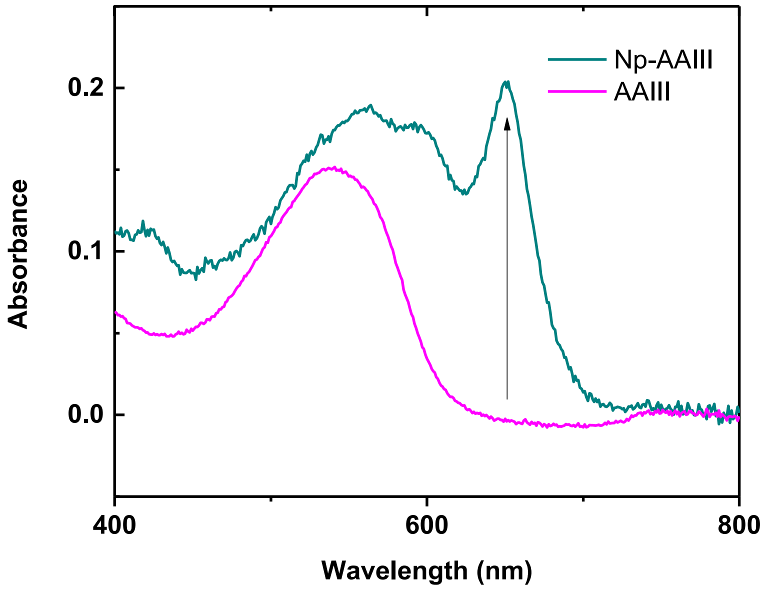
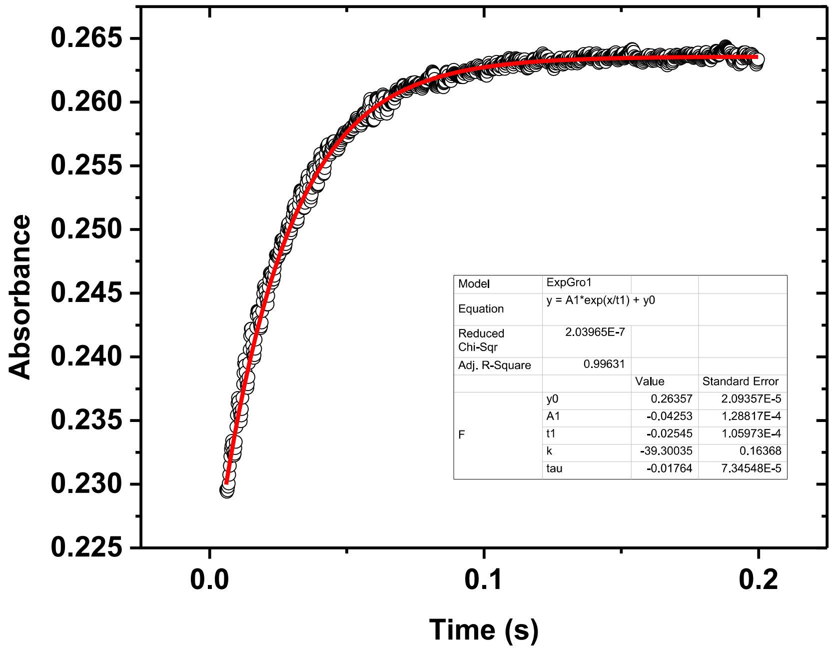


Figure 4. Optical absorbance spectra of (—) neptunium complex with AA-III and (—) decomplexed AA-III. [Np(V)] = 1x10^{-5} M, [AA-III] = 1x10^{-5} M, acetate buffer = 0.005 M Solution pH 3.0, T = 21 ± 1˚C.



Model	ExpGro1		
Equation	y = A1*exp(x/t1) + y0		
Reduced Chi-Sqr	2.03965E-7		
Adj. R-Square	0.99631		
		Value	Standard Error
F	y0	0.26357	2.09357E-5
	A1	-0.04253	1.28817E-4
	t1	-0.02545	1.05973E-4
	k	-39.30035	0.16368
	tau	-0.01764	7.34548E-5

Figure 5. Sample absorption growth kinetics trace from the stopped flow spectrophotometer measuring the rate of reaction of Np(V) with AAIII at 650 nm. [Np] = 5x10-5 M, [AAIII] = 1x10-5 M I = 0.1 M, pH= 4.0, T = 21 ± 1˚C. Open circles represent the measured data the red line represents the fit.

Unlike the lanthanide work performed previously[20] the kinetic traces measured here fit to a single exponential kinetic function, indicating a simple A + B → C type reaction mechanism. The reaction was studied as a function of pH to examine the acid dependence of the complex formation and dissociation. The values calculated for the first order rate parameter k (s^{-1}) are shown in this system as a function of increasing Np concentration in Table 3. Figure 6 displays the calculated second order rate constant for these reactions, with k = $(2.89 \pm 0.11) \times 10^5$ and $(7.26 \pm 0.51) \times 10^5$ ($M^{-1}s^{-1}$) at pH 3 and 4 respectively. Both sets of reactions conditions show a positive finite intercept, that decreases with increasing pH, the intercept of the second order plots gives the rate of the decomplexation reaction.

Table 3. Rate constants for the reaction of Np(V) + AAIII as a function of Np concentration at pH 3 and pH 4.

pH 3		pH 4	
[Np] (M)	k_{obs} (s^{-1})	[Np] (M)	k_{obs} (s^{-1})
1.0×10^{-5}	16.49 (±1.85)	1.0×10^{-5}	18.78 (±3.73)
2.5×10^{-5}	19.21 (±2.23)	2.5×10^{-5}	26.09 (±0.42)
5.0×10^{-5}	27.15 (±0.63)	5.0×10^{-5}	41.45 (±1.25)
7.5×10^{-5}	34.46 (±0.80)	7.5×10^{-5}	68.07 (±0.86)
1.0×10^{-4}	43.63 (±4.62)	1.0×10^{-4}	77.62 (±0.87)

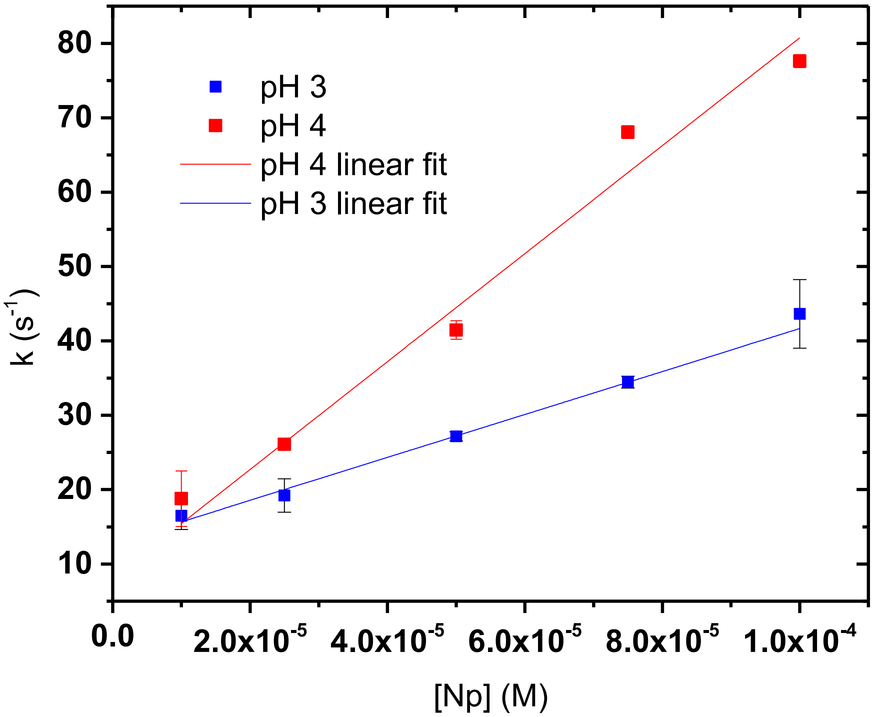


Figure 6. Second order plot of rate constants for Np(V) + AAIII at pH 3 and pH 4. pH 3 slope corresponds to a value of $(2.89 \pm 0.11) \times 10^5$ $M^{-1}s^{-1}$, intercept of 12.79 ± 0.60 with an R^2 of 0.995; pH 4 slope corresponds to a value of $(7.26 \pm 0.51) \times 10^5$ $M^{-1}s^{-1}$, intercept of 8.19 ± 2.73 with an R^2 of 0.980.

To identify if AAIII and/or ionic strength have any influence on the reaction rate, experiments were performed at an increased AAIII concentration and also higher ionic strength. These experiments were both performed at pH 4. The calculated values for the first order rate parameter k (s^{-1}) for both systems are shown in Table 4 as a function of increasing Np concentration. The calculated second order rate constant for these reactions are (2.22 ± 0.14) x 10^5 where the AAIII concentration was 2.5 x 10^{-5} M and I=0.1 M and (4.18 ± 0.43) x 10^5 ($M^{-1}s^{-1}$) for 1.0 x 10^{-5} M AAIII at I = 1.0. From Figure 7 it can be seen that both sets of reactions conditions show a positive finite intercept.

Table 4. Rate constants for the reaction of Np(V) + AAIII as a function of Np concentration for solution composition of [AAIII] = 2.5x10^{-5}M, I=0.1 M at pH 4 and [AAIII] = 1x10^{-5}M, *I*=1.0 M at pH 4.

[AAIII]=2.5x10^{-5}M, I=0.1 M		[AAIII] = 1x10^{-5}M, *I*=1.0 M	
[Np] (M)	k_{obs} (s^{-1})	[Np] (M)	k_{obs} (s^{-1})
1.0x10^{-5}	9.54 (±0.10)	1.0x10^{-5}	8.07 (±0.07)
2.5x10^{-5}	12.11 (±0.05)	2.5x10^{-5}	11.77 (±0.35)
5.0x10^{-5}	17.21 (±0.05)	5.0x10^{-5}	21.99 (±0.29)
7.5x10^{-5}	22.18 (±1.03)	7.5x10^{-5}	37.24 (±0.53)
1.0x10^{-4}	30.21 (±0.14)	1.0x10^{-4}	53.25 (±0.79)

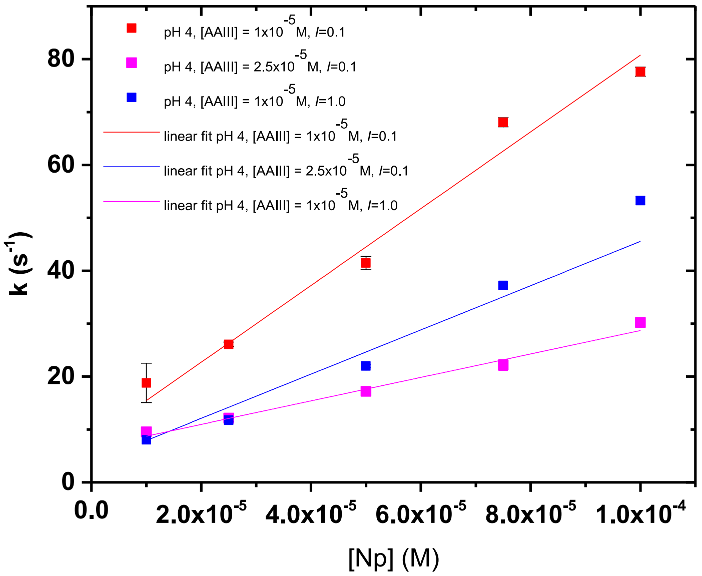


Figure 6. Second order plot of rate constants for Np(V) + AAIII at pH 4 showing effects of variation of ionic strength and [AAIII]. [AAIII] = 2.5x10^{-5} M slope corresponds to a value of (2.22 ± 0.14)x10^5 $M^{-1}s^{-1}$, intercept of 6.52 ± 0.60 with an R^2 of 0.984, *I* = 1.0 slope corresponds to a value of (4.18 ± 0.43)x10^5 $M^{-1}s^{-1}$, intercept of 3.73 ± 0.84 with an R^2 of 0.985.

Finally a data set was measured to identify if there were significant changes by varying the charge on the actinyl ion by studying Np(VI) binding kinetics. The values calculated for the first order rate parameter k (s^{-1}) are shown in Table 5, and Figure 7 compares the second order plots for Np(V) and Np(VI) reaction with AAIII. The calculated second order rate constant for Np(VI) with AAIII was found to be (5.53 ± 0.70) x 10^5 at pH 4 and I=0.1 M.

Table 5. Rate constants for the reaction of Np(VI) + AAIII as a function of Np concentration at pH 4, [AAIII] = $1x10^{-5}$ M and *I*= 0.1 M.

[Np] (M)	k_{obs} (s^{-1})
$1.0x10^{-5}$	11.01 (±0.28)
$2.5x10^{-5}$	21.35 (±0.48)
$5.0x10^{-5}$	41.34 (±0.29)
$7.5x10^{-5}$	48.48 (±0.70)
$1.0x10^{-4}$	59.38 (±0.39)

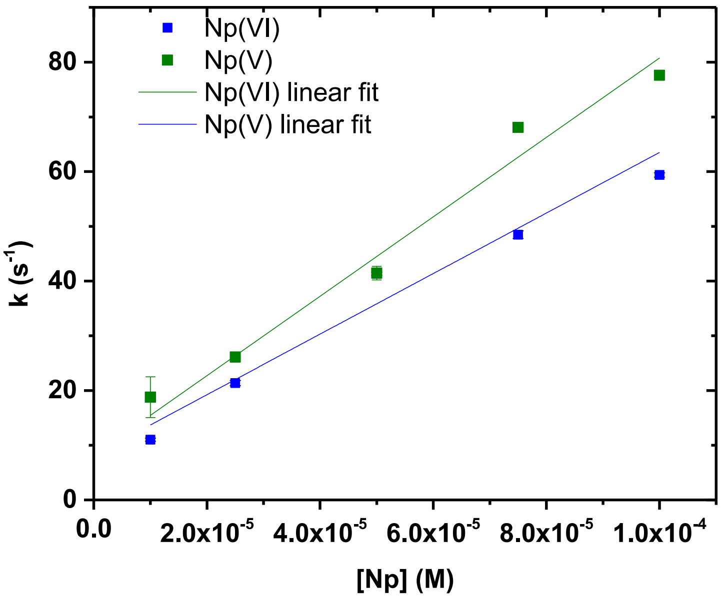


Figure 7. Second order plot of rate constants for Np(V) + AAIII at pH 4 and Np(VI) + AAIII. Np(V) slope corresponds to a value of (7.26 ± 0.51) x 10^5 $M^{-1}s^{-1}$, intercept of 8.19 ± 2.73 with an R^2 of 0.980. Np(VI) slope corresponds to a value of (5.53 ± 0.70) x 10^5 $M^{-1}s^{-1}$, intercept of 8.17 ± 3.80 with an R^2 of 0.939.

4. Discussion

There are some significant differences between the study performed here and that of Fugate et al.,[17] primarily the ionic meda (Fugate used perchlorate not nitrate), however in the instance where our neptunium and AAIII concentrations were similar the 1st order rates obtained were within reasonable agreement see Table 6. Fugate's result was slightly slower, however, the neptunium concentration was lower than that of this study.

Table 6. Comparison of rate parameters for the reaction of Np(V) and AAIII between this study and that of Fugate et al.[17]

Fugate et al.				This Study			
[Np(V)]x10^{-5} (M)	[AAIII]x10^{-5} (M)	T (°C)	k_{obs} (s^{-1})	[Np(V)]x10^{-5} (M)	[AAIII]x10^{-5} (M)	T (°C)	k_{obs} (s^{-1})
2.0	1.0	24.6	22.25 (±0.08)	2.5	1.0	21.0	26.01 (±0.41)

It should be noted that in all experiments the absorbance vs. time plots (see Figure 3 for example) were adequately fit with the first order rate law, which is consistent with prior work with the actinyl ions.[15,17,18,21,22] This is significantly different to the previous work performed under this work package with the lanthanide elements, there the absorbance vs. time plots had to be fit with two exponential functions.[20] As these data can be fit in this manner, under second order conditions, this indicates that the rate determining step is an intramolecular process.[23] The linear dependence of the rate on neptunium concentration is shown in Figures 6-8 for all conditions studied.

It was seen in this study that the reaction rate is influenced by [H$^+$] in solution, increasing the pH was seen to significantly increase the rate of the forward reaction (~2.5 times faster). However, the rate of the reverse (decomplexation) reaction was seen to be little affected by pH within the experimental error. Increasing the AAIII concentration in these experiments appeared to suppress the reaction rate which is consistent with the findings of Fugate et al.[17] When adjusting the ionic strength, the rate of reaction was also seen to decrease for Np(V) complexation. This is found to be the reverse trend observed for investigations of CL-AAIII binding to Np(V). However, those studies were performed in high acid medium and therefore a different binding mechanism may be the explanation for the difference in these two systems. Further investigation is required to assess the true impacts, and possible mechanistic differences, in these systems.

The most significant result from these tests is the comparison of the relative rates of complexation of Np(V) by AAIII with that of Np(VI) and AAIII wherein $k_{Np(V)}/ k_{Np(VI)} = 7.26 \times 10^5\ M^{-1}s^{-1} / 5.53 \times 10^5\ M^{-1}s^{-1} = 1.31$.[17] This difference in relative rates is in contrast to those observed in the prior literature. When such comparisons have been made with U(VI) and Np(V) the hexavalent uranium has always been seen to be greater than those of the Np(V) species in solution. The difference may be due to the strength of the final complex between these two species, however if this is the case this would infer that the strength of the Np(VI)-AAIII complex is significantly weaker than that of the U(VI)-AAIII complex (relative rates analysis for U(VI) vs. Np(VI) = $k_{U(VI)}/ k_{Np(VI)} = 1.69 \times 10^7\ M^{-1}s^{-1} / 5.53 \times 10^5\ M^{-1}s^{-1} = 30.54$).[17] The difference may also lie in comparing the U(VI)-AAIII complex to the Np(V)-AAIII complex as opposed to the Np(V)-AAIII vs Np(VI)-AAIII. Although researchers use actinides of the same valence state interchangeably as surrogates, there is significant evidence in the open literature that these comparisons should be done so with caution. Indeed, this phenomenon warrants further study to identify if there is a trend of decreasing complexation rates across the series it would be prudent to study Pu(VI) in addition.

It is worthy of note that another factor to be considered is the role of acetate. In the uranyl system it has been assumed that this does not interfere with the kinetics of the reaction however, this may not be the case for the neptunyl(VI) system. A more extensive study of the Np(VI)-acetate complexation constants would be required alongside a kinetics study varying the concentration of acetate.

Although good second order rate constants were obtained for most data sets in this study, the errors were higher than expected which was consistent with the Fugate study.[17,18] One source of possible error is that the Np(V) or Np(VI) may be changing oxidation state inbetween the time it is produced to the time that the solution is used in an experiment. In future studies, this uncertainty will be minimized by running UV-vis spectra after the kinetics measurements have been made.

5. Conclusions and Future Direction

The binding kinetics of a chromotropic acid, Arsenazo III, to Np(V) and Np(VI) has been studied under mildly acidic conditions using stopped flow spectrophotometry. For both Np(V) and Np(VI) reactions the absorbance vs time plots were fitted with the simple first order rate law under second order conditions. This is indicative of the rate determining step for the reaction being intramolecular in nature. In the Np(V) system increasing the pH was seen to significantly increase the rate of reaction, however increasing the ionic strength and AAIII concentration led to a decrease in the reaction kinetics.

The Np(VI) system studied displayed slower binding kinetics at pH 4 than that of the Np(V) reaction. This may be due to a weaker complex formation between the Np(VI) and AAIII however further study would be required to confirm this hypothesis. The relative rates analysis between the Np(VI) and U(VI) system reported in the prior literature demonstrated that the U(VI) system is ~30 times faster. It is not clear from the experiments performed if the acetate is interfering with the complexation in the Np(VI) system.

The results presented here begin to identify that complex stability of actinyl systems may be related to the rate of formation of the complex. Further there may be significant differences in the binding kinetics for one valence state as you move across the actinide series. Future experiments are planned to asses these trends across the actinide series, with a more extensive study of ionic strength, pH and acetate dependencies. In addition to these studies, rates of reaction will be measured as a function of temperature to determine the activation energy and entropy of these systems.

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