Tc(IV) COMPLEXATION WITH ORGANIC LIGANDS

BY

MARK ANTONY BOGGS

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
WASHINGTON STATE UNIVERSITY
MAY 2012
To the faculty of Washington State University:

The members of the committee appointed to examine the dissertation of MARK
ANTONY BOGGS find it satisfactory and recommend that it be accepted:

__________________________________________
Nathalie A. Wall, Ph.D., Chair

__________________________________________
Ken Nash, Ph.D.

__________________________________________
Sue Clark, Ph.D.

__________________________________________
Jim Harsh, Ph.D.
Acknowledgement

I would like to first acknowledge my advisor and mentor Professor Nathalie A. Wall. Without her help and guidance none of this work would have been possible. Nathalie has not only had a great influence on my chemistry but on my way of thinking and attitude toward life. I like to think that over the last four years I have matured, and this is greatly due to the help and guidance of Nathalie. Her influence on me will not stop when I leave this institute, and for that I am thankful.

I would also like to thank my committee of Prof. Sue Clark, Prof. Ken Nash, and Prof. Jim Harsh. Each of which have played different, but necessary, roles in my education. I have been able to talk candidly with them whenever the need has arisen. They have treated me with respect, and have always been willing to offer me guidance in research and on how to be a successful scientist. Their guidance has helped me to become the scientist that I am today.

There is absolutely no way that I would be writing this thesis without the help of everyone in the A.E.R. I have benefited greatly from the camaraderie and friendship of everyone in the division, as well as many others outside the division.

Lastly I would have not made it far in school, and life, without the support of my family.
99Technetium poses a difficult problem at multiple Department of Energy sites, where there are currently vast quantities in storage. 99Tc has a half-life of $2.3 \times 10^5$ years, thus it will have to be accounted for a long time. This problem is compounded by past releases of significant amounts of Tc into the environment. At the Hanford Site, Washington state, it is projected that 30 Ci of Tc have been released into the vadose zone, while 30,000 Ci of Tc has been added to underground tanks.

It is known that in the +7 oxidation state Tc is highly mobile in the environment, and can travel at 90% the rate of ground water. Tc can be found, to a lesser extent, in the environment and waste in the +4 oxidation state. Very little is currently known about how this lower oxidation state interacts with organic ligands in the environment, and which may also be found in many of the different waste forms. In particular how these interactions may influence its environmental migration rates.

The interaction of Tc(IV) with the organic ligands acetate and EDTA were determined using solvent extraction. Both ligands formed complexes with Tc(IV), as expected the complexes formed with EDTA were much stronger than those of acetate. Using these findings the solubility of Tc(IV) in the presence of these ligands was modeled. It was
shown that EDTA could cause a two order of magnitude increase in solubility of Tc(IV), which could have a great impact on its environmental mobility.

The interaction of Tc(IV) and a variety of humic substance was determined using a solvent extraction system. Large binding constants were also determined for Tc(IV) with both humic and fulvic acids. In order to include the dynamic nature of humic substances in the complexation of Tc(IV), ultracentrifugation was used to selectively sediment humic acid size fractions. From these studies it was found that, independent of humic acid source, ionic strength, pH, and background electrolyte, there was a constant ratio of Tc(IV) to humic acid. These studies pave the way for future work on the characterization of Tc(IV) interactions in the environment.
# TABLE OF CONTENTS

ACKNOWLEDGEMENT ........................................................................................................................ III

ABSTRACT ........................................................................................................................................ IV

TABLE OF FIGURES .......................................................................................................................... X

TABLE OF TABLES ............................................................................................................................. XIII

CHAPTER 1 ........................................................................................................................................ 1

INTRODUCTION .............................................................................................................................. 1

99\text{Te}chnetium ................................................................................................................................ 1

IV and VII Oxidation States ................................................................................................................ 2

Metal Complexation ............................................................................................................................. 3

Humic Substances and Colloids .......................................................................................................... 6

Scope and Impact of This Research .................................................................................................. 13

Bibliography ....................................................................................................................................... 14

CHAPTERS 2 AND 3 ........................................................................................................................... 25

Preface ............................................................................................................................................... 25

CHAPTER 2 ........................................................................................................................................ 27

Complexation of TC(IV) with Acetate at Varying Ionic Strengths .............................................. 27

Introduction ........................................................................................................................................ 28

Experimental ...................................................................................................................................... 29

Data treatment .................................................................................................................................... 30

Results and Discussion ....................................................................................................................... 32

References .......................................................................................................................................... 34

List of Tables: ..................................................................................................................................... 37
LIST OF FIGURES: .................................................................................................................. 37
Appendix A. Experimental data .......................................................................................... 44

CHAPTER 3 ............................................................................................................................... 48

COMPLEXATION OF TC(IV) WITH EDTA AT VARYING IONIC STRENGTH OF NACl .... 48

ABSTRACT ................................................................................................................................. 48
INTRODUCTION ......................................................................................................................... 49
EXPERIMENTAL ......................................................................................................................... 51
RESULTS AND DISCUSSION ..................................................................................................... 56
ACKNOWLEDGEMENTS ............................................................................................................ 58
REFERENCES ............................................................................................................................ 58
LIST OF TABLES ......................................................................................................................... 63
LIST OF FIGURES ....................................................................................................................... 63

APPENDIX A: EXAMPLES OF SOLVENT EXTRACTION DATA ................................................. 70

CHAPTER 4 ............................................................................................................................... 72

PREFACE .................................................................................................................................. 72

CHAPTER 4 ............................................................................................................................... 73

INTERACTIONS OF TC(IV) WITH HUMIC SUBSTANCES ....................................................... 73

ABSTRACT ................................................................................................................................. 73
INTRODUCTION ........................................................................................................................ 73
EXPERIMENTAL ....................................................................................................................... 76
Humic solution preparations .................................................................................................. 76
Potentiometric titration .......................................................................................................... 77
Solvent extraction .................................................................................................................. 78
Data treatment ....................................................................................................................... 80
PROCEDURE................................................................................................................................. 128
RESULTS AND DISCUSSION ........................................................................................................... 129
REFERENCES .................................................................................................................................. 132
LIST OF TABLES .............................................................................................................................. 135
LIST OF FIGURES ........................................................................................................................... 135

CHAPTER 7 ...................................................................................................................................... 140

CONCLUSIONS ............................................................................................................................... 140
SUMMARY ........................................................................................................................................ 140
FUTURE WORK ................................................................................................................................. 143
REFERENCES .................................................................................................................................. 146

APPENDIX 1 ..................................................................................................................................... 149

APPENDIX 2 ..................................................................................................................................... 154
Table of Figures

Figure 1. List of some fission products, decay energy, yield and activity created during common operation conditions of light water reactors. Adapted from Choppin et. al. \(^2\) .................................................................................................................................................. 20

Figure 2 A: Solubility of Tc(IV) under anoxic conditions in the presence of different organic ligands. ................................................................................................................................. 21

Figure 3 Sedimented particle size as a function of speed at 600, 900, and 3600 seconds, using a Fisher F65L rotor ........................................................................................................................................... 22

Figure 4 Change in charge as function of distance from the surface of a particle........ 23

Figure 5 Work flow diagram for humeomics type humic substance analysis adapted from Nabisco et. al. 2011 ........................................................................................................................................ 24

Figure 6. PHREEQC predicted Tc(IV) species distribution using Table 1 hydrolysis constants at I = 0 in the absence of ligand and assuming total [Tc(IV)] = 10^{-6} M under O_2- and CO_2-free conditions. Total [Tc(IV)] is over-saturated at pH \geq 2 with regard to the solubility of TcO_2 \cdot 1.6 H_2O(s). ..................................................................................................................... 38

Figure 7 Experimental data of (D_0/D-1) as a function of free acetate concentration and its linear regression. (I = 0.5 M (NaCl), 25°C, pCH 4.75 \pm 0.03, and pO_2 = PCO_2 = 0). ..................................................................................................................................... 39

Figure 8 PHREEQC modeled solubility of Tc(IV)O_2 \cdot 1.6 H_2O in presence varying amount
of acetate in the pH range 3.5 - 6.5 using Table 2 reaction constants and the stability constant of TcO(OH)Ac complex obtained in this work at I = 0 M. .................... 40

**Figure 12:** Tc(IV) speciation in the absence of HA. Total Tc concentration is $10^{-7}$ M. Calculations were performed using PHREEQC. (Note that the concentration of the species TcO$^{2+}$ and TcO(OH)$_3^-$ are negligible). ....................................................... 91

**Figure 13:** Tc(IV) speciation in the presence of 20 ppm FRCHA. Total Tc concentration is $10^{-7}$ M. Calculations performed using PHREEQC. (Note that the concentration of the species TcO$^{2+}$, TcO(OH)$^+$, TcO(OH)$_3^-$, and TcO(OH)-Ac are negligible) .... 91

**Figure 14:** Soluble Tc-HA species concentrations as a function of FRCHA concentration. Total Tc concentration is $10^{-7}$ M. Calculations performed using PHREEQC. ...... 91

Figure 15 .................................................................................................................................. 121

Figure 16: Zeta potentials, in mV, for different pH, ionic strength, and humic acid sources after selective sedimentation by ultracentrifugation. Errors are $2\sigma$, and all measurements were performed in at least duplicate .................................................. 122

Figure 17: ATR-FTIR spectra of selected humic acid dry filtrates (0.45 µm) at different pH and ionic strength........................................................................................................... 123

**Figure 15:** Extraction of ca. $2\cdot10^{-7}$ M Tc(VII) from an aqueous phase of 1 mM sodium acetate (pH 3.0) and 1 mM TAPS (pH 8.0) buffers into an organic phase chloroform. Results are from triplicate experiments; errors are reported as $3\sigma$................................. 135

**Figure 16:** Percent Tc Remaining in the Aqueous Phase as a function of pH (0.1 I) with
solubility of Tc(IV) into chloroform: ................................................................. 135

Figure 17: UV-Vis Spectra of 0.02 mM INT in aqueous phase ................................. 135

Figure 15: Extraction of ca. 2·10^{-7} M Tc(VII) from an aqueous phase of 1 mM sodium acetate (pH 3.0) and 1 mM TAPS (pH 8.0) buffers into an organic phase chloroform. Results are from triplicate experiments; errors are reported as 3 sigma........... 136

Figure 16: Percent Tc Remaining in the Aqueous Phase as a function of pH (0.1 I) with 0.8 mM INT; errors are reported as 3σ. The Tc(IV) data is corrected for the small solubility of Tc(IV) into chloroform: ........................................................................ 137

Figure 17: UV-Vis Spectra of 0.02 mM INT in aqueous phase. ............................... 138
Table of Tables

Table 1 Select δ* values for ions in solution, assuming a standard error of ± 128............ 19

Table 2 Selected stability constants for Tc(IV) reactions at zero ionic strength considered in this work ........................................................................................................................................... 41

Table 3 Values necessary for the determination of the Tc complex stability constants and SIT parameters. pcH 4.5 ± 0.2 ........................................................................................................................................... 42

Table 4 Results of experimentally determined log β_{1,1} for Tc(IV) acetate at ionic strengths 0.5-3.0 M (NaCl) and value modeled at zero ionic strength using SIT..... 43

Table 5 EDTA pK_{a}, pK_{w} and data necessary for stability constant calculations ............... 64

Table 6 Selected stability constants for Tc(IV) hydrolysis and interaction with acetate (Ac⁻). ........................................................................................................................................... 65

Table 7 Stability constants for Tc(IV)/[EDTA^{4-}] at ionic strengths 0.5–3.0 M (NaCl) and calculated stability constants at zero ionic strength determined with SIT modeling. Errors are indicated as 2σ of replicate results ................................................................. 66

Table 8. Electrode calibration as a function of the ionic strength (NaCl): V = s pcH + y_0, where V is the electrode potential in mV and pcH is –log[H⁺]. Errors are 2σ of replicates. ........................................................................................................................................... 91

Table 9. Selected Tc(IV) reactions and associated thermodynamic constants at zero ionic strength considered in this work. .................................................................................................................. 91
Table 10. Additional data necessary for $\beta_{1,-1,1}$ calculations. ............................................. 91

Table 11. HS potentiometric titration results and binding constants with $\text{Tc}^4(\text{OH})^+$

$(\log \beta_{1,-1,1})$ and $\text{Tc}^4(\text{OH})_{2}^{0}$ $(\log \beta_{1,-2,1})$. Errors are 2$\sigma$ of replicates ......................... 91

Table 12 Separation of Tc VII/VI oxidation states (0.01 I) with 0.8 mM INT and vary
concations of Tc(VII). Errors are 3$\sigma$ of triplicates. ......................................................... 135

Table 12 Separation of Tc VII/VI oxidation states (0.01 I) with 0.8 mM INT and vary
concations of Tc(VII). Errors are 3$\sigma$ of triplicates. ......................................................... 139

Table 13 Stability constants with various ligands and Tc(IV) at 0.5 I (NaCl). ............... 148
Dedication

This dissertation is dedicated to my father, Kenneth Arthur Boggs

Even though he is no longer with us, he is always by our side to guide us
Chapter 1

INTRODUCTION

**99**-Technetium

Technetium-99 (**99**Tc), a pure beta emitter (E\text{max} = 294 keV)\(^1\), is a major environmental contaminant produced during fission processes (i.e., fission of \(^{235}\)U or \(^{239}\)Pu) in nuclear reactors. For a light water reactor with a burnup of 33,000 MWd/t IHM, after 3 years of cooling \(^{99}\)Tc will constitute 0.77 kg per 5 m\(^3\) of waste\(^2\) (Figure 1). The combination of the large amounts produced and a long half-life (2.13 × 10\(^5\) years) makes \(^{99}\)Tc an important factor in the disposal of nuclear waste, as well as remediation of past nuclear facilities.

\(^{99}\)Tc is of major concern at many Department of Energy (DOE) sites, such as at the Hanford site, in Washington state, where an estimated 30 Ci of technetium has entered the vadose zone and is projected to reach the Columbia River in the future\(^3\). Similar trends in migration have been observed at the Field Research Center at Oak Ridge, Tennessee, where \(^{99}\)Tc can be found in the vadose zone waters at concentrations up to 40,000 pCi/L\(^4\).

These sites also have very large quantities of Tc stored on site that may be at risk of being released into the environment. Furthermore, there is currently no proposed fuel cycle that would not end up with large quantities of \(^{99}\)Tc at the back end. Using current estimates, the Hanford site features an estimated upper value of 30,000 Ci\(^5\) of \(^{99}\)Tc in storage, 50%
of which is held in underground tanks\(^6\); the tank capabilities in containing the nuclear material is questionable and the tank contents characterization difficult to obtain.

**IV and VII Oxidation States**

\(^{99}\)Tc exists predominantly in the VII oxidation state as the highly environmentally mobile pertechnetate anion (TcO\(_4^–\)). Most minerals display anionic surfaces in nature and will have very limited interactions with other anions, such as TcO\(_4^–\). While there have been some laboratory studies that have shown sorption of pertechnetate onto hydrotalcite, or similar minerals, such sorption is usually quite weak and difficult to use in large-scale remediation plans. Sorption onto hydrotalcite has been used to separate \(^{99}\)Tc from multiple matrices but has thus far proven problematic to control. Studies that have shown sorption involved a calcination of hydrotalcite prior to Tc sorption and have not been able to fully address the problem of aqueous anions such as NO\(_3^–\) or ClO\(_4^–\) competition\(^7^8\).

While these methods show promise these minerals are not environmentally abundant, and there are no known field studies using them at this time.

While the VII oxidation state is the predominant state for Tc under reducing conditions it can be found in the IV oxidation state as the sparingly soluble TcO\(_2\cdot\)H\(_2\)O amorphous solid\(^3\). Studies of waste tanks at the Hanford site demonstrated that up to 75% of the Tc waste is not in the VII oxidation state, with the most likely oxidation state being IV\(^9\). In order to understand the mechanism of reduction, samples of Tc(VII) were exposed to conditions that are relevant for nuclear waste storage. It was found that within 3 days a solution of gluconate was able to reduce over 75% of Tc(VII) to the IV oxidation state.
This trend was observed with many other organic carbohydrates, with the majority of these reducing at least 65% of Tc(VII)\textsuperscript{10}.

Other mechanistic studies have been performed to determine if metal catalysts present in the waste lead to Tc(VII) reduction. In these studies it was found that a combination of Rh, Pd, and Pt, likely to be found in the tank waste, lead to reduction of at least 99% of Tc in a short period\textsuperscript{11}. An increase in the rate of reduction was observed when organic ligands such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were added to solution; however NTA leads to less than 10% reduction. The literature does not offer any explanation for this difference, but EDTA would be expected to form a stronger complex with reduced Tc, which may induce greater stabilization of the IV oxidation state.

Further studies of the Hanford wastes noted that the majority of the Tc present is in the aqueous phase\textsuperscript{6}, which is up to 3M in NaOH, despite it being in a reduced oxidation state. This is particularly surprising as the predicted solubility of $\text{TcO}_2\cdot\text{H}_2\text{O}$ is many order of magnitudes lower than what was found in the Hanford waste solutions\textsuperscript{12}. This is a very important finding, as oxidation state, speciation, and chemical form of any Tc released into the environment will have a very large influence on its environmental mobility.

\textbf{Metal Complexation}

Due to the low solubility of the Tc(IV) solids, the IV oxidation state is thought to have rather low environmental migration rates. However complexing ligands can increase Tc(IV) solubility and therefore its mobility. Complexants such as acetate, oxalate, EDTA,
and humic substances are ubiquitous in the environment and/or present in nuclear wastes and very little data currently exists to determine their effect on the solubility and speciation of Tc(IV).

One common way of illustrating the interaction of a complexant, $L^-$, and a metal, $M^+$, is:

$$mM + nH + zL \rightleftharpoons M_{m}H_{n}L_{z} \quad (2)$$

with the stability constant ($\beta$) defined as:

$$\beta_{m,n,z} = \frac{[M_{m}H_{n}L_{z}]}{[M]^m[H]^n[L]^z} \quad (3)$$

where a negative $n$ would indicate a hydroxide. Understanding the nature and the strength of metal-ligand complexes is an important step to determine the fate of radionuclides in the environment, as well as the contaminant speciation that can be expected in specific environments.

Recent studies performed by Felmy et al. present the determination of Tc(IV)/oxalate complex stability constants and the influence of oxalate on Tc(IV) solubility$^{13,14}$. These studies show a large increase in the solubility of Tc(IV) in the presence of oxalate. The logarithm of the stability constant for the formation of the TcOOH-OX species was determined to be $6.66 \pm 0.27$ at zero ionic strength, using Pitzer modeling. The authors also observed an increase in solubility at high pH that could not be explained by the presence of a 1:1 complex – the authors hypothesize that the TcOOH(OX)$_2^{3-}$ or TcO(OH)$_2$OX$^-$ species may be present. The formation of a carbonate species was ruled
out, as recent studies have shown that Tc(IV) does not form complexes with carbonate, even at high pH\textsuperscript{12}. Felmy \textit{et al.} were unable to obtain data that would directly prove any of the speciation assumptions, but experimental data could be modeled without the inclusion of at least one of these complexes. The formation of anionic species is of particular interest to environmental migration of radionuclides, as negatively charged species have higher mobilities, because they do not sorb to negatively charged minerals or interact with organic matter. These studies show that organic ligands can greatly increase the solubility of Tc(IV), and must be taken into consideration in future mobility models.

Experiments carried out by Gu \textit{et al.}\textsuperscript{15} demonstrate a two fold increase in solubility of Tc(IV) after 4 days in the presence of 2.5 mM EDTA, at neutral pH (Figure 2). In these studies the amount of complexed Tc(IV) in solution increased during the first 3 days, before reaching equilibrium. The solubility of Tc(IV) increased over this same time period, but began to decrease as the experiments continued. The decrease in solubility may be due to colloid formation, which would not have been included as part of the solution phase as samples were filtered prior to analysis. The formation of Tc(IV) colloids has been well documented\textsuperscript{16} in the literature. Gu \textit{et al.} studies also show that complexation with EDTA stabilized the IV oxidation state in an oxic environment. Only ca. 20 \% of the Tc(IV) was oxidized back to the VII oxidation state after one week of exposure to oxic conditions. Such work indicates that the complexation of Tc(IV) species with EDTA is not negligible and it will play an important role in planning safe future waste storages, as well as in assessing the potential environmental impact complexants may have in currently contaminated sites in need of remediation. However, little
information is currently available on the quantification of Tc(IV) complexation with EDTA and its effect on Tc(IV) speciation and solubility.

Gu’s studies also highlight the importance of humic substances on metal transport, as humic substances show a similar increase in Tc solubility as was found with EDTA. This is of interest because the increase in Tc solubility due to humic substances is higher than expected, in comparison with EDTA; EDTA habitually form stronger complexes than humic substances do. The humic substances in this study also provided interesting results with respect to their influence on Tc oxidation state stability. After equilibration of Tc(IV) in presence of humic acids (International Humic Substances Society, Elliot Soil Humic Acid) under anoxic conditions, the rate of Tc(IV) oxidation under oxic conditions is faster in presence of the humics than 1) for the control sample that does not contain organic ligand or 2) in sample containing EDTA, which stabilizes the IV oxidation state. This tendency of humics to oxidize Tc(IV) is important from the standpoint of the mobilization of Tc in the environment, as humics can promote the re-oxidation of Tc to the highly mobile VII oxidation state.

**Humic substances and Colloids**

Humic substances are of particular interest due to their strong complexing nature and environmental ubiquity. Humic substances arise from the decomposition of organic matter and are traditionally segregated into three groups: humin, which is insoluble under all conditions; humic acid, which is insoluble at low pH; and fulvic acid which is soluble at all pH. Humic substance’s elemental composition is predominately determined by their place of origin, but primarily consist of 40-60% carbon, 30-50%, oxygen 4-5% hydrogen,
1-4% nitrogen, 1-2% sulfur, and 0-0.3% phosphorus\textsuperscript{17}. In addition to their solubility, the general distinction between humic and fulvic acids is that humic acids are enriched in carbon and somewhat larger in size than fulvic acid. While humin is elementally more similar to humic acid, it is commonly found strongly sorbed to clays and minerals\textsuperscript{18}.

Colloids are entities that are suspended in solution and range roughly from 1nm to 1\textmu m in size, allowing them to remain in suspension. Due to their size being considerably larger than most organic compounds, while still remaining suspended in solution, colloids are often considered to be a “third phase”; not being well characterized by models of solids or aqueous ions alone. Colloids have a much higher surface area than that of other particles and have a greater number of sites capable of interacting with metals. Higher surface area combined with small size allows colloids to allow for the migration of contaminants at high rates in the environment. Humic substances are considered colloids, based on their colloidal-like sizes and while there is a wide range of discrete sites possible for metal binding on a humic molecule, most binding occurs through carboxylic acid groups, prominent on humic materials.

Colloids have long been known to be essential for the mechanisms of transport for a myriad of soil nutrients\textsuperscript{19}. Recent studies, performed at the nuclear test sites in Nevada, have attributed Pu migration, of distances of over 1.5 km from the site of detonation, to colloidal transport\textsuperscript{20,21}. In these studies up to 90% of Cs and 50 % or more for Eu/Pu/Co were found to be associated with colloids, leading to a potential increase in environmental mobility. Large variations in the amount the nuclides associated with different size fractions present simultaneously in solution were observed.
Size distribution of colloids largely dictates the rate of colloidal transport. It is important to note that humic acids can be found over a wide range of sizes simultaneously in solution. Colloids of different sizes have different complexing characteristics and environmental mobilities. Studies performed with size fractionated humic acids and Am$^{3+}$ have shown that the smaller the humic acid size the stronger the interaction with Am$^{3+}$ at the same time, Am$^{3+}$ complexes with small entities are more environmentally mobile. Therefore, it is of great importance to understand how the sizes of humic acids are affected by physical and chemical conditions of specific environments.

The size of the humic acids moieties is a variable parameter that is influenced by a number of solution conditions. pH, will affect the surface charge of humic acids: at high pH, sites are deprotonated at the surface of the particles, thus the surface charge is high and electrostatic repulsions maintain humic acids moieties from increasing in size and coagulating. An increase of the hydrogen ions concentration in solution leads to a decrease of the number of charged surface sites, which limits electrostatic repulsion between particles, allowing for coagulation and eventually precipitation. Studies performed by Alvarez et al. observed a nearly 500% increase in humic acid particle size, when decreasing from pH 9 to 2.

One method that is commonly used to differentiate between sized particles is differential centrifugal sedimentation. A modification of Stokes Law can be used to determine the size of the particle precipitated by velocity and time (Equation 4):

$$D = \sqrt{\frac{18\eta \ln \left(\frac{R_f}{R_0}\right)}{(\rho_p - \rho_f)\omega^2 t}}$$

(Equation 4)
Where D is the diameter of the particle, η is the viscosity of the fluid, ω is the angular velocity of the rotor, ρp is the density of the particle and ρf is the density of the fluid the particle is suspended in. A representation of the application of this is presented in Figure 3.

An increase in particle size is also observed when ionic strength is increased. However, an increase in size also affects the pH at which precipitation occurs, thus lowering the rate of environmental migration. Studies performed by Wall et al. have shown that increasing the charge of electrolytes in solution decreases the stability of humic acid and precipitation will occur at a higher pH. Analogous studies of the dissolution of humic acid, rather than precipitation, have observed similar trends.

Accurate determination of the surface charge is important to monitor humic surface modifications and trends of behavior of humic acids. Because direct measurements of surface potentials are not possible, the zeta potential (ζ) is measured, as illustrated in Figure 4. When a charged particle is introduced into aqueous media, it will influence the surrounding solution, whether the solution is pure water or highly concentrated electrolytes. If this particle was to move through the medium, it would drag along some of the electrolyte particles with it. The point at which the particle no longer has influence on the solution, i.e. Slipping Plane, is where the zeta potential is located. Thus the zeta potential is not defined at an exact distance from the surface of a particle, rather its
located at the Slipping Plane and is based off the influence that the particle has on the solution.

Zeta potentials can be measured by a variety of methods, but recent advancements in laser technology has made Electrophoretic Light Scattering (ELS) the predominant method. Zeta potential measurements by ELS are performed by applying a potential across a capillary containing a solution of charged particles. Upon application of the potential the particles’ rate of migration through the capillary is measured by light scattering. The mobility of the particle can then be related to the zeta potential using Smuluchowski’s equation (Equation 5).

\[
\zeta = \frac{\eta}{\varepsilon_0 \varepsilon_r} U
\]  

(Equation 5)

Where \( \zeta \) is the zeta potential, \( \eta \) is the solution viscosity, \( U \) is the mobility of the particle, and \( \varepsilon_0 \) and \( \varepsilon_r \) are the dielectric constant in vacuum and of the solvent respectively.

Dielectric constants (\( \varepsilon \)) that were not available in the literature\textsuperscript{27} were determined by Equation 6\textsuperscript{28}

\[
\varepsilon = \varepsilon_\omega + 2\delta c
\]  

(Equation 6)

Where \( \varepsilon_\omega \) is the dielectric of water, \( c \) is the concentration of solution in moles per liter, and \( \delta \) is (Equation 7):

\[
\delta = \frac{(\delta^- + \delta^+)}{2}
\]  

(Equation 7)
where \( \delta^- \) and \( \delta^+ \) are contributions from the anion and cation respectively in solution and some examples are shown in Table 1.

Electrophoretic light scattering has some limitations in zeta potential determination due to instrumentation. For example, particles of sizes smaller than 10 nm do not scatter light efficiently and therefore large amounts of such small particles are needed for accurate measurements; additionally, ELS is not suitable for zeta potential determination at high ionic strengths (e.g. 0.5 M NaCl), as joule heating may cause an increase of temperature and create microenvironments of altering diffusion and dielectric constants. Despite these drawbacks, ELS is a powerful method that is finding increasing uses in laboratory studies.

For the environmental transport of Tc via humic acid bindings, it is very important to 1) systematically characterize humic acids as described above, 2) understand humic binding of Tc(IV), 3) accurately predict humic coagulation and zeta potential. To the best of the authors’ knowledge, a model with the ability to accurately understand and interlink these three points is not currently available. There is also a lack of the fundamental knowledge of the differences, if any, between the different size fractions of humic acid. It is not known whether Tc binding with different humic size fractions occurs through the same functional groups, or if sorption into the bulk of the humic acids plays an important role in metal interactions.

Some recent studies have taken a more stepwise approach to the analysis of humic acids, coining the term “humeomics”. Much like many other “-omics”, humeomics uses a wide range of instrumentation and separation techniques to determine the chemical make-up of humic substances. A major publisher in this field is Piccolo et. al., who have
contributed large quantities of data and knowledge to this field of study\textsuperscript{19,30,31}. A work flow chart, by Nabisco \textit{et. al.}\textsuperscript{32}, for the breakdown of humic acid into its subsequent constituents is show in Figure 5.

Nabisco method involves at least 12 steps, at least 6 different techniques and 4 different analytical instruments. Using this method, vast quantities of data can be obtained from a single source of humic substances. While the results from this method are scientifically valid, the method itself may not be practical in most settings. This type of analyses is very time consuming and instrument intensive, and would also need to be performed on a wide variety of sources before the ability to predict traits for different humic acid sources could be obtained. While the major components of humic acids can be determined, this method lacks the ability to elucidate what influence, if any, humic acids would have on complexation and aggregation. These types of studies also appear to make a vast assumption that humic substances can only be understood by looking at their individual building blocks. This has yet to be proven, and this may not be the case at all for the case of metal binding. However, this method, and the ones like it, may be of use to complement humic-metal binding studies, as they can help determine if different size fractions are made of the same fundamental building blocks.

The literature currently lacks a method to simultaneously address humic acid dynamic nature and its binding with metals, although there are many different methods to characterize humic substances. Aside from humeomics, other method to characterize humic substances include potentiometric titrations, CPMAS-NMR, IR, UV-Vis, size exclusion chromatography, etc. Combining multiple methods is essential to gaining a greater understanding of humic substance behaviors towards metals and contaminants. If
there is to be greater knowledge learned from these studies there must also be a more conscientious effort of the researchers to take the conditions in which the experiments are conducted into consideration. For instance, many experiments are conducted under one condition (e.g. ionic strength, pH, concentration humic substances) and no attempt to extend the conclusions to greater relevance is attempted. Not only will conditions in the environment vary, but there is very little continuity in the way that Tc, among other contaminants, is kept in storage. There have also been many different scenarios described for long-term radionuclide storage, whether it be in dense rock or natural salt formations. It is essential to understand how all these conditions will affect radionuclide migration. Thus, it is crucial to find methods and conditions during analysis that are relevant to a wide range of situations.

Scope and impact of this research

The experiments presented in this thesis were designed to help fill in some of the gaps of knowledge mentioned here. Complexation between Tc(IV) and acetate was characterized, which allowed us to build from these studies and use more complex ligands. The complexation of EDTA – a strong complexing ligand – with Tc(IV) was studied to obtain a better understanding of the ligand influence on Tc(IV) solubility and speciation.

The interaction of Tc(IV) and humic substances was also investigated by determining the binding constants of the moieties formed between the metal and the organic molecule, in a similar fashion to those of EDTA and acetate. Finally, in order to fully address the dynamic nature of humic substances, Tc(IV) complexation with humic acid has been
investigated as a function of humic size, size distribution, background electrolyte nature and ionic strength, and humic zeta potential.

Bibliography


**List of Tables and Figures**

**Table 1.** Select δ* values for ions in solution, assuming a standard error of ± 1.28

**Figure 1.** List of some fission products, decay energy, yield and activity created during common operation conditions of light water reactors. Adapted from Choppin et. al.2

**Figure 2.** A: Solubility of Tc(IV) under anoxic conditions in the presence of different organic ligands.

   B: Oxidation over time of Tc(IV) in oxic environment in the presence of different organic ligands. Adopted from Gu. et. al.15

**Figure 3.** Sedimented particle size as a function of speed at 600, 900, and 3600 seconds, using a Fisher F65L rotor.

**Figure 4:** Change in charge, as function of distance, from the surface of a particle.

**Figure 5:** Work flow diagram for humeomics type humic substance analysis adapted from Nabisco et. al. 2011.
<table>
<thead>
<tr>
<th>Ion</th>
<th>$\delta^+$, $\delta^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>-8</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-8</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-24</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>-3</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>-13</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>-7</td>
</tr>
</tbody>
</table>

Table 1 Select $\delta^+$ and $\delta^-$ values for ions in solution, assuming a standard error of $\pm 1^{28}$. 
Figure 1. List of some fission products, decay energy, yield and activity created during common operation conditions of light water reactors. Adapted from Choppin et. al. 

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Energy (MeV)</th>
<th>Yield (%) (^{**})</th>
<th>Activity (TBq/(\ell) U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{79})Se</td>
<td>(&lt;6.5 \times 10^4)</td>
<td>0.1509</td>
<td>0.0443</td>
<td>0.0151</td>
</tr>
<tr>
<td>(^{85})Kr</td>
<td>10.72</td>
<td>0.6874</td>
<td>1.318</td>
<td>183</td>
</tr>
<tr>
<td>(^{87})Rb</td>
<td>(4.8 \times 10^3)</td>
<td>0.2823</td>
<td>2.553</td>
<td>7.7 \times 10^{-7}</td>
</tr>
<tr>
<td>(^{90})Sr \rightarrow (^{90})Y</td>
<td>28.5</td>
<td>0.5463 + 2.2845</td>
<td>5.772</td>
<td>2180</td>
</tr>
<tr>
<td>(^{92})Zr \rightarrow (^{92})Nb</td>
<td>(1.5 \times 10^4)</td>
<td>0.0905</td>
<td>6.375</td>
<td>0.068 + 0.028</td>
</tr>
<tr>
<td>(^{94})Tc</td>
<td>(2.13 \times 10^7)</td>
<td>0.2936</td>
<td>6.074</td>
<td>0.484</td>
</tr>
<tr>
<td>(^{107})Pd</td>
<td>(6.5 \times 10^6)</td>
<td>0.033</td>
<td>0.147</td>
<td>0.0042</td>
</tr>
<tr>
<td>(^{120})Sn \rightarrow (^{120m})Sn</td>
<td>(&lt;1 \times 10^5)</td>
<td>0.368 + 3.670</td>
<td>0.0536</td>
<td>0.029</td>
</tr>
<tr>
<td>(^{129})I</td>
<td>(1.57 \times 10^8)</td>
<td>0.192</td>
<td>0.757</td>
<td>0.0012</td>
</tr>
<tr>
<td>(^{133})Cs</td>
<td>2.002</td>
<td>2.0585</td>
<td>0</td>
<td>201</td>
</tr>
<tr>
<td>(^{135})Cs</td>
<td>(3.0 \times 10^6)</td>
<td>0.205</td>
<td>6.536</td>
<td>0.0098</td>
</tr>
<tr>
<td>(^{137})Cs \rightarrow (^{137m})Ba</td>
<td>30.0</td>
<td>0.5134</td>
<td>6.183</td>
<td>3060</td>
</tr>
<tr>
<td>(^{137})Sn</td>
<td>90</td>
<td>0.0763</td>
<td>0.4196</td>
<td>12</td>
</tr>
<tr>
<td>(^{154})Eu</td>
<td>8.8</td>
<td>1.9689</td>
<td>0</td>
<td>169</td>
</tr>
<tr>
<td>(^{155})Eu</td>
<td>4.96</td>
<td>0.2527</td>
<td>0.0320</td>
<td>59</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Only for the longer lived mother nuclides. \(^{\ddagger}\) Decay energy, not particle energy (see decay schemes).

\(^{**}\) Thermal fission of \(^{235}\)U (fission of \(^{239}\)U, fission of Pu isotopes and \(n,\gamma\)-reactions are important effects in a nuclear reactor).
Figure 2 A: Solubility of Tc(IV) under anoxic conditions in the presence of different organic ligands.

B: Oxidation over time of Tc(IV) in oxic environment in the presence of different organic ligands. Adapted from Gu. et. al.
Figure 3 Sedimented particle size as a function of speed at 600, 900, and 3600 seconds, using a Fisher F65L rotor.
Figure 4 Change in charge as function of distance from the surface of a particle.
Figure 5 Work flow diagram for humeomics type humic substance analysis adapted from Nabisco et. al. 2011
Chapters 2 and 3

PREFACE

This introductory project was designed as a first step to determine the stability constant of Tc(IV) with acetate, as well as a stepping stone to further studies with more complicated systems. At the onset of these studies little information was available for complexation of Tc(IV), including thermodynamic constants, complexation constants, as well as sparse experimental details in the literature. While acetate is an important complexant in the environment and many waste forms, it is also a useful buffer, and characterization of its interaction with Tc(IV) was necessary for many of the studies that were conducted after this one.

Chapter 2 focuses on the use of a solvent extraction system to quantify the interaction of acetate with Tc(IV), specifically the TcOOH$^+$ species. While the complexation between these two species was not exceptionally strong ($\log \beta_{1.1,1} = 2.8 \pm 0.16$), we were able to show proof of concept for further studies of Tc(IV) complexation. This paper is shown in the final manuscript form that was published in the journal Radiochimica Acta in 2010, and is included in its published form in Appendix 1.

Chapter 3 represents the results obtained for Tc(IV) complexation with EDTA. It represents a separate journal article submitted to Radiochimica Acta, which is currently under review. As EDTA is a much stronger complexant than acetate, this would allow us to get a better idea at how strong Tc(IV) could bind to organic complexants. In order to examine all possible complexes, studies were performed at pH 4.5, as well as pH 7. This allowed us to study solution conditions were TcOOH$^+$ and TcO(OH)$_2$ were predominate species respectively.
The stability constants of the Tc(IV) EDTA complexes were many order of magnitudes higher than those for acetate, and were in agreement with those determined for other transition metals. Modeling of the solubility of Tc(IV), in the presence of EDTA highlights the importance of this work, as a two fold increase in solubility was observed. The modeled solubility is also in agreement with experimental results obtained by Gu. et. al.
Experimental

All solutions were prepared from reagent-grade chemicals in de-ionized distilled water (DDIW). NaCl (Fisher) solutions were used as a background electrolyte to control the ionic strength, from 0.5 to 3.0 M, in all experiments. Sodium acetate (0.5 M Fisher) solutions were prepared at appropriate ionic strengths. NaCl and sodium acetate solutions were filtered over 0.22 μm pore size Nalgene filters. A 0.1 M Bis-(2-Ethylhexyl) phosphoric acid (HDEHP) (Sigma-Aldrich) in hexane (Fisher) solution, used as the organic phase for all extractions, was shielded from light for the duration of the experiments. A Tc(IV) stock solution was prepared according to Hess et al., (8). Briefly, an aliquot of 0.29 M NH₄TcO₄ (Oak Ridge) was added to water and freshly prepared 0.195 M Na₂S₂O₄ (Mallinckrodt); the solution pH was raised to 12 to form a TcO₂·xH₂O(am) black slurry, which was then washed three times with 0.01 M Na₂S₂O₄. The Tc(IV) precipitate was separated by centrifugation, after a 72 h equilibration period, and dissolved in concentrated HCl (Fisher). The Tc(IV) stock solution was authenticated using an Ocean Optics USB4000 UV-Vis spectrometer, showing the TcCl₆²⁻ peak (8). An aliquot of this solution was diluted to obtain 4000 cpm per 20 μl, in 1 M HCl. Tc reduction and all subsequent experiments were performed in an oxygen-free glove box (< 1ppm O₂(g)), to maintain Tc in its reduced form. Solvent extraction experiments were performed by vigorously shaking 1.5 mL of NaCl solutions with varying amounts of acetate, 4000 cpm Tc(IV) and at pH adjusted to 4.5 (± 0.2), with equal volume of the 0.1 M HDEHP solution for at least 4 h. All experiments were conducted at room temperature (25 ± 1°C). 1.0 mL aliquots were drawn from each phase and diluted with Eco-scint cocktail for liquid scintillation counting (LSC) (Beckman Coulter LS6500 liquid scintillation counter). Each aqueous phase pH was measured using a Denver Instruments combination glass electrode and a Thermo-Fisher pH-meter. The electrode was calibrated daily.
with pH 4.01 and 7.00 buffers (Fisher) and the pH-meter readings (i.e. pHr) were converted to pcH values (i.e. \(-\log[H^+]\)) by the following equation, determined as explained elsewhere (9,10):

\[
\text{pcH} - \text{pHr} = 0.30 \cdot I + 0.04
\]

(1)

where I is the ionic strength in M (NaCl)

Additionally, aliquots of the aqueous phase of selected samples were equilibrated with 0.001M methyltriocytammonium bromide in methylene chloride, which has been shown to extract Tc(VII) anionic species only, not Tc(IV) cationic species (11). Results showed that Tc(IV) did not oxidize to Tc(VII) over the course of the experiments.

**Data treatment**

The metal-ligand complexation reactions are generally described as (charges omitted for simplicity):

\[
mM + nH + zL = M_mH_nL_z
\]

(2)

with the stability constant defined as:

\[
\beta_{m,n,z} = \frac{[M_mH_nL_z]}{[M]^m[H]^n[L]^z}
\]

(3)

where a negative n value indicates a hydroxo species. For the solvent extraction system in question the distribution ratio (D) is defined as:

\[
D = \frac{\Sigma[M_{org}]}{\Sigma[M_{aq}]}
\]

(4)

Labeling \(D_0\) as the distribution of metal without ligand, using known stability constants for the metal hydrolysis, considering the formation of only one ML complex, and the absence of CO\(_2(g)\) or any buffer in the system, Eq.(4) becomes:
\[
\frac{D_0}{D-1} = \beta_{ML} \cdot [L] \cdot (1 + ^{+OH}\beta_1 \cdot [OH] + ^{+OH}\beta_2 \cdot [OH]^2 \ldots) \tag{5}
\]

With, in the case of a monoprotic acid:

\[
[L]_T = [L]_T/(1+10^{(pK_a-pH)}) \tag{6}
\]

And \[ ^{+OH}\beta_1 = [MOH]/([M] \cdot [OH]) \tag{7} \]

\[ ^{+OH}\beta_2 = [M(OH)_2]/([M] \cdot [OH]^2) \tag{8} \]

In the particular case of our work, the experiments were performed at pH 4.50 ± 0.2. TcOOH\(^+\) and TcO(OH)\(_2\) are the only species present at such pH, as shown on Figure 6. TcO\(^2+\) is negligible. As a result, in the case of the formation of one MOHL complex, Eq.(5) is modified:

\[
\frac{D_0}{D-1} = \beta_{TcOOHAc} \cdot [Ac^-]/(1 + ^{+OH}\beta_1 \cdot [OH]) \tag{9}
\]

with \[ ^{+OH}\beta_1 = [TcO(OH)_2]/([TcOOH\(^+\)] \cdot [OH]) \tag{10} \]

Eq. (9) shows that \( \beta_{TcOOHAc} \) values can be determined from the linear plot of \( \frac{D_0}{D-1} \) as a function of [Ac\(^-\)], which slope is \( \beta_{TcOOHAc}/(1 + ^{+OH}\beta_1 \cdot [OH^-]) \). Values of acetic acid pK\(_a\) and pK\(_w\) at specific ionic strength are presented in Table 3. The value of \( ^{+OH}\beta_1 \) \(^0\) (i.e. at zero ionic strength) was used for all calculations, because of the lack of information currently available for the determination of this parameter at higher ionic strengths; its value, calculated from Table 2 and Table 3 data, is \( 10^{10.01} \).

Specific Ion Interaction Theory (SIT) (12) was used to determine the stability constant of the TcOOHAc complex at zero ionic strength, from the experimental data obtained within the 0.5-3.0 M ionic strength range. SIT modeling is expressed in the following way:

\[
\log\beta^{0}_{1.11} = \log\beta_{1.11} - \Delta Z^2 D + \Delta \varepsilon \cdot I_m \tag{11}
\]
where \( I_m \) is the ionic strength expressed in molality. The stability constant of the TcOOHAc complex at zero ionic strength is log\( \beta^o_{1,11} \) and log\( \beta_{1,11} \) is the experimental stability constants at a non-zero ionic strength. \( \Delta Z^2 \) is relative to the change in charge from the uncomplexed to complexed metal ligand couple and is defined as:

\[
\Delta Z^2 = (Z_{MHL})^2 + Z_H^2 - Z_M^2 - Z_L^2
\]

(12)

And D is the Debye-Hückle term with A and aB defined as 0.509 kg\(^{1/2}\)·mol\(^{1/2}\) and 1.5 kg\(^{1/2}\)·mol\(^{1/2}\), respectively (3):

\[
D = A \cdot I_m^{1/2} / (1 + aB \cdot I_m^{1/2})
\]

(13)

The term \( \Delta \varepsilon \) is the ion interaction parameter for the cation anion pair in question; it is mostly independent of the ionic strength (15). The stability constant of the TcOOHAc complex at zero ionic strength is extrapolated from the fitting of the plot of \{log\( \beta_{1,11} \) - \( \Delta Z^2 D \)\} as a function of \( I_m \).

Predicted aqueous speciation and solubility were calculated from the SIT data using the publicly available geochemical equilibrium speciation code PHREEQC (16).

**Results and discussion**

Figure 7 shows an example of a \( D_0 / D - 1 \) as a function of [Ac\(^-\)], for the system at 0.5 M (NaCl) ionic strength and pcH 4.75 ± 0.03. The linear regression of the plot indicates the presence of a single TcOOHAc complex; supplementary experiments performed at pH 6.5 showed no complexation between TcO(OH)\(_2\) and acetate. Table A1 of Appendix A presents data obtained for each ionic strength studied, 0.5 M, 1.0 M, 1.5 M, 2.0 M, 2.5 M, and 3.0 M; only one set of data is presented for each ionic strength, for conciseness, but the experiments were performed in triplicate. Table 4 Results of experimentally determined log \( \beta_{1,11} \) for Tc(IV) acetate at ionic strengths 0.5-3.0 M (NaCl) and value modeled at zero ionic strength using SIT shows that the
TcOOHAc complex stability constant varies from 2.46 (± 0.03) to 3.09 (± 0.08), from 0.5 M to 3.0 M ionic strength, respectively. The value of logβ⁰₁₋₁₁ was determined to be 2.8 ± 0.16 with Δε at -0.28 ± 0.08.

As previously mentioned, the value of OH⁻ was used for all calculations, because tools are not yet available to calculate it at non-zero ionic strength. While stability constants vary with ionic strength, this does not significantly alter our final calculations, in this case. For instance, the first and second hydrolysis of UO₂²⁺ stability constants decreases by only 3% and 1%, with experimental error respectively.
Acknowledgement. This work was supported by the Office of the Biological and Environmental Research, Office of Science, US Department of Energy under the grant DE-FG02-08ER64696 with Washington State University and under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, which is managed by UT-Battelle LLC.

References


8. Hess, N. J., Xia, Y., Rai D.: Thermodynamic Model of the Solubility of TcO$_2$·xH$_2$O$_{am}$ in the


List of Tables:

Table 2. Selected stability constants for Tc(IV) reactions at zero ionic strength considered in this work.

Table 3. Values necessary for the determination of the Tc complex stability constants and SIT parameters. pcH 4.5 ± 0.2.

Table 4. Results of experimentally determined log $\beta_{1,-1,1}$ for Tc(IV) acetate at ionic strengths 0.5-3.0 M (NaCl) and value modeled at zero ionic strength using SIT.

List of Figures:

Figure 6. PHREEQC predicted Tc(IV) species distribution using Table 1 hydrolysis constants at I = 0 in the absence of ligand and assuming total [Tc(IV)] = $10^{-6}$ M under O$_2$- and CO$_2$-free conditions. Total [Tc(IV)] is over-saturated at pH ≥ 2 with regard to the solubility of TcO$_2$·1.6 H$_2$O(s).

Figure 7. Experimental data of ($D_0$/D-1) as a function of free acetate concentration and its linear regression. (I = 0.5 M (NaCl), 25°C, pcH 4.75 ± 0.03 , and pO$_2$ = pCO$_2$ = 0).

Figure 8. PHREEQC modeled solubility of Tc(IV)O$_2$·1.6 H$_2$O in presence varying amount of acetate in the pH range 3.5 - 6.5 using Table 1 reaction constants and the stability constant of TcO(OH)Ac complex obtained in this work at I = 0 M.
Figure 6. PHREEQC predicted Tc(IV) species distribution using Table 1 hydrolysis constants at $I = 0$ in the absence of ligand and assuming total $[\text{Tc(IV)}] = 10^{-6}$ M under $O_2$- and $CO_2$-free conditions. Total $[\text{Tc(IV)}]$ is over-saturated at $pH \geq 2$ with regard to the solubility of $\text{TcO}_2 \cdot 1.6 \text{H}_2\text{O(s)}$. 
Table 2 Selected stability constants for Tc(IV) reactions at zero ionic strength considered in this work

<table>
<thead>
<tr>
<th>Reactions</th>
<th>log K&lt;sup&gt;0&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TcO&lt;sup&gt;2+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O = TcOOH&lt;sup&gt;+&lt;/sup&gt; + H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.0072</td>
<td>8</td>
</tr>
<tr>
<td>TcOOH&lt;sup&gt;+&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O = TcO(OH)&lt;sub&gt;2&lt;/sub&gt; + H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-4.00</td>
<td>12</td>
</tr>
<tr>
<td>TcO(OH)&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O = TcO(OH)&lt;sub&gt;3&lt;/sub&gt; + H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>-14.9</td>
<td>12</td>
</tr>
<tr>
<td>TcO&lt;sub&gt;2&lt;/sub&gt;·1.6 H&lt;sub&gt;2&lt;/sub&gt;O (s) = TcO(OH)&lt;sub&gt;2&lt;/sub&gt; + 1.6 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-8.4 ± 0.5</td>
<td>12</td>
</tr>
<tr>
<td>I (m)</td>
<td>pKw&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Acetate pK&lt;sub&gt;a&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>0.51</td>
<td>13.72</td>
<td>4.50</td>
</tr>
<tr>
<td>1.02</td>
<td>13.70</td>
<td>4.52</td>
</tr>
<tr>
<td>1.55</td>
<td>13.74</td>
<td>4.60</td>
</tr>
<tr>
<td>2.09</td>
<td>13.78</td>
<td>4.65</td>
</tr>
<tr>
<td>2.65</td>
<td>13.86</td>
<td>4.73</td>
</tr>
<tr>
<td>3.20</td>
<td>13.93</td>
<td>4.96</td>
</tr>
</tbody>
</table>

<sup>a</sup>ref. (13)

<sup>b</sup>ref.(14)

Table 3 Values necessary for the determination of the Tc complex stability constants and SIT parameters. pH 4.5 ± 0.2.
<table>
<thead>
<tr>
<th>$I_m$</th>
<th>$p$cH</th>
<th>$\log \beta_{1,-1,1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.5 ± 0.2</td>
<td>2.8 ± 0.16</td>
</tr>
<tr>
<td>0.51</td>
<td>4.75 ± 0.04</td>
<td>2.46 ± 0.03</td>
</tr>
<tr>
<td>1.02</td>
<td>4.59 ± 0.05</td>
<td>2.66 ± 0.06</td>
</tr>
<tr>
<td>1.55</td>
<td>4.57 ± 0.05</td>
<td>2.81 ± 0.08</td>
</tr>
<tr>
<td>2.09</td>
<td>4.77 ± 0.08</td>
<td>2.84 ± 0.05</td>
</tr>
<tr>
<td>2.65</td>
<td>4.67 ± 0.07</td>
<td>2.98 ± 0.09</td>
</tr>
<tr>
<td>3.20</td>
<td>4.80 ± 0.05</td>
<td>3.09 ± 0.08</td>
</tr>
</tbody>
</table>

Table 4 Results of experimentally determined $\log \beta_{1,-1,1}$ for Tc(IV) acetate at ionic strengths 0.5-3.0 M (NaCl) and value modeled at zero ionic strength using SIT
Appendix A. Experimental data

Table A1. Examples of distribution data for Tc(IV) acetate extraction (0.1M HDEHP) experiments.

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>$[\text{Ac}]_{\text{total}}$(M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I=0.5 M (NaCl)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>526</td>
<td>671</td>
<td>0.391</td>
<td>0.0183</td>
<td>4.78</td>
</tr>
<tr>
<td>551</td>
<td>758</td>
<td>0.363</td>
<td>0.0217</td>
<td>4.74</td>
</tr>
<tr>
<td>609</td>
<td>675</td>
<td>0.451</td>
<td>0.00667</td>
<td>4.93</td>
</tr>
<tr>
<td>674</td>
<td>802</td>
<td>0.420</td>
<td>0.0133</td>
<td>4.84</td>
</tr>
<tr>
<td>559</td>
<td>716</td>
<td>0.390</td>
<td>0.02</td>
<td>4.92</td>
</tr>
<tr>
<td>549</td>
<td>767</td>
<td>0.357</td>
<td>0.0267</td>
<td>4.92</td>
</tr>
<tr>
<td>494</td>
<td>741</td>
<td>0.333</td>
<td>0.033</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>I=1.0 M (NaCl)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>619</td>
<td>1171</td>
<td>0.528</td>
<td>0.0216</td>
<td>4.57</td>
</tr>
<tr>
<td>904</td>
<td>987</td>
<td>0.915</td>
<td>0.005</td>
<td>4.57</td>
</tr>
<tr>
<td>827</td>
<td>1104</td>
<td>0.749</td>
<td>0.00833</td>
<td>4.58</td>
</tr>
<tr>
<td>712</td>
<td>1030</td>
<td>0.691</td>
<td>0.0116</td>
<td>4.5</td>
</tr>
<tr>
<td>Organic (cpm)</td>
<td>Aqueous (cpm)</td>
<td>D</td>
<td>$[Ac]_{\text{total}}$ (M)</td>
<td>pcH</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>-----</td>
<td>--------------------------</td>
<td>-----</td>
</tr>
<tr>
<td><strong>I = 1.5 M (NaCl)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>619</td>
<td>1171</td>
<td>0.528</td>
<td>0.021</td>
<td>4.57</td>
</tr>
<tr>
<td>904</td>
<td>987</td>
<td>0.915</td>
<td>0.005</td>
<td>4.57</td>
</tr>
<tr>
<td>827</td>
<td>1104</td>
<td>0.749</td>
<td>0.0083</td>
<td>4.58</td>
</tr>
<tr>
<td>712</td>
<td>1030</td>
<td>0.691</td>
<td>0.0116</td>
<td>4.5</td>
</tr>
<tr>
<td>713</td>
<td>1120</td>
<td>0.636</td>
<td>0.015</td>
<td>4.48</td>
</tr>
<tr>
<td>728</td>
<td>1084</td>
<td>0.671</td>
<td>0.0166</td>
<td>4.59</td>
</tr>
<tr>
<td>634</td>
<td>1159</td>
<td>0.547</td>
<td>0.0183</td>
<td>4.7</td>
</tr>
<tr>
<td>610</td>
<td>1144</td>
<td>0.533</td>
<td>0.0216</td>
<td>4.59</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>$[Ac]_{\text{total}}$ (M)</th>
<th>pcH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I = 2.0 M (NaCl)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic (cpm)</td>
<td>Aqueous (cpm)</td>
<td>D</td>
<td>[Ac]_{total}(M)</td>
<td>pcH</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>------</td>
<td>----------------</td>
<td>-----</td>
</tr>
<tr>
<td>585</td>
<td>844</td>
<td>0.693</td>
<td>0.005</td>
<td>4.56</td>
</tr>
<tr>
<td>518</td>
<td>879</td>
<td>0.589</td>
<td>0.0083</td>
<td>4.63</td>
</tr>
<tr>
<td>448</td>
<td>806</td>
<td>0.555</td>
<td>0.015</td>
<td>4.48</td>
</tr>
<tr>
<td>466</td>
<td>875</td>
<td>0.532</td>
<td>0.018</td>
<td>4.57</td>
</tr>
<tr>
<td>441</td>
<td>847</td>
<td>0.520</td>
<td>0.01</td>
<td>4.57</td>
</tr>
<tr>
<td>438</td>
<td>853</td>
<td>0.513</td>
<td>0.016</td>
<td>4.58</td>
</tr>
<tr>
<td>400</td>
<td>935</td>
<td>0.427</td>
<td>0.023</td>
<td>4.54</td>
</tr>
<tr>
<td>380</td>
<td>920</td>
<td>0.413</td>
<td>0.03</td>
<td>4.55</td>
</tr>
<tr>
<td>372</td>
<td>924</td>
<td>0.402</td>
<td>0.033</td>
<td>4.5</td>
</tr>
<tr>
<td>356</td>
<td>883</td>
<td>0.403</td>
<td>0.036</td>
<td>4.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[Ac]_{total}(M)</th>
<th>pcH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 2.5 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>707</td>
<td>0.707</td>
<td>0.005</td>
<td>4.89</td>
</tr>
<tr>
<td>625</td>
<td>838</td>
<td>0.745</td>
<td>0.0083</td>
<td>4.88</td>
</tr>
<tr>
<td>502</td>
<td>761</td>
<td>0.659</td>
<td>0.011</td>
<td>4.85</td>
</tr>
<tr>
<td>435</td>
<td>826</td>
<td>0.526</td>
<td>0.018</td>
<td>4.83</td>
</tr>
<tr>
<td>Organic (cpm)</td>
<td>Aqueous (cpm)</td>
<td>D</td>
<td>[Ac]_{total} (M)</td>
<td>pcH</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>-----</td>
<td>------------------</td>
<td>-----</td>
</tr>
<tr>
<td>I = 3.0 M (NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>634</td>
<td>939</td>
<td>0.675</td>
<td>0.005</td>
<td>4.79</td>
</tr>
<tr>
<td>563</td>
<td>1017</td>
<td>0.553</td>
<td>0.00833</td>
<td>4.72</td>
</tr>
<tr>
<td>572</td>
<td>1112</td>
<td>0.514</td>
<td>0.0116</td>
<td>4.79</td>
</tr>
<tr>
<td>519</td>
<td>1152</td>
<td>0.450</td>
<td>0.015</td>
<td>4.76</td>
</tr>
<tr>
<td>545</td>
<td>1140</td>
<td>0.478</td>
<td>0.0166</td>
<td>4.81</td>
</tr>
<tr>
<td>517</td>
<td>1224</td>
<td>0.422</td>
<td>0.0183</td>
<td>4.86</td>
</tr>
<tr>
<td>378</td>
<td>1220</td>
<td>0.309</td>
<td>0.025</td>
<td>4.86</td>
</tr>
</tbody>
</table>
Introduction

Technetium-99 ($^{99}$Tc), a pure beta emitter ($E_{\text{max}} = 294$ keV) [1], is a major environmental contaminant produced during fission processes in nuclear reactors. For a light water reactor with a burnup of 33,000 MWday per ton of initially present heavy metals, $^{99}$Tc will constitute 0.77 kg per $5\text{m}^3$ of waste after 3 years of cooling time [2]. The combination of the large amounts produced and long half-life ($2.13 \times 10^5$ years) makes $^{99}$Tc an important factor for the disposal of nuclear wastes, as well as for remediation of past nuclear facilities. For example, an estimated 500 Ci of Tc has been released into the vadose zone at the Hanford Site in Washington state [3]; and Tc concentrations can be found as high as 95 pCi/g and 31,000 pCi/L in sediments and groundwater, respectively, at the Field Research Center at Oak Ridge, Tennessee [4].

The environmental behavior of Tc is controlled by chemistry of soils, sediments, water and biological activity. Tc exists predominately in valence states VII and IV, under oxidizing and reducing conditions, respectively. Dissolved Tc can be present as the aqueous Tc(VII) oxyanionic species $\text{TcO}_4^{-}$ in oxic systems, having non-adsorptive properties and high solubility under most solution conditions. For these reasons, Tc(VII) concentration in the vadose zone and groundwater is not limited by adsorption or solubility processes, but displays a high mobility in oxic environments. Under reducing conditions, Tc can be found as Tc(IV), which form sparingly soluble species [5] and able to sorb onto mineral surfaces [6]. As a result, Tc(IV) is thought to be relatively immobile, in reducing subsurface environments [7].

Nuclear fuel production facilities, such as those at Hanford and Oak Ridge, have generated large amounts of highly radioactive, non-radioactive, and hazardous waste. About 50% of the radioactive waste is confined in underground storage tanks and contain large quantities of various inorganic compounds, chelating agents (e.g. ethylenediamine tetraacetic acid (EDTA),
citric acid, oxalic acid), and organic solvents [8, 9]. Some of the organic ligands present in the tanks have been shown to form stable soluble complexes with radioactive contaminants [10-12], which is significant for the standpoint of the performance assessment of long term radioactive disposals – in particular, minute quantity of EDTA (e.g. < 1 mg/L) can enhance metal migration processes [12, 13].

Recent studies have shown that up to 75% of Tc waste currently in storage under high pH (> 2 M NaOH) at Hanford, can be found in an oxidation state lower than VII [9]. This is of particular importance as these lower oxidation states – generally considered insoluble – were found to exist under a wide range of solution conditions, predominantly in the aqueous phase, and as stable moieties [14]. The specific mechanism for increased Tc solubility has yet to be determined, but is likely associated with reduction followed by complexation with organic ligands (e.g. gluconate, EDTA). This explanation for the increase in solubility agrees with published complexation studies, as Tc(IV) was shown to form soluble complexes with oxalic acid [15], acetate [16], and humic substances [17].

In fact, experiments carried out by Gu et al. [18] demonstrated an increase in solubility of Tc(IV)(s) from 1.5x10^{-7} to 2.5x10^{-7} M after 4 days in the presence of 2.5 mM EDTA and at neutral pH. In these studies the amount of complexed Tc(IV) in solution remained constant after about 3 days, while the solubility of the free Tc(IV) decreased over time. This is likely due to the formation of insoluble Tc(IV) colloids, as have been previously documented [19, 20]. Gu et al. studies also show that complexation with EDTA actually stabilized the IV oxidation state in oxic environment, with only ~20 % being oxidized to Tc(VII) after one week, after a change from anoxic to oxic conditions. Such work indicates that the complexation of Tc(IV) species with EDTA cannot be neglected, as it will play an important role in planning safe future waste
storages, as well as in assessing the potential environmental impact these complexes may have on contaminated sites in need of remediation. However, little information is currently available on the quantification of Tc(IV) complexation with EDTA and its effect on Tc(IV) speciation and solubility. This study describes the experimental data and modeling work conducted to determine the stability constants of Tc(IV)/EDTA complexes at pH 4.5 and 6.5 and at varying ionic strengths, using a solvent extraction method and PHREEQC calculations.

**Experimental**

All solutions were made from reagent grade chemicals using de-ionized distilled water (DDIW) for aqueous solutions or hexane for organic phases. Electrolyte solutions were prepared by dissolving NaCl (Fisher) to the desired ionic strengths, with 10 mM 2-(N-morpholino)ethanesulfonic acid (MES) or sodium acetate (Fisher), and adjusting to pH at 6.5 and 4.5, respectively. All aqueous solutions were filtered using 0.22 μm pore size Nalgene filters. Stock solutions of 0.1 M EDTA solutions at desired ionic strength were prepared from Na₂EDTA·H₂O (Fisher), without further purification or filtration. Organic phases of all extractions performed at pH 6.5 were 0.05 M Tri-n-octylphosphine oxide (TOPO, Acros 99 %) and 0.05 M Cyanex 272 (Cytec Industries) in hexane (Fisher). Extractions at pH 4.5 were performed with organic phases of 0.1 M bis(2-ethylhexyl) phosphoric acid (HDEHP) (Sigma Aldrich 99%) in hexane (Fisher). Solutions of freshly prepared 1 mM iodonitrotetrazolium chloride (INT) in chloroform were used to determine oxidation state pre- and post-extraction [21]. All organic solutions were stored in the dark for the duration of experiments.

Tc(IV) was prepared according to Hess *et al.* [22] and Boggs *et al.* [16] using a 0.29 M NH₄TcO₄ (Oak Ridge) stock solution. The resulting Tc(IV) precipitate was dissolved in concentrated HCl (Fisher) and aliquots were used to prepare a working solution of ca. 4000 cpm/20 μl. The Tc(IV)
stock solution was confirmed using an Ocean Optics USB4000 UV-Vis spectrometer, indicating the \( \text{TcCl}_6^{2-} \) peak [22]. The reduction of Tc(VII) and all subsequent experiments were conducted in an oxygen-free glove box (< 1 ppm \( \text{O}_2 \) (g), \( \text{N}_2 \) 99.999%) to maintain Tc in its reduced state. Experiments were carried out by vigorously shaking 1.5 mL of aqueous solutions of varying concentrations of EDTA and ca. 1700 cpm Tc(IV) with equal volume of organic solution for at least 24 hours, as EDTA/Tc(IV) complexes have been shown to have relatively slow rates of formation [23]. All experiments were conducted at room temperature (25 ± 1°C). Upon equilibration, 0.75 mL aliquots were drawn from each phase (organic and aqueous), for liquid scintillation counting, while pH of aqueous phases were measured using a Denver Instruments combination of glass electrode combined to a Thermo-Fisher pH-meter. The electrode was calibrated on a daily basis with pH 4.01 and 7.00 buffers (Fisher). All experiments were carried out with one electrode, calibrated at each ionic strength, following the procedure previously described [24]; the reading (\( i.e. \) pHr) can be converted to \(-\log[\text{H}^+]\) values (\( i.e. \) pcH) using the equation:

\[
\text{pcH} - \text{pHr} = 0.28 \cdot I + 0.03
\]

where \( I \) indicates the ionic strength in M (NaCl).

To ensure that Tc(IV) did not oxidize to Tc(VII) during the course of the experiments, selected aqueous solutions were back-extracted, using INT in chloroform [21]. Analysis showed that there was no observed oxidation of Tc(IV) under all experimental conditions. This is also in agreement with previous studies of this author [18].

Metal-ligand complexation reactions can be expressed as (omitting charges for simplification):

\[
m \text{M} + n \text{H} + z \text{L} \leftrightarrow M_{n}H_{n}L_{z}
\]
with the stability constant defined as:

$$\beta_{m,n,z} = \frac{[M_mH_nL_z]}{([M]^m[H]^n[L]^z)}$$  \hspace{1cm} (3)$$

where a negative $n$ value is indicative of a hydroxo species.

With respect to the solvent extraction system, the distribution ratio ($D$) of Tc(IV) between the phases is defined as:

$$D = \frac{\sum [Tc]_{org}}{\sum [Tc]_{aq}}$$  \hspace{1cm} (4)$$

where $\sum [Tc]_{org}$ and $\sum [Tc]_{aq}$ are the sum of Tc(IV) species concentrations in the organic and aqueous phases, respectively; the distribution of metal in absence of ligand labeled as $D_0$. In this work, the concentration of free ligand, [EDTA$^{4-}$], was calculated using previously published pKa values [25, 26] and presented with Table 5. Tc(IV) hydrolysis stability constants were also published [5, 27] and shown with Table 6; we define the following terminology for the hydrolysis:

$$\beta_{1,-1,0} = \frac{[TcOOH^+]}{[TcO^{2+}][OH^-]}$$
The plot of \( \left\{ \frac{D_0}{D - 1} \right\}_{\text{pH 4.5}} \) as a function of \([\text{EDTA}^4^-]\) is a straight line at fixed pH, which slope allows for the determination of \( \beta_{1,1,1} \) (\( \beta_{1,0,1} \) was determined with Equation 10). Table 6 presents the pK\(_a\) values for EDTA and acetate, and pK\(_w\), at ionic strengths applicable to the present work. Many different and reliable sources can be found that have precisely determined the deprotonation constants of EDTA and acetate, and the data used for these calculations is considered reasonable as they do not differ greatly from those other references. The greatest differences are found with the calculation of the 5\(^{th}\) and 6\(^{th}\) pKa, associated with the amine groups. For the discussion of the current experiments these pKa are not included as they are not expected to play a major role in metal complexation. Values for Tc(IV) hydrolysis at zero ionic strength was used for all calculations, as there are no published values at higher ionic strengths and the slight effect of the ionic strength on these values was deemed negligible [16].

Specific Ion Interaction Theory (SIT) [5] was used to determine the stability constant of the two Tc(IV)/EDTA complexes at zero ionic strength, from the experimental data obtained within the 0.5-3.0 M ionic strength range. SIT modeling is expressed as:

\[
\log \beta^{\circ}\text{MHL} = \log \beta_{\text{MHL}} - \Delta Z^2 D + \Delta \epsilon \cdot I_m
\]  
(14)

where \( I_m \) is the ionic strength expressed in molality. The stability constant of the Tc(IV)/EDTA complex at zero ionic strength is \( \log \beta^{\circ}\text{MHL} \), while \( \log \beta_{\text{MHL}} \) represents the experimental stability constants at a non-zero ionic strength. \( \Delta Z^2 \) is relative to the change in charge from the uncomplexed to complexed metal ligand couple is defined as:

\[
\Delta Z^2 = (Z_{\text{MHL}})^2 - Z_H^2 - Z_M^2 - Z_L^2
\]  
(15)
And $D$ is the Debye-Hückle term with $A$ and $aB$ defined as $0.509 \text{ kg}^{1/2} \cdot \text{mol}^{1/2}$ and $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{1/2}$, respectively [28]:

$$D = A \cdot I_m^{1/2}/(1 + aB \cdot I_m^{1/2})$$  \hspace{1cm} (16)

The values of $D\Delta Z^2$ calculated for the complexes in this study are included in Table 1. Upon determination of the stability constants of the Tc(IV)/EDTA complexes based on the solvent extraction data, predicted aqueous speciation and solubility were calculated, using the publicly available geochemical equilibrium speciation code PHREEQC [29].

**Results and discussion**

Back-extractions with INT confirmed that Tc(IV) was not oxidized to Tc(VII) during the course of the experiments. The plot of $D_0/D - 1$ as a function of $[\text{EDTA}^4^-]$ at 0.5 M (NaCl) ionic strength and $\text{pH}$ 6.6 (Figure 9) is provided as an example of data obtained from solvent extraction; presence of a single Tc(IV)/EDTA complex is indicated by the linear regression of the plot. **Table A1** of Appendix A presents one set of data obtained for each ionic strength 0.5, 1.0, 2.0, and 3.0 M, however each experiment was actually conducted in triplicate. Tc(IV)/EDTA complex stability constants determined in the present work are presented in Table 7.

The value for $\beta^0_{1,0,1}$ was found to be $20.0 \pm 0.4$ for Tc(IV)/EDTA complexation (with $\Delta \varepsilon = 0.73$) and the value for $\beta^0_{1,1,1}$ was found to be $25.3 \pm 0.5$ (with $\Delta \varepsilon = 0.58$). Our value for $\beta^0_{1,0,1}$ is much larger than stability constant for complexes with other carboxylic ligands, such as acetate [16] ($\log \beta^0_{1,-1,1} = 2.8$) and oxalate [15] ($\log \beta^0_{1,0,1} = 7.2 \pm 0.2$) – an expected trend due to the larger number of carboxylate sites for EDTA. The stability constant for the EDTA complex with TcO$_2^{2+}$ determined in the present work is similar to that of free tetravalent vanadium (VO$_2^{2+}$) with $\log \beta^0_{1,0,1} = 18.7$ at 0.1 M ionic strength for vanadium [30], while this work reports $\log \beta^0_{1,0,1}$ at
20.0 ± 0.4 and 17.1 ± 0.4, at 0 and 0.5 ionic strength, respectively, for TcO$_{2}^{2+}$. Furthermore, the increased stability constant from TcOEDTA$_{2}^{2+}$ to TcOHEDTA$^{+}$ complexes observed in these studies (log$\beta_{1,0,1}$ = 17 ± 0.4 and log$\beta_{1,1,1}$ = 21 ± 0.5 at 0.5 ionic strength) was also observed with VO$_{2}^{2+}$, with log$\beta_{1,0,1}$ = 18.7 and log$\beta_{1,1,1}$ = 21.6 (both at 0.1 ionic strength) [30].

The majority of studies on Tc(IV)/EDTA systems, available in the literature at this time, were performed at a pH value where the TcOEDTA$_{2}^{2-}$ species would be predicted to either be the predominant or only species present [18, 23, 31], but there have been no studies to date discussing possible mechanisms for the formation of Tc(IV)/EDTA complexes. Past investigations of crystal structures of Tc(IV)/EDTA complexes showed a planar four membered Tc$^{IV}$($\mu$-O)$_2$Tc$^{IV}$ ring with the full structure of (H$_2$EDTA)Tc$^{IV}$($\mu$O)$_2$Tc$^{IV}$(H$_2$EDTA)-5H$_2$O) [31]. However, this structure may not be directly comparable to our results as the concentration of $^{99}$Tc was 0.1 mmol, which would result in a large amount of polymerized Tc(IV) [19]. Further studies confirmed this structure, but these systems again contained relatively high concentrations of Tc [23]. Additionally, these studies were also performed at low pH (2-3), where TcO$_{2}^{2+}$ would be the predominant species. The present work was based on low Tc concentrations to avoid possibility of polymerization; however, there is no evidence to prove that polymerization may not have been induced by EDTA complexation. A more precise analysis of the structure, under similar solution conditions, is needed to allow for determination of further properties of this complex.

The solubility of Tc(IV) in the presence of EDTA was modeled with PHREEQC and the data obtained in the present work. The EDTA concentration was set at 2.5 mM to compare the present results to previous work; solubility results are shown with Figure 10, which illustrates Tc solubility median data along with upper and lower limits of calculated values (i.e. addition or
subtraction of error), to allow for a more accurate data representation. The solubility of Tc(IV) greatly decreases with increased pH; literature shows that very alkaline pH leads to a subsequent increase in solubility [32]. Gu et al. [18] found the solubility of Tc(IV) to be about 3\cdot10^{-7} M, in the presence of 2.5 mM EDTA and at neutral pH, which agrees with the calculated solubility of 3.9\cdot10^{-7} M obtained in the present work. The speciation of 10^{-7} M Tc(IV) in presence of 0.171 M EDTA was calculated at 0.1 ionic strength using PHREEQC, the stability constants determined in the present work, and Tc(IV) hydrolysis constants (Figure 11). The speciation results are shown with the associated standard error; error bars were omitted from the non-dominant species for simplicity. Figure 11 shows that the predominant species in the acidic region is TcOEDTA^{2-}, while TcO(OH)_{2} is predominant in the basic region.

This work offers some explanation on the previous observations of high concentrations of soluble Tc(IV) in the high pH waste tanks. Strong stability of soluble Tc-EDTA complexes will increase the mobility of Tc in the environment. It should be noted that a wide range of complexing ligands are expected to be present under environmental and waste storage conditions and may greatly impact Tc(IV) speciation.
Figure 10 Modeled solubility of Tc(IV) in presence of 2.5 mM EDTA.
Figure 11 Modeled speciation of Tc(IV) in the presence of 0.171 mM EDTA
### Appendix A: Examples of solvent extraction data

**Table A1.** Solvent extraction data in 0.5 M (NaCl).

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[EDTA]_{tot(M)}</th>
<th>pcH</th>
</tr>
</thead>
<tbody>
<tr>
<td>525.4</td>
<td>1260.3</td>
<td>0.41688</td>
<td>0.00081</td>
<td>5.03</td>
</tr>
<tr>
<td>552.4</td>
<td>1261.9</td>
<td>0.43775</td>
<td>0.00094</td>
<td>4.9</td>
</tr>
<tr>
<td>504.6</td>
<td>1265.4</td>
<td>0.39877</td>
<td>0.00107</td>
<td>4.99</td>
</tr>
<tr>
<td>464</td>
<td>1212.2</td>
<td>0.38278</td>
<td>0.00121</td>
<td>4.98</td>
</tr>
<tr>
<td>456.7</td>
<td>1305.4</td>
<td>0.34985</td>
<td>0.00134</td>
<td>4.95</td>
</tr>
<tr>
<td>415.9</td>
<td>1274.1</td>
<td>0.32643</td>
<td>0.00174</td>
<td>4.97</td>
</tr>
</tbody>
</table>

**Table A2.** Solvent extraction data in 1.0 M (NaCl).

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[EDTA]_{tot(M)}</th>
<th>pcH</th>
</tr>
</thead>
<tbody>
<tr>
<td>385.6</td>
<td>940.5</td>
<td>0.409</td>
<td>0.001</td>
<td>4.42</td>
</tr>
<tr>
<td>397.6</td>
<td>1320</td>
<td>0.301</td>
<td>0.0013</td>
<td>4.53</td>
</tr>
<tr>
<td>400.6</td>
<td>1447.5</td>
<td>0.277</td>
<td>0.0015</td>
<td>4.65</td>
</tr>
<tr>
<td>264.8</td>
<td>718.3</td>
<td>0.369</td>
<td>0.0017</td>
<td>4.36</td>
</tr>
<tr>
<td>437.9</td>
<td>1000.7</td>
<td>0.438</td>
<td>0.00066</td>
<td>4.43</td>
</tr>
<tr>
<td>229.8</td>
<td>1152.8</td>
<td>0.199</td>
<td>0.00067</td>
<td>4.3</td>
</tr>
</tbody>
</table>

**Table A3.** Solvent extraction data in 2.0 M (NaCl).

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[EDTA]_{tot(M)}</th>
<th>pcH</th>
</tr>
</thead>
<tbody>
<tr>
<td>811.5</td>
<td>1306.4</td>
<td>0.70905</td>
<td>0.00000</td>
<td>4.96</td>
</tr>
<tr>
<td>529.5</td>
<td>1377.4</td>
<td>0.38442</td>
<td>0.00067</td>
<td>4.86</td>
</tr>
<tr>
<td>599.2</td>
<td>1430.5</td>
<td>0.41887</td>
<td>0.00100</td>
<td>4.81</td>
</tr>
<tr>
<td>483</td>
<td>1472.5</td>
<td>0.32801</td>
<td>0.00133</td>
<td>4.86</td>
</tr>
<tr>
<td>Organic (cpm)</td>
<td>Aqueous (cpm)</td>
<td>D</td>
<td>[EDTA]_{tot(M)}</td>
<td>pcH</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
<td>-------</td>
<td>----------------</td>
<td>-----</td>
</tr>
<tr>
<td>476.4</td>
<td>1529.3</td>
<td>0.31152</td>
<td>0.00167</td>
<td>4.79</td>
</tr>
<tr>
<td>415</td>
<td>1505.1</td>
<td>0.27573</td>
<td>0.00200</td>
<td>4.77</td>
</tr>
<tr>
<td>389.3</td>
<td>1499.3</td>
<td>0.25965</td>
<td>0.00233</td>
<td>4.77</td>
</tr>
<tr>
<td>385.2</td>
<td>1584.6</td>
<td>0.24309</td>
<td>0.00267</td>
<td>4.73</td>
</tr>
<tr>
<td>337.5</td>
<td>1624.1</td>
<td>0.20781</td>
<td>0.00300</td>
<td>4.77</td>
</tr>
<tr>
<td>337.4</td>
<td>1577.9</td>
<td>0.21383</td>
<td>0.00333</td>
<td>4.79</td>
</tr>
</tbody>
</table>

**Table A4.** Solvent extraction data in 3.0 M (NaCl).
Chapter 4

PREFACE

These studies marked the beginning of my studies to characterize the interaction of Tc(IV) with humic acid. Like in the previous experiments the stability constants for the interaction of Tc(IV) with humic substances were determined. Three different sources were used Integrated Field Research Center (IFRC), International Humic Substance Society (IHSS), and Sigma Aldrich to compare how the place of origin affects its properties.

A solvent extraction system similar to the one used for acetate and EDTA was used for these studies, but they were chronologically performed before the EDTA experiments. As with EDTA, the stability constant at two different pH was determined. Strong complexation constants were observed at both pH, and were the same independent of the origin of the humic substances. They were also found to be in agreement with the limited studies previously published by Maes et. al.

We did observe no difference in the binding constant between humic and fulvic acids, which normally have about 1-2 order of magnitude difference. This has yet to be fully explained, but the fulvic acid source (IFRC) was not used in further experiments. The humic and fulvic acid from the IFRC were not very stable in solution and there appeared to be a fungal growth in some of the samples.

These studies were published in journal *Environmental Science and Technology* in 2011. The full text, as published, can be found in Appendix 3.
Chapter 4

Interactions of Tc(IV) with humic substances

By Mark A. Boggs¹, Travis Minton¹, Samuel Lomasney¹, Mohammed R. Islam¹, Wenming Dong², Baohua Gu², and Nathalie A. Wall¹

¹ Department of Chemistry, Washington State University, Pullman, WA 99164-4630
² Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Abstract

To understand the key processes affecting ⁹⁹Tc mobility in the subsurface and help with the remediation of contaminated sites, the binding constants of several humic substances (humic and fulvic acids) with Tc(IV) were determined, using a solvent extraction technique. The novelty of this paper lies in the determination of the binding constants of the complexes formed with the individual species TcO(OH)⁺ and TcO(OH)₂⁰. Binding constants were found to be 6.8 and between 3.9 and 4.3, for logβ₁₁,₁ and logβ₁₂,₁, respectively; these values were not modified by a change of ionic strength between 0.1 M to 1.0 M, nor were they by the nature and origin of the humic substances. Modeling calculations based on these show TcO(OH)-HA to be the predominant complex in a system containing 20 ppm HA and in the 4-6 pH range, while TcO(OH)₂⁰ and TcO(OH)₂-HA are the major species, in the pH 6-8 range.

Keywords: Technetium / organic matter / complexation / Solvent Extraction

Introduction

⁹⁹Tc is a significant environmental contaminant, with a long half-life of 2.1·10⁵ y, found in sites such as the U.S. Department of Energy (DOE) Oak Ridge Integrated Field Research Center (IFRC) and Hanford site. At Oak Ridge, ⁹⁹Tc is present in groundwater and sediments at
concentrations as high as 31 nCi/L and 95 pCi/g, respectively; the Hanford site shows four large
and 15 µCi/kg \(^{99}\)Tc has been found in the vadose zone, near underground tanks [3]. \(^{99}\)Tc presents
a challenge for clean up because of its complex chemistry, making critical to understand the key
processes that affect its mobility in the environment.
Although Tc valence state can vary from VII to III [4], Tc(VII) (in the form of pertechnetate
oxyanion, \(\text{TcO}_4^{-}\)) is the most stable in natural oxic environments, rendering it highly mobile in
environmentally relevant pH conditions, because of its high solubility in water and essentially
nonadsorptive properties towards sediment minerals. However, Tc(VII) can be reduced in the
environment, to produce relatively immobile and sparingly soluble Tc(IV) species. The biogenic
Fe(II) reduction of \(\text{TcO}_4^{-}\) has been observed in many instances; for example, in unamended soil,
representative of a United Kingdom nuclear site [5, 6] clay minerals [7]; subsurface materials
from the US Department of Energy’s Hanford and Oak Ridge sites [1, 8, 9] and core samples
from a shallow sandy aquifer that contained Fe(II) [10]. Interestingly, even if biological activity
is eliminated by pasteurization, previously bioreduced materials still reduced \(\text{TcO}_4^{-}\), but the
reduction rate depends on Fe(II) concentrations [1]. Tc reduction can be amplified by the
addition of organic electron donors (e.g. acetate and lactate) to the system, leading to a microbial
reduction of Fe(III) [9, 10]. However, Tc(VII) reduction can be limited by several factors such
as the presence of unreduced Mn [1]; the presence of large quantities of layer silicates (e.g.
illites) [1]; and in non-neutral pH condition if Fe(II) is present at low concentration (less than
1mM) [7].
Tc(IV)\(\text{O}_2\cdot x \text{H}_2\text{O(s)}\) has a very low solubility of \(10^{-8} \text{ m}\), under reducing conditions and in a pH
ranging from 4 to 9 [4, 11], but Tc(IV) is more soluble at higher pH: \(10^{-6.5} \text{ M}\) at pH 14.3 [12] and
is especially soluble in acidic solution: $10^{-3}$ m at pH -1 [13]. The species issued from the solubility of TcO$_2$·1.6 H$_2$O(am) were identified as the hydrolyzed species TcO$_{2+}$(aq), TcO(OH)$^+$ (aq), TcO(OH)$_2^0$(aq), and TcO(OH)$_3^-$ (aq), in absence of carbonate; Guillaumont et al. reported that the presence of carbonate leads to the formation of the species Tc(CO$_3$)(OH)$_2^0$(aq) and Tc(CO$_3$)(OH)$_3^-$ (aq) [11], however a more recent work demonstrates that at least 0.01 M carbonate must be present to induce the formation of Tc(IV) carbonatespecies [14]. Yet, Tc(IV) solubility can increase in the presence of complexing organic ligands; for example, Tc(IV) forms complexes with oxalate and acetate [15, 16] and experiments showed that an increase of oxalate concentration from $10^{-6}$ M to $10^{-0.5}$ M increased Tc(IV) solubility from $10^{-8}$ M to $10^{-3}$ M, at pH 4 [17].

Humic substances (HS), organic colloids derived from the degradation of natural organic matter, are traditionally segregated in three major groups, humic acids (HA) that precipitate at low pH, fulvic acids (FA) that are soluble at all pH, and humin that is insoluble at all pH. The last decade literature has shown evidences of Tc(IV)-humics species, using a combination of XANES and gel permeation chromatography [18] or by surface-enhanced Raman spectroscopy (SERS) [19]. As predicted, such complexes affect Tc solubility; it was suggested that the presence of organic matter maintained Tc in a soluble form, in buried pets, in spite of an excess of Fe(II) [10], while a study showed that the 160 ppm of organic matter contained in Gorleben groundwater enhanced Tc dissolution by 2 orders of magnitudes, under neutral and alkaline anoxic conditions [18]. Studies also showed that HS increase Tc(IV) mobility [20]. While the formation of soluble Tc(IV)-HS species had been studied in terms of ligand-metal complexation, for solutions of low Tc(IV) concentrations (e.g. [21]), a combination of XANES and EXAFS measurements implied an HS sorption onto Tc(IV) colloids, in suspensions containing near-to-millimolar amounts of
Tc, under slightly basic pH and reducing conditions [22]. Trace levels of Tc(IV) interactions with Boom Clay HS samples in synthetic clay water of neutral pH were quantified using a modified Schubert method; the logarithm of the binding constants of the TcO(OH)$_2$-HS complexes was found to be 5.3 ± 0.3 [21]. Though, in neutral to basic pH solution, the logarithm of the conditional binding constant between colloidal Tc(IV) (for Tc concentrations as high as 6·10$^{-4}$ M) and Gorleben HS, describing the overall distribution between Tc(IV) and HS, was found to be 2.6 ± 0.3, using Schubert plots [23] and 2.3 ± 0.3, with a method involving HS precipitation by La$^{3+}$ [24, 25]. The experiments described in the literature presented above were performed with HS, without segregation of HA from FA; and, more importantly, the experiments have been performed only in pH regions where neutral and negative Tc(IV) species occur, but the binding constant to each individual species have not been determined. This paper present the experimental determination of the binding constant of several HA and one FA samples with TcO(OH)$^+$ and TcO(OH)$_2^0$, at different ionic strengths, using a solvent extraction method and modified Schubert calculations. Speciation calculations were also conducted based on these results.

**Experimental**

**Humic solution preparations**

All solutions were prepared from reagent-grade chemicals in de-ionized distilled water. The Oak Ridge IFRC HA (FRCHA) and FA (FRCFA) were obtained from a background topsoil at the U.S. Department of Energy’s Integrated Field Research Challenge (IFRC) site at the Y-12 National Security Complex in Oak Ridge, Tennessee. Details of the extraction procedures and characteristics of these humic materials were given elsewhere [26-28]. Humic acids purchased from Sigma Aldrich HA were purified according to the literature [29]; purified Sigma Aldrich
HA will be referred to as SAHA for the continuation of this paper. The purified Elliot soil humic acids (ESHA) were purchased from The International Humic Substances Society (IHSS) and used without further purification. All stock humic substances solutions were prepared in deionized water and were stored at 1-3°C when not in use.

**Potentiometric titration**

Potentiometric titrations were conducted with a Denver Instrument Model 352 autotitrator, connected to a PHC2401-a Denver electrode and a TitraMaster 85 software Version 5.0.0 (Radiometer Analytical). All titrations were performed at 25ºC, in a jacketed vessel, and under a blanket of N$_2$(g). The electrode was calibrated daily, by conducting a titration of standardized 0.5 M HCl (Fisher) with carbon-free standardized 0.5 M NaOH (Fisher), at the desired ionic strength (NaCl, Fisher). The daily electrode calibration also provided the equation for the potential expression, V, as a function of the calculated pcH ($-\log[H^+]$), for each ionic strength studied, as presented in Table 1. HS potentiometric titrations were then carried out by measuring the weight of 0.02 g HS to the 4$^{th}$ decimal, to which a known amount of DDIW was added and enough 5.0 M NaCl to reach the appropriate ionic strength. Small aliquots of carbon-free standardized 0.1 M NaOH (Fisher) and set at the appropriate ionic strength (NaCl) were slowly added, under constant stirring, until pH was measured to be between 10.75 and 11.00; the total amount of added NaOH was recorded (the NaOH solution added was too small to modify the sample ionic strength). The HS solution was allowed to equilibrate for at least 20 min before titrated with standardized 0.05 M HCl (Fisher) set at the appropriate ionic strength (NaCl); the titrant was added at a maximum rate of 0.1 mL/min., allowing a next titrant addition only if the potential deviation between two consecutive measurements did not exceed 0.6 mV/min (a difference of 0.01 pH unit/min), after a 30 sec measurement; when an inflection point was
detected, the autotitrator automatically decreased the amount of titrant addition. The titration was set to be completed when the potential reached a value of 260 mV (pH 2.5). pKₐ values and carboxylic site capacities were determined graphically, from the titration curve first derivatives, as described elsewhere [30]. Each HS titration was performed in triplicates.

**Solvent extraction**

A Tc(IV) stock solution was prepared according to the literature [13]. Briefly, an aliquot of 0.29 M NH₄TcO₄ (Oak Ridge) was added to water and freshly prepared 0.195 M Na₂S₂O₄ (Mallinckrodt); the solution pH was raised to 12 to form a TcO₂·xH₂O(amp) black slurry, which was then washed three times with 0.01 M Na₂S₂O₄. The Tc(IV) precipitate was separated by centrifugation, after a 72 h equilibration period, and dissolved in concentrated HCl (Fisher). The Tc(IV) stock solution was authenticated using an Ocean Optics USB4000 UV-Vis spectrometer, showing the characteristic TcCl₆²⁻ peak [13]. For the extraction performed at ionic strengths equal or larger than 0.5 M, the Tc(IV) stock solution was prepared by diluting an aliquot of the previous Tc(IV) solution in 1 M HCl to obtain 4000 cpm per 20 μl. For extractions performed at 0.1 M ionic strength, a second Tc(IV) stock solution was prepared; 1 mL of the previous Tc(IV) stock solution prepared in concentrated HCl was evaporated to dryness, using acetone (Fisher) and re-dissolved in 5 mL of DDIW. Tc reduction and solvent extraction experiments were performed in an oxygen-free glove box (< 1ppm O₂(g)), to maintain Tc in its reduced form. NaCl (Fisher) solutions were used as a background electrolyte to control the ionic strength, from 0.1 to 1.0 M, in all experiments. Sodium acetate (Fisher) or MES (Sigma-Aldrich) solutions were used to buffer NaCl solutions at pH 4.8 and 6.8, respectively. NaCl and sodium acetate solutions were filtered over 0.22 μm pore size Nalgene filters. A solution of 0.05M Cyanex 272 (Cytec Industries) with 0.05M Tri-Octylphosphine oxide (TOPO) (Sigma-Aldrich -99%) in hexane was
used for the extractions at pH 6.8. A 0.1 M Bis-(2-Ethylhexyl) phosphoric acid (HDEHP) (Sigma-Aldrich-97%) in hexane (Fisher) solution was used for the extractions at pH 4.8, kept in the dark when not in use.

Solvent extraction experiments were performed by vigorously shaking, for 24 hours and at room temperature (25 ± 1°C), 1.5 mL of an aqueous solution with an equal volume of organic extractant solution (Cyanex+TOPO in hexane for extractions at pH 6.8 and HDEHP in hexane for experiments at pH 4.5); the NaCl aqueous solutions contained varying amounts of HS, 6000 cpm Tc(IV), either 0.005 M sodium acetate or 0.01 M MES, and enough NaOH or HCl to adjust the pH to the desired value. Upon equilibration, 750 µL aliquots were drawn from each phase and diluted to 7.0 mL with Eco-scint cocktail for liquid scintillation counting (Beckman Coulter LS6500 liquid scintillation counter). Each aqueous phase pH was measured using a Denver Instruments combination glass electrode and a Thermo-Fisher pH-meter. The electrode was calibrated daily with pH 4.01 and 7.00 buffers (Fisher) and the pH-meter readings (i.e. pHr) were converted to pcH values (i.e. –log[H⁺]) by the following equation, determined as explained elsewhere [29, 31]:

\[
\text{pcH} – \text{pHr} = 0.30 \cdot I + 0.04
\]

(17)

where \( I \) is the ionic strength in M (NaCl)

It was ensured that no HS was loss during this procedure by spectrophotometrically measuring their concentration in the aqueous phases, before and after extraction.
Data treatment

At pH 6.8, TcO(OH)$_2^0$ is the dominant aqueous species according to previous calculations (16) since the experiments were performed in the presence of MES buffer, which does not complex metals. Therefore, the equilibria of concern at such pH are:

\[ TcO(OH)_2^0 + HS \rightleftharpoons TcO(OH)_2 - HS \]  
(18)

and

\[ TcOOH^+ + OH^- \rightleftharpoons TcO(OH)_2^0 \]  
(19)

with the complex binding and stability constants defined as follow:

\[ \beta_{1-2,1} = \frac{[TcO(OH)_2^0 - HS]}{[TcO(OH)_2][HS]} \]  
(20)

\[ \beta_{1-2,0} = \frac{[TcO(OH)_2^0]}{[OH^-][TcOOH^+]} \]  
(21)

The humic concentrations account for the carboxylic capacity, the humic pKa values, and the pH at which the experiments are performed:

\[ [HS] = C_{HS} \alpha_{HS} \text{Capacity}_{HS} \]  
(22)

where $C_{HS}$ is the total HS concentration; $\alpha_{HS}$ the degree of ionization of HS at the experiment pH; and $\text{Capacity}_{HS}$ the HS capacity determined in this paper by potentiometric titration.

The distribution coefficient (D) of Tc between the organic and aqueous phases is defined as the ratio between the sum of Tc species in the organic phase and the sum of Tc species in the aqueous phase:

\[ D = \Sigma[Tc_{org}] / \Sigma[Tc_{aq}] \]  
(23)
Labeling \( D_0 \) as the distribution of metal without ligand, in absence of \( \text{CO}_2(\text{g}) \) or any metal complexing buffer in the system, the equation becomes:

\[
\frac{D_0}{D} = \frac{[\text{TcO}(\text{OH})^0] + [\text{TcO}(\text{OH})_2 - \text{HS}]}{[\text{TcO}(\text{OH})^0_2]} \quad (24)
\]

Therefore:

\[
\frac{D_0}{D} - 1 = \beta_{1,-2,1}[\text{HS}] \quad (25)
\]

The plot of \( D_0/D-1 \) as a function of \([\text{HS}]\) is a linear regression, which slope is \( \beta_{1,-2,1} \).

However, at pH 4.5, about 34% of \( \text{Tc(IV)} \) is present as \( \text{TcOOH}^+ \) species, and 66% as \( \text{TcO}(\text{OH})^0_2 \) according to calculations [16]. Therefore, the following equilibrium is considered in addition to Eq. (2):

\[
\text{TcOOH}^+ + \text{HS} \rightleftharpoons \text{TcOOH} - \text{HS} \quad (26)
\]

With the associated binding constant expressions:

\[
\beta_{1,-1,1} = \frac{[\text{TcOOH} - \text{HS}]}{[\text{TcOOH}^+][\text{HS}]} \quad (27)
\]

Considering \( \text{Tc} \) second hydrolysis shown in Eq. (3) and \( \text{Tc} \) complexation with acetate, used to buffer pH:

\[
\text{TcOOH}^+ + \text{Ac}^- \rightleftharpoons \text{TcOOH} - \text{Ac} \quad (28)
\]

and its respective stability constant:

\[
\beta_{1,-1,1\text{Ac}} = \frac{[\text{TcOOH} - \text{Ac}]}{[\text{Ac}^-][\text{TcOOH}^+]} \quad (29)
\]

the ratio of \( \text{Tc} \) distribution coefficients, described in Eq. (7) to Eq. (9), becomes:
\[
\frac{D_0}{D} = \frac{[\text{TcOOH}^+]+[\text{TcO(OH)}_2]+[\text{TcOOH} - \text{Ac}]+[\text{TcOOH} - \text{HS}]+[\text{TcO(OH)}_2 - \text{HS}]}{[\text{TcOOH}^+]+[\text{TcO(OH)}_2]+[\text{TcOOH} - \text{Ac}]} \tag{30}
\]

and:
\[
\frac{D_0}{D} - 1 = \frac{\left(\beta_{1,-1,1} + \beta_{1,-2,0}[\text{OH}^-]\right)}{1 + \beta_{1,-2,0}[\text{OH}^-] + \beta_{1,-1,1,\text{Ac}}[\text{Ac}^-]} \times [\text{HS}] \tag{31}
\]

where \([\text{HS}]\) is defined by Eq. (6) and \([\text{Ac}^-]\) is the concentration of deprotonated acetate at the experiment pH and ionic strength. The plot of \(D_0/D-1\) as a function of \([\text{HS}]\) provides a linear regression; the only unknown term of the slope expression is \(\beta_{1,-1,1}\), as \(\beta_{1,-2,1}\) was determined in this work, from the experiments conducted at pH 6.8, \(\beta_{1,-2,0}\) can be calculated from the literature [11, 13], and \(\beta_{1,-1,\text{Ac}}\) was previously determined by this group [16]. The data necessary to calculate \(\beta_{1,-1,1}\) are presented in Tables 2 and 3. The value for \(\log \beta_{1,-1,\text{Ac}}\) at 0.1M was extrapolated using the Specific Ion Interaction Theory (SIT) modeling and the parameters described by Boggs et al. [16].

**Results and Discussion**

**HS Potentiometric**

HS titration curves were similar to that presented in previous published work [30]. For each potentiometric titration, 3 inflection points were detected, corresponding to two different carboxylic sites (the two first inflection points) and one phenolic site (the last inflection point, at higher pH), as explained elsewhere [30]. The pK\(_a\) values of each HS functional group (determined at the half equivalence points) and the total carboxylic capacities are presented in Table 1. The values of pK\(_{a1}\) and pK\(_{a2}\) are that of carboxylic groups and pK\(_{a3}\) of phenolic groups. Table 1 results are in accordance with those presented elsewhere with other humic substances, including the fact that the ionic strength has little influence on the pK\(_a\) values [30].
The carboxylic capacity of the IFRC humics is little affected by a change of ionic strength; however, it is decreased by a factor of 2 for SAHA, with an increase of ionic strength from 0.1 M to 0.5 M. This decreasing capacity can be attributed to SAHA size growth, as additional data (not shown here) have demonstrated that, at neutral pH, the average size of SAHA remains unchanged between solution at ionic strengths from 0.01 M to 0.1 M, but increases between solutions at ionic strengths 0.1 M and 0.5 M. Also, previous work showed SAHA size remains unchanged as the ionic strength increases from 1.0 m to 5.0 m [29], which explains a constant capacity between ionic strengths 0.5 and 1.0 M, in this work.

**HS-Tc binding constants**

Data used to calculate $\beta_{1-2,0}$ (*Table 9*) are only available at zero ionic strength. The use of these data does not affect significantly our final results, although we conducted experiments at non-zero ionic strengths. The deviation we would obtain, had we had access to non-zero ionic strength Tc hydrolysis constants, would fall within the errors of our reported binding constants, as explained elsewhere [16].

Our results for the binding constants of humic and fulvic acids with TcO(OH)$_2^+$ (log$\beta_{1-1,1}$) and TcO(OH)$_2^0$ (log$\beta_{1-2,1}$) are presented in *Table 11*. The values of log$\beta_{1-1,1}$ were determined at 0.1 M, 0.5 M, and 1.0 M ionic strengths, for FRCFA, FRCHA, and SAHA; the similarity of the results between each humic and at the three ionic strengths lead to conclude that log$\beta_{1-2,1}$ values would not vary either between humics at a fixed ionic strength, or for one particular humic material between different ionic strengths. Therefore, log$\beta_{1-2,1}$ values were determined at only one ionic strength, 0.5 M, for all the humic substances studied. Similar stability constants between humic acids of different origin have been observed in the past, in particular for the binding of other humic acids with uranyl [30]. However, Tc(IV) binding constants are
unexpectedly similar between HA and FRCFA complexes, while previous works have shown a difference of at least one order of magnitude between HA and FA binding constants with actinides, with HA complexes being the strongest [30, 32]. The logβ_{1-2,1} value of the Tc(IV) complex with the IHSS HA sample ESHA is again similar to those obtained with the other humics studied in this work. It is unsure at this point, if the similar strength of complexes between the HA samples and FRCFA is due to the nature of FRCFA, which may be a stronger complexant than other FA samples, or to a difference of humic interactions between actinides and transition metals. The data also showed that the binding constants of HS with the cationic Tc(IV) species are substantially larger (by two orders of magnitude) than with the neutral TcO(OH)$_2^0$, as would be expected.

Previous work showed a logarithm of the binding constant of Tc(IV)-HA complex of 5.3 ± 0.3, for tracer levels of Tc(IV) and at pH 8.0, where TcO(OH)$_2^0$ is the only species present (Figure 12) [22]. Maes’ studies were performed in synthetic clay water consisting of a variety of background electrolytes, and HA and FA were not discriminated, rendering a difficult comparison with our results. However, our work lead to remarkably similar data; our results for logβ_{1-2,1} range from 3.9 ± 0.3, for FRCFA, to 4.6 ± 0.1, for ESHA, in solution of ionic strength of 0.5 M. The binding constant data we obtained, in conjunction with Tc(IV) thermodynamic data of Table 9, allowed performing speciation calculations, using the publicly available geochemical equilibrium speciation code PHREEQC [33]. Figure 13 presents Tc(IV) speciation in presence of 20 ppm FRCHA. While TcO(OH)$^+$ and TcO(OH)$_2^0$ are the two major species in the 4-5 pH range in absence of HA (Figure 12), the addition of 20 ppm HA allows the complex TcO(OH)-HA to be predominant in the same pH array. Also, the presence of 20 ppm HA allows the species TcO(OH)$_2$-HA to be predominant at pH 7, while the neutral TcO(OH)$_2^0$ is in absence
of HA. Figure 14 presents a compilation of data obtained from PHREEQC calculations, to show the maximum HA concentration necessary to obtain maximal Tc(IV)-HA species concentration (i.e. the addition of TcO(OH)-HA and TcO(OH)$_2$-HA concentrations). In a solution containing $10^{-7}$ M Tc(IV), while less than 20 ppm HA is sufficient to obtain an absolute dominance of the soluble humic complexes at pH 4.5, 75 ppm HA is necessary to reach the maximum predominance of humic complexes at pH 6.8. Additionally, 100 ppm HA is still not quite enough for the humic complexes to be the absolute dominant species at pH 6.8, due to the smaller binding constant of the neutral Tc(IV) species at this pH; a small amount of TcO(OH)$_2$ is still present at this pH, as shown on Figure 13.

This paper provides a novel method to determine the binding constants of several humic substances with the individual Tc(IV) species, TcO(OH)$^+$ and TcO(OH)$_2$.$^0$. While confirming the literature finding that neutral Tc(IV) species binds to humic substances, this work also demonstrates the importance of an accurate knowledge of solution pH; in absence of carbonate, the singly charged Tc(IV) species, predominant at pH 4, has a much higher binding constants with humics than the neutral TcO(OH)$_2$.$^0$ (the major species between pH 5 and 8), by three orders of magnitude. In turn, a more accurate knowledge of Tc(IV) behavior with humic substances, over a wide pH range, allows a more realistic modeling of the speciation of the Tc(IV) in presence of the naturally occurring ligand. Calculations show TcO(OH)-HA is the predominant complex in a system containing 20 ppm HA and in the 4-6 pH range, while TcO(OH)$_2$.$^0$ and TcO(OH)$_2$-HA are the major species, in such system between pH 6 and 8. Current research focuses on experimentally quantifying Tc(IV) solubility in presence of the humic substances and verifying the accuracy of the modeling presented in this paper.
Acknowledgements

This work was supported by the Office of the Biological and Environmental Research, Office of Science, US Department of Energy (DOE) under the grant DE-FG02-08ER64696 with Washington State University and under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, which is managed by UT-Battelle LLC for DOE.

References


List of Tables:

Table 8. Electrode calibration as a function of the ionic strength (NaCl): \( V = s \cdot p\text{cH} + y_0 \), where \( V \) is the electrode potential in mV and \( p\text{cH} \) is \(-\log[H^+]\). Errors are 2\( \sigma \) of replicates.

Table 9. Selected Tc(IV) reactions and associated thermodynamic constants at zero ionic strength considered in this work.

Table 10. Additional data necessary for \( \beta_{1,-1,1} \) calculations.

Table 11. HS potentiometric titration results and binding constants with TcO(OH)\(^+\) (log\( \beta_{1,-1,1} \)) and TcO(OH)\(_2^0\) (log\( \beta_{1,-2,1} \)). Errors are 2\( \sigma \) of replicates

List of Figures:

Figure 12: Tc(IV) speciation in the absence of HA. Total Tc concentration is \( 10^{-7} \) M. Calculations were performed using PHREEQC. (Note that the concentration of the species TcO\(^2^+\) and TcO(OH)\(_3^-\) are negligible).

Figure 13: Tc(IV) speciation in the presence of 20 ppm FRCHA. Total Tc concentration is \( 10^{-7} \) M. Calculations performed using PHREEQC. (Note that the concentration of the species TcO\(^2^+\), TcO(OH)\(^+\), TcO(OH)\(_3^-\), and TcO(OH)-Ac are negligible)

Figure 14: Soluble Tc-HA species concentrations as a function of FRCHA concentration. Total Tc concentration is \( 10^{-7} \) M. Calculations performed using PHREEQC.
Table 8. Electrode calibration as a function of the ionic strength (NaCl): $V = s \cdot \text{pH} + y_0$, where $V$ is the electrode potential in mV and pH is $-\log[H+]$. Errors are $2\sigma$ of replicates.

<table>
<thead>
<tr>
<th>Ionic Strength (NaCl, M)</th>
<th>s</th>
<th>$y_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>-57.6 ± 0.02</td>
<td>370.2 ± 0.1</td>
</tr>
<tr>
<td>0.50</td>
<td>-58.8 ± 0.02</td>
<td>381.4 ± 0.2</td>
</tr>
<tr>
<td>1.00</td>
<td>-59.1 ± 0.02</td>
<td>386.5 ± 0.2</td>
</tr>
</tbody>
</table>
Table 9. Selected Tc(IV) reactions and associated thermodynamic constants at zero ionic strength considered in this work.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>log $K^0$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TcO}^{2+} + \text{H}_2\text{O} = \text{TcOOH}^+ + \text{H}^+$</td>
<td>0.0072</td>
<td>[13]</td>
</tr>
<tr>
<td>$\text{TcO}^{2+} + 2 \text{H}_2\text{O} = \text{TcO(OH)}_2^0 + 2 \text{H}^+$</td>
<td>-4.00</td>
<td>[11]</td>
</tr>
<tr>
<td>$\text{TcO}^{2+} + 3 \text{H}_2\text{O} = \text{TcO(OH)}_3^- + 3 \text{H}^+$</td>
<td>-14.9</td>
<td>[11]</td>
</tr>
</tbody>
</table>
Table 10. Additional data necessary for $\beta_{1,-1,1}$ calculations.

<table>
<thead>
<tr>
<th>I (M, NaCl)</th>
<th>$pK_w^a$</th>
<th>Acetate $pK_a^b$</th>
<th>$\log \beta_{1,-1,Ac}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>13.83</td>
<td>4.56</td>
<td>2.74*</td>
</tr>
<tr>
<td>0.5</td>
<td>13.72</td>
<td>4.50</td>
<td>2.46 ± 0.06</td>
</tr>
<tr>
<td>1.0</td>
<td>13.70</td>
<td>4.52</td>
<td>2.7 ± 0.1</td>
</tr>
</tbody>
</table>

$^a$ [34]  
$^b$ [35]  
$^c$ [16]  

* Data calculated using SIT and published parameters [16]
Table 11. HS potentiometric titration results and binding constants with TcO(OH)$_2^+$ ($\log\beta_{1,-1,1}$) and TcO(OH)$_{20}^-$ ($\log\beta_{1,-2,1}$). Errors are 2σ of replicates

<table>
<thead>
<tr>
<th></th>
<th>FRCFA</th>
<th>FRCHA</th>
<th>SAHA</th>
<th>ESHA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ionic strength: 0.1 M</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$pK_{a1}$</td>
<td>4.0 ± 0.4</td>
<td>3.3 ± 0.2</td>
<td>3.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>$pK_{a2}$</td>
<td>6.9 ± 0.3</td>
<td>6.4 ± 0.2</td>
<td>6.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>$pK_{a3}$</td>
<td>8.8 ± 0.3</td>
<td>8.8 ± 0.3</td>
<td>8.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Capacity (COO$^-$) (meq/g HS)</td>
<td>4.0 ± 0.8</td>
<td>4.8 ± 0.4</td>
<td>4.2 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>$\log \beta_{1,-1,1}$</td>
<td>6.5 ± 0.3</td>
<td>6.2 ± 0.2</td>
<td>5.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td><strong>ionic strength: 0.5 M</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$pK_{a1}$</td>
<td>3.4 ± 0.2</td>
<td>3.4 ± 0.2</td>
<td>4.2 ± 0.2</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>$pK_{a2}$</td>
<td>6.4 ± 0.1</td>
<td>6.5 ± 0.2</td>
<td>6.9 ± 0.3</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>$pK_{a3}$</td>
<td>8.9 ± 0.1</td>
<td>8.9 ± 0.1</td>
<td>9.5 ± 0.1</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td>Capacity (COO$^-$) (meq/g HS)</td>
<td>4.2 ± 0.3</td>
<td>4.8 ± 0.3</td>
<td>2.4 ± 0.4</td>
<td>4.6 ± 0.1</td>
</tr>
<tr>
<td>$\log \beta_{1,-1,1}$</td>
<td>6.8 ± 0.3</td>
<td>6.8 ± 0.4</td>
<td>6.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>$\log \beta_{1,-2,1}$</td>
<td>3.9 ± 0.3</td>
<td>4.3 ± 0.4</td>
<td>4.3 ± 0.3</td>
<td>4.6 ± 0.1</td>
</tr>
<tr>
<td><strong>ionic strength: 1.0 M</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$pK_{a1}$</td>
<td>3.1 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>4.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>$pK_{a2}$</td>
<td>6.2 ± 0.2</td>
<td>6.1 ± 0.6</td>
<td>6.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>$pK_{a3}$</td>
<td>9.1 ± 0.1</td>
<td>8.9 ± 0.3</td>
<td>8.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Capacity (COO$^-$) (meq/g HS)</td>
<td>6 ± 1</td>
<td>5 ± 1</td>
<td>2.5 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>$\log \beta_{1,-1,1}$</td>
<td>6.4 ± 0.3</td>
<td>6.5 ± 0.3</td>
<td>6.5 ± 0.3</td>
<td></td>
</tr>
</tbody>
</table>
Figure 12: Tc(IV) speciation in the absence of HA. Total Tc concentration is $10^{-7}$ M. Calculations were performed using PHREEQC.
Figure 13: Tc(IV) speciation in the presence of 20 ppm FRCHA. Total Tc concentration is $10^{-7}$ M. Calculations performed using PHREEQC.
**Figure 14:** Soluble Tc-HA species concentrations as a function of FRCHA concentration. Total Tc concentration is $10^{-7}$ M. Calculations performed using PHREEQC.
Supporting Information: Example of extraction data. The extractant is 0.1 M HDEHP in hexane, for experiments conducted at pH 4.5 and 0.05 M Cyanex 272 + 0.05 M TOPO in hexane, for experiments conducted at pH 6.8. Ionic strength maintained with NaCl. The terms cpmorg and cpmaq stand for “count per minute” in the organic and aqueous phases aliquots, respectively, obtained from liquid scintillation counting.

Table S1. SAHA, ionic strength 0.5 M, pH = 4.3 ± 0.1

<table>
<thead>
<tr>
<th>cpm_{org}</th>
<th>cpm_{aq}</th>
<th>D</th>
<th>[HA]_{ppm}</th>
<th>pcH</th>
<th>D_0/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>790</td>
<td>2078</td>
<td>0.38</td>
<td>0.00</td>
<td>4.32</td>
<td>0</td>
</tr>
<tr>
<td>734</td>
<td>2573</td>
<td>0.285</td>
<td>10.00</td>
<td>4.27</td>
<td>0.332</td>
</tr>
<tr>
<td>672</td>
<td>2605</td>
<td>0.257</td>
<td>13.33</td>
<td>4.29</td>
<td>0.473</td>
</tr>
<tr>
<td>594</td>
<td>2484</td>
<td>0.239</td>
<td>16.66</td>
<td>4.38</td>
<td>0.589</td>
</tr>
<tr>
<td>761</td>
<td>2405</td>
<td>0.316</td>
<td>6.66</td>
<td>4.34</td>
<td>0.200</td>
</tr>
<tr>
<td>728</td>
<td>2639</td>
<td>0.275</td>
<td>10.00</td>
<td>4.42</td>
<td>0.377</td>
</tr>
<tr>
<td>669</td>
<td>2651</td>
<td>0.252</td>
<td>13.33</td>
<td>4.32</td>
<td>0.505</td>
</tr>
<tr>
<td>643</td>
<td>2683</td>
<td>0.239</td>
<td>20.00</td>
<td>4.33</td>
<td>0.585</td>
</tr>
</tbody>
</table>

Table S2. FRCHA, ionic strength 1.0 M. pH = 4.8 ± 0.1

<table>
<thead>
<tr>
<th>cpm_{org}</th>
<th>cpm_{aq}</th>
<th>D</th>
<th>[HA]_{ppm}</th>
<th>pcH</th>
<th>D_0/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2375</td>
<td>808</td>
<td>2.93</td>
<td>20.00</td>
<td>4.80</td>
<td>0.701</td>
</tr>
<tr>
<td>2141</td>
<td>1030</td>
<td>2.07</td>
<td>30.00</td>
<td>4.75</td>
<td>1.40</td>
</tr>
<tr>
<td>1905</td>
<td>1009</td>
<td>1.88</td>
<td>40.00</td>
<td>4.79</td>
<td>1.64</td>
</tr>
<tr>
<td>1615</td>
<td>1055</td>
<td>1.53</td>
<td>45.00</td>
<td>4.81</td>
<td>2.26</td>
</tr>
<tr>
<td>1669</td>
<td>1314</td>
<td>1.27</td>
<td>50.00</td>
<td>4.74</td>
<td>2.93</td>
</tr>
<tr>
<td>1583</td>
<td>1438</td>
<td>1.10</td>
<td>55.00</td>
<td>4.80</td>
<td>3.54</td>
</tr>
</tbody>
</table>
Table S3. FRCFA, ionic strength 1.0 M, pH = 4.6 ± 0.1

<table>
<thead>
<tr>
<th>cpm_{org}</th>
<th>cpm_{aq}</th>
<th>D</th>
<th>[HA]_{ppm}</th>
<th>pcH</th>
<th>D_0/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1035</td>
<td>957</td>
<td>1.08</td>
<td>9.85</td>
<td>4.72</td>
<td>0.85</td>
</tr>
<tr>
<td>1011</td>
<td>1057</td>
<td>0.956</td>
<td>13.10</td>
<td>4.69</td>
<td>1.09</td>
</tr>
<tr>
<td>950</td>
<td>918</td>
<td>1.03</td>
<td>16.40</td>
<td>4.54</td>
<td>0.93</td>
</tr>
<tr>
<td>907</td>
<td>1036</td>
<td>0.875</td>
<td>19.70</td>
<td>4.64</td>
<td>1.28</td>
</tr>
<tr>
<td>1047</td>
<td>1715</td>
<td>0.610</td>
<td>22.90</td>
<td>4.62</td>
<td>2.28</td>
</tr>
<tr>
<td>872</td>
<td>1761</td>
<td>0.495</td>
<td>26.20</td>
<td>4.63</td>
<td>3.04</td>
</tr>
<tr>
<td>817</td>
<td>1467</td>
<td>0.556</td>
<td>29.50</td>
<td>4.68</td>
<td>2.59</td>
</tr>
<tr>
<td>1054</td>
<td>1769</td>
<td>0.595</td>
<td>32.80</td>
<td>4.53</td>
<td>2.36</td>
</tr>
<tr>
<td>786</td>
<td>1940</td>
<td>0.405</td>
<td>36.10</td>
<td>4.61</td>
<td>3.94</td>
</tr>
</tbody>
</table>

Table S4. FRCHA, ionic strength 0.5 M, pH = 6.8 ± 0.4

<table>
<thead>
<tr>
<th>cpm_{org}</th>
<th>cpm_{aq}</th>
<th>D</th>
<th>[HA]_{ppm}</th>
<th>pcH</th>
<th>D_0/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>629</td>
<td>1688</td>
<td>0.300</td>
<td>0.00</td>
<td>6.59</td>
<td>0.00</td>
</tr>
<tr>
<td>325</td>
<td>1468</td>
<td>0.221</td>
<td>6.67</td>
<td>6.54</td>
<td>0.36</td>
</tr>
<tr>
<td>245</td>
<td>1793</td>
<td>0.137</td>
<td>10.00</td>
<td>6.81</td>
<td>1.20</td>
</tr>
<tr>
<td>223</td>
<td>1754</td>
<td>0.127</td>
<td>13.33</td>
<td>7.00</td>
<td>1.36</td>
</tr>
<tr>
<td>182</td>
<td>1912</td>
<td>0.095</td>
<td>16.67</td>
<td>7.13</td>
<td>2.15</td>
</tr>
<tr>
<td>217</td>
<td>2004</td>
<td>0.108</td>
<td>20.00</td>
<td>6.58</td>
<td>1.77</td>
</tr>
<tr>
<td>402</td>
<td>1605</td>
<td>0.250</td>
<td>3.33</td>
<td>6.78</td>
<td>0.20</td>
</tr>
<tr>
<td>342</td>
<td>1680</td>
<td>0.204</td>
<td>4.67</td>
<td>6.90</td>
<td>0.47</td>
</tr>
<tr>
<td>256</td>
<td>1683</td>
<td>0.152</td>
<td>6.67</td>
<td>7.00</td>
<td>0.97</td>
</tr>
<tr>
<td>223</td>
<td>1897</td>
<td>0.118</td>
<td>10.00</td>
<td>7.08</td>
<td>1.55</td>
</tr>
<tr>
<td>247</td>
<td>2076</td>
<td>0.119</td>
<td>13.33</td>
<td>6.64</td>
<td>1.52</td>
</tr>
<tr>
<td>244</td>
<td>2098</td>
<td>0.116</td>
<td>16.67</td>
<td>6.62</td>
<td>1.58</td>
</tr>
<tr>
<td>234</td>
<td>2136</td>
<td>0.110</td>
<td>20.00</td>
<td>6.58</td>
<td>1.74</td>
</tr>
</tbody>
</table>
Table S5. SAHA, ionic strength 0.5 M, pH = 6.8 ± 0.2

<table>
<thead>
<tr>
<th>cpm_{org}</th>
<th>cpm_{aq}</th>
<th>D</th>
<th>[HA]_{ppm}</th>
<th>pcH</th>
<th>D_0/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>590</td>
<td>1618</td>
<td>0.365</td>
<td>0.00</td>
<td>6.67</td>
<td>0.00</td>
</tr>
<tr>
<td>406</td>
<td>1585</td>
<td>0.256</td>
<td>6.67</td>
<td>6.65</td>
<td>0.42</td>
</tr>
<tr>
<td>355</td>
<td>1719</td>
<td>0.207</td>
<td>10.00</td>
<td>6.75</td>
<td>0.77</td>
</tr>
<tr>
<td>278</td>
<td>1545</td>
<td>0.180</td>
<td>13.33</td>
<td>6.77</td>
<td>1.03</td>
</tr>
<tr>
<td>400</td>
<td>1593</td>
<td>0.251</td>
<td>6.67</td>
<td>7.00</td>
<td>0.45</td>
</tr>
<tr>
<td>523</td>
<td>1327</td>
<td>0.394</td>
<td>0.00</td>
<td>6.77</td>
<td>-0.07</td>
</tr>
<tr>
<td>416</td>
<td>1626</td>
<td>0.256</td>
<td>6.67</td>
<td>6.72</td>
<td>0.43</td>
</tr>
<tr>
<td>404</td>
<td>1442</td>
<td>0.280</td>
<td>6.67</td>
<td>6.84</td>
<td>0.30</td>
</tr>
<tr>
<td>348</td>
<td>1822</td>
<td>0.191</td>
<td>10.00</td>
<td>6.82</td>
<td>0.91</td>
</tr>
<tr>
<td>284</td>
<td>1622</td>
<td>0.175</td>
<td>13.33</td>
<td>6.92</td>
<td>1.08</td>
</tr>
<tr>
<td>281</td>
<td>1650</td>
<td>0.170</td>
<td>13.33</td>
<td>6.87</td>
<td>1.14</td>
</tr>
</tbody>
</table>
Chapter 5

PREFACE

These studies were meant as a continuum to the previous humic substances complexation studies. In the previous studies, as well as in many literature papers, the dynamic nature of humic substances is generally ignored. The tendency for humic acid, in particular, to form large aggregates as pH is decreased, or ionic strength increased, is usually not well addressed. There are many gaps in the literature that could be filled if studies were done in a more systematic nature. These studies set out to determine what affect, in any, changes in ionic strength and pH would have on complexation of Tc(IV) and humic acid.

These works were accomplished by using carbon analysis, electrophoretic light scattering, and ultracentrifugation in tandem. When possible, IR and C\textsuperscript{13} CP-MAS NMR measurements were performed on filtered dry solids. My results show that despite large differences in the percentage of humic acid present in the different size ranges, there are trends between the amount of humic and Tc(IV) complexed. Once the size of the humics increases above the colloidal range, there is no discernable trend, but this may be due to our lack of ability to characterize these larger sizes. We are able to explain this by the zeta potential results, as the larger size has a much less negative zeta potential and would thus be expected to not form as strong of complexes.

Results of this nature are important to the modeling of currently contaminated areas, as well as future storage of radionuclides as they point towards ways that the interactions of metals and humic substances can be modeled and predicted.

Chapter 5 is a direct copy of a manuscript submitted to the journal *Environmental Science and Technology* for publication in 2012.
Size fractionated complexation of Tc(IV) with soil humic acids at varying solution conditions: correlations and observations from zeta potential, dynamic light scattering, ATR-IR, and NMR

Mark A. Boggs, Samantha E. Nulle, and Nathalie A. Wall

Abstract
Currently there are multiple Department of Defense sites that have large quantities of $^{99}$technetium stored under a variety of conditions. At at-least two of these sites, Hanford and Oak Ridge, located in Washington and Tennessee respectively, substantial releases in to the environment have been documented. While it is known that Tc in the VII oxidation state has a very high rate of environmental migration, little is know about the IV oxidation state; which is expected to be present under anoxic conditions. In these studies the complexation of Tc(IV) with humic acid particles of 10 nm and greater was determined by ultracentrifugation and total organic carbon analysis. It was observed, that independent of pH, ionic strength, background electrolyte and source, that there is a consistent ratio of Tc(IV) to humic acid for the size range of 10 – 1000 nm. While for the largest size fraction of > 1000 nm there was no discernable trend. The zeta potential of these particles was determined and showed that the largest size fraction had a considerably less negative zeta potential, while the zeta potential of the colloidal size fraction was independent of solution conditions. Solid filtrate, from selected samples, was analyzed by $^{13}$C CP-MAS NMR and ATR-IR to determine structural characteristics. It was observed that the two sources of humics used had distinct spectra, with very little in common, but these spectra were not affected by changes in
solution conditions. This work shows that we are able to use zeta potential measurements to accurately describe the binding characteristics of humic acid with Tc(IV).

**Introduction:**

$^{99}$Tc is of major concern at many U.S. Department of Energy (DOE) sites, such as at the Hanford site in Washington state where an estimated 30 Ci of technetium is projected to reach the Columbia River in the near future[1]. Similar trends in migration have been observed at the Field Research Center at Oak Ridge (Tennessee), where $^{99}$Tc can be found in vadose zone waters at concentrations up to 40,000pCi/l[2]. Large quantities of Tc are stored on site and there is a risk of further release into the environment. Additionally, there is currently no proposed advanced fuel cycles that would not end up with large quantities of $^{99}$Tc at the back end. Using current estimates, the Hanford site has up to 30,000 Ci of $^{99}$Tc in storage[3], with 50% of this being held in underground tanks[4] that have been shown to be hard to maintain and many of the waste forms present in them have not been fully characterized.

Technetium can exist in a variety of oxidation states, with Tc(VII) being the most abundant and stable under oxic conditions. However, recent analysis of tanks at the Hanford site suggest that up to 75% of the Tc present in the waste is not in the VII oxidation state[5]; while Tc oxidation state could not be determined, this portion would most likely be Tc(IV). While the reduction mechanism was not specifically addressed, it is likely due to catalysis from transition metals and Tc(IV) may be stabilized by organic ligands present in the waste[6]. Further analysis also showed that contrary to solubility predictions over 50% of the Tc was present in the aqueous phase, which is much higher than would be predicted at high pH[5]. Reduction of Tc(VII) to Tc(IV) has also been widely shown to occur in environmental conditions[7],[8],[9].
Recent studies report that organic ligands (e.g. oxalate, acetate, and EDTA) can form complexes with Tc(IV) and increase Tc(IV) solubility[10-13]. The role of humic acids in the mobilization and transport of Tc(IV) in the environment has also been investigated[14, 15]. In particular, Gu et. al[15]. have shown a ten fold increase in the solubility of Tc(IV) in the presence of humic substances at near neutral pH and demonstrated that humic acids mobilize Tc(IV) to the same extent as EDTA. However, the comparable effect of humics and EDTA on Tc(IV) solubility is quite unexpected based on the fact that Tc(IV) was recorded to form stronger complexes with EDTA than with a variety of humic substances[13, 16]. EXAFS analyses of Tc(IV)-humic acids[17] complex did not show any Tc(IV) oxygen bonds, but only observed Tc(IV)-Tc(IV) bonds, indicating a Tc(IV) colloid layer on the surface of the humics, as opposed to actually complexed Tc to humic carboxylic acid functional groups. However, these studies were performed at concentrations beyond Tc(IV) solubility limit, at which colloidal Tc(IV) would have likely formed; structural information for Tc(IV) complexes with humic substances at tracer concentrations is still not available.

One aspect that has not been well addressed in past studies is whether humic colloidal size can affect complexation characteristics; past published work on the interaction of Tc(IV) with humic substances did not account for the size and size distribution of the humic acid. Studies performed with size fractionated humic acids and Am$^{3+}$ have shown that humic acids of smaller size induce stronger interaction with Am$^{3+}$, while Am$^{3+}$ complexes with small size humics are more environmentally mobile[18]. Therefore, it is of great importance to know the effect of the size of humic acids on their interaction with Tc(IV).

Colloids (entities of size ranging from 1 to 1000 nm) play an important role in the migration of metals in the environment, in particular for the transport of radionuclides in the
subsurface[19][20][21][22]. Studies at the Nevada nuclear test site have determined that more than 90% of Pu, Cs, Eu and Co in the ground waters close to the site are associated with colloids [23]. While this specific case may not involve humic acid colloids, it shows the importance of colloids in contaminant migration. Many studies have investigated the influence of humic acid colloids on contaminant transports, but this particular body of literature sometimes lacks a systematic characterization of the humics used for the study. In particular, what role zeta potential may have in the behavior of colloidal humic acid. Recent advancements in laser technology have allowed for easy determination of mobility in solution and allow for measuring natural organic matter zeta potential. For example, the influence of Al$^{3+}$ on humic acids coagulation was correlated with the colloid zeta potential. There have however been very few studies that correlate zeta potentials and the binding of humics with metals. This paper presents a systematic study of the influence of humic acid origin, size, size distribution, and electrolyte nature on the humic binding with Tc(IV), using tools such as FTIR, NMR, and zeta potential determination.

**Experimental:**

Humic acids purchased from Sigma-Aldrich (SAHA) were purified following previously published works[14]. Briefly, the purchased solid was purified by dissolution in 0.02 M NaOH followed by precipitation with HCl or NaNO$_3$, depending on what background electrolyte the humic acid was to be used with. The solution was then centrifuged at 2000 rpm for 30 minutes and the supernatant discarded; the solid was then dissolved and re-precipitated twice more. The final precipitate was freeze-dried and stored at 2°C. Elliot Soil humic acid (ESHA) was purchased from the International Humic Substances Society with no further purification. Stock solutions of humic acid were prepared by dissolving the purified humic acid in freshly prepared
0.002 M NaOH, with the appropriate electrolyte, to produce 1000 ppm; the humic stock solutions were subsequently stored at 2°C for no longer than 1 month.

For experiments involving Tc(IV), 100 ppm humic acid solutions were prepared in an inert atmosphere (N₂) glovebox; solution pH were adjusted with NaOH and acid form of background electrolyte (HCl, HNO₃, HClO₄). Tc(IV) was prepared as explained elsewhere[12]. Humic samples were then spiked with 900 cpm/ml of Tc(IV). Spiked samples were allowed to equilibrate between 24 and 36 hours, the time necessary to reach a constant pH. Upon equilibrium, aliquots from each sample were centrifuged to separate desired size fractions. Using centrifugation once can selectively sediment sizes of specific diameter, leaving the smaller sizes in the supernatant. The size range sedimented is determined by a modification of Stokes Law (Equation 1):

\[
D = \sqrt{\frac{18\eta \ln \left( \frac{R_{max}}{R_{min}} \right)}{(\rho_p - \rho_f) \omega^2 t}}
\]

(Equation 1)

Where D is the diameter of the particle, η is the viscosity of the fluid, ω is the angular velocity of the rotor, ρp is the density of the particle and ρf is the density of the fluid the particle is suspended in. Rₘₐₓ and Rₘᵢₙ are the maximum and minimum distances of the sample vials from the middle of the rotor. For all particle sedimentation for sizes of 10 – 1000 nm ultracentrifugation was needed and performed on a Sorvall WX Ultra Series centrifugation was conducted under high vacuum (~1 mBar) and lasted between 15 and 30 minutes. A Thermo Fisher CL2 bench top centrifuge was used for sedimentation of particle sizes great than 1000 nm. Aliquots of 750 µl from each supernatant were put into 7 ml of EcoScint-O cocktail and counted using a Beckman-Coulter liquid scintillation counter (LSC). Oxidation state of selected samples
containing Tc was determined before and after centrifugation[24], to ensure that Tc(IV) did not oxidize to Tc(VII). In order to minimize error, the total amount of Tc(IV) was determined for selected samples and did not vary by more than 100 cpm/ml. Denver Instruments combination glass electrode and a Thermo-Fisher pH-meter and the electrode was calibrated daily with pH 4.01, 7.00, and 10.00 buffers (Fisher).

Dynamic light scattering (DLS) and zeta potential measurements were performed with a Beckman-Coulter DELSA-nano instrument. Sizing results were performed using a 1.0 cm quartz cell and calculated using the cumulants and polydispersion methods. Zeta potential (ζ) measurements were performed in triplicate at 30 V and calculated using Smuluchowski’s equation.

\[
\zeta = \frac{n \eta}{\varepsilon_0 \varepsilon_r} U
\]

Where \(\eta\) is the solution viscosity, \(U\) is the mobility of the particle, and \(\varepsilon_0\) and \(\varepsilon_r\) are the dielectric constant in vacuum and in the sample solvent respectively. All dielectric constants were obtained from the literature[25] or the instrument software database.

The percentage of humic acid in each size fraction was determined by taking the total percent carbon from an uncentrifuged aliquot of the sample and subtracting subsequent size fractions from this total (equation 3).

\[
\frac{\text{carbon fraction 1} - \text{carbon fraction 2}}{\text{Total carbon}} \times 100
\]

Where the Fraction 1 and 2 carbon are relative amount of carbon determined by TOC analysis for subsequent size fractions (i.e 1000 nm and 750 nm) and total is the total amount of carbon present in the sample.

The percent of Tc(IV) was calculated the same way, using counts from LSC to determine percentages in place of carbon.
Humic acid concentrations were quantified by measuring solution total organic carbon (TOC). Samples containing 100 ppm of humic acid were prepared using degassed DDI water and pH adjusted using NaOH and HCl or HNO₃. Samples were constantly stirred and stored in a light free environment for between 24 and 36 hours. Eight ml aliquots were sampled from each solution and centrifuged to separate desired size fractions, as explained above. After centrifugation, aliquots were taken from each sample and TOC was determined with a Shimadzu TOC-V instrument. Samples were purged with purified air for 90 seconds prior to analysis. Tc(IV) binding to humics and TOC analyses were performed in separate experiments; because these experiments were performed at very low Tc(IV) concentrations, the addition of Tc is not expected to affect humic size distribution.

Samples used in Attenuated Total Reflectance FT-IR (ATR-FTIR) and $^{13}$C Cross Polarization and Magic Angle Scattering NMR (CPMAS-NMR) analysis were filtered through 0.45 μm Wattman membrane filter, and the recovered solid was freeze dried. ATR-FTIR was performed using a diamond/ZeSe attachment on a Perking Elmer Spectrum 400 FTIR spectrometer. CPMAS results are from 20,000 scans on a Bruker DRX 400 NMR spectrometer (Oxford 9.4T, 89 mm magnet) using a Chemagnetics 5mm Triple Resonance HXY MAS probe.

Results and Discussion:

Figure 15 presents examples of results obtained for the humic size distribution and the concentration of Tc(IV) associated with each size fraction, at different pH, ionic strengths, and for SAHA and ESHA; additional examples are provided in the supplementary data. These data illustrate that an increasing ionic strength promotes larger humic sizes and greater amount of coagulation – as has been observed previously [21] – regardless of the origin of humic acids. This trend was also observed, but not as pronounced, with changes in pH. The size fraction
larger than 1000 nm is of particular interest, it accounts for $14 \pm 3\%$ of SAHA humic, at pH 4.5 in 0.1 M NaCl, while it increases drastically to $63 \pm 3\%$ at the same pH but in 1.0 M NaCl. Supplementary data show that such increase of the largest size fraction was also observed at pH 7.0, but to a much lesser extent. Figure 15 also presents the fraction of Tc(IV) bound to each humic size fraction. At lower ionic strengths, there is generally less Tc(IV) associated to the humic colloidal range than associated to the particles larger than colloids (> 1 μm), for both SAHA and ESHA. There is an overall increase in the fraction of Tc(IV) associated with humics as the concentration of larger humic particle sizes become more predominant. ESHA displays a smaller size increase with increasing ionic strength than SAHA does, but there is a significant increase in the amount of Tc(IV) bound to ESHA with an increasing ionic strength from 0.1 and 0.5 M, occurring simultaneously with a decrease of the concentration of the smallest size moieties (10-50 nm) and a significant increase of the concentration of the 250 – 1000 nm size range. In the case of SAHA, the largest contribution to the increase in humic acid is due to the > 1000 nm size fraction, while this size fraction increases drastically in overall percent of the humic acid there is little to no increase in the amount of Tc(IV) associated with it.

The ratios between the fraction of Tc associated with humic acid and the amount of humic acid that comprises the specific sizes are presented in Table 12. In the case of SAHA colloidal size fraction (10-1000 nm), the Tc(IV)-to-HA ratio remains at ca. 1:2, over the 0.1-to-1.0 ionic strength range (NaCl) and is pH independent. Such finding is significant as it can simplify future Tc/humics binding studies, allowing for the investigation of the strength of the Tc/humic moieties without an extended experimental matrix. Additionally, the 10-50 nm size range was dominate for ESHA until 0.5 I at pH 4.5 and 1.0 I at pH 7.0, while this size fraction was not prevalent in SAHA above 0.1I.
Table 12 also demonstrates that the Tc(IV)/SAHA ratio is independent of the sodium-based background electrolyte (NaCl, NaClO₄, or NaNO₃), as expected due to the small interactions between anions and humic acids. However, a change of electrolyte from NaCl to MgCl₂ leads to a humic size increase, as expected because of the larger cation charge in the case of MgCl₂, as explained previously [21]. However, the Tc-to-humic ratio is similar between solution in NaCl and MgCl₂.

In the case of the size fraction greater than 1000 nm, Table 12 reveals that the Tc-to-SAHA ratio varies significantly as ionic strength is increased from 0.1 to 1.0. This may be caused by a difference in mechanism of complexation (adsorption vs. complexation) or a substantial loss of carboxylic acid sites, which are expected to be responsible for metal complexation. Some variation in size within this range, observable by DLS, may be responsible for this but is not currently quantifiable. Further separation within this size range may be necessary but is difficult, as these particles are not stable in solution and precipitate without centrifugation.

The zeta potential for the smallest size fractions is not always measurable, as small sizes do not scatter light efficiently; additionally, zeta potential cannot be determined for high ionic strength solutions (0.5 M), as joule heating may influence results [24]. The zeta potential of the different humic acid size fractions for selected pH values and ionic strengths systems are presented with Figure 16. The zeta potentials determined for the bulk humic samples are within accepted literature values for similar systems [25][26]. Upon systematic sedimentation there was no observed change in the zeta potential at 0.1 I at both pH measured. This is would indicate that the colloidal range particles have the same, or similar, charges. Once the Ionic strength is increased to 0.5 I the zeta potential of the uncentrifuged bulk solution is less negative, which coincides with the increase in the greater than 1000 nm size fraction. After centrifuging to sediment
subsequent size fractions, the zeta potential remains constant with the results at 0.1. This is in agreement with the complexation data in this study, showing that there is a constant ratio of Tc(IV)/HA. The less negative zeta potential for the larger size fraction also explains their lack of stability in solution, as it is theorized that a zeta potentials between +20 mV and -20 mV will not be stable in solution and precipitate[25]. At ionic strength of 0.5 there was not enough humic left in solution to obtain reproducible zeta potential measurements for size fractions below 250 nm, they are expected to be similar to those at lower ionic strength.

Similar zeta potentials were observed when changing background electrolytes and SAHA, as well as for NaCl and ESHA. While the zeta potential with NaNO$_3$ is slightly more negative than that of NaCl (-52 ± 2, pH 7.0 : -43 ± 3, pH 4.5), there is no increase in complexation over the colloidal range. It would be expected that a more negative zeta potential would lead to more efficient complexation, but the difference in potential may not be great enough to change the complexation characteristics in this case.

For an electrolyte with a cation of larger charge, MgCl$_2$, the humic zeta potential is 15 ± 1 mV, at both pH 4.5 and 7 and 0.1 I. The less negative zeta potential is expected to lead to more coagulation and eventual precipitation. Due to the gross amounts of coagulation, we were unable to obtain zeta potential results after size discrimination. Even thought nearly 100% of the humic is in the colloidal and > 1000 nm size range, the same Tc(IV)/HA ratio is observed, while no overall trend in the > 1000 nm range is observed. The lack of change in humic metal binding characteristics when the background electrolytes are varied shows that humic binding with metals may be modeled as independent of the background electrolyte, as long as humic sizing and humic zeta potential properties are known. This may prove to be an important step in simplifying future attempts at modeling colloidal complexation.
From these results we can conclude that the zeta potential of the colloidal range is not affected by changes in ionic strength, and is minimally affected by changes in background anion. These findings are in agreement with the Tc(IV)/HA ratios determined in this study as well as previously published stability constant data [11, 27]. This may also provide an explanation for the fact that less Tc(IV) binding is observed when the lowest size fraction is dominant. For similar concentrations of different humic size fractions, the humic of smaller sizes will have much larger surface area and, consequently, the larger sizes will be able to “out compete” the smaller sizes for metal binding. It may also be that while this size fraction is included in the definition of colloidal, composition may differ between colloidal fraction and the fraction of larger sizes. Due to its low abundance and small size, it is difficult to single out this size range for further analysis by the means currently available. It would be prudent to investigate these quasi-colloidal ranges to determine specifically if there is any difference in its chemical composition.

There is also a rather constant Tc(IV) binding ratio observed between pH 4.5 and pH 7 (Table 12). Tc(IV)/humic binding constants previously determined were two orders of magnitude greater for the TcOOH\(^+\) species, which is present at pH 4.5 [13]. Although there is great differences between binding constants between pH 4.5 and pH 7, large difference in complexation is not expected to be present under these conditions, because 91 ± 4 and 99 ± 3 % of the Tc(IV) is expected to be complexed at pH 7.0 and pH 4.5, respectively, with 100 pmm humic. These binding constant are also determined based on experiments that did not differentiate humic size fractions.

ATR-FTIR analysis of dried humic filtrates are shown in Figure 17. The ESHA solid spectrum is in agreement with spectrum published by the International Humic Substance Society. The FTIR
data show that the solid forms of ESHA and SAHA are very different, with both having stretches from many different carbon functional groups. However, there is little influence of the ionic strength on the FTIR data for SAHA. While there is a large difference in the overall spectra for SAHA and ESHA, there is little difference in the COO\(^{-}\) asymmetrical stretches at ca. 1560 cm\(^{-1}\) between the two humics. We believe that this is the most important portion of the spectra as these functional groups are the most important in metal binding. While the COO\(^{-}\) functional groups appear to be the major factor in metal binding, further analysis of all of the carbon functional groups needs to be completed to determine how they may influence size distribution.

Solid state C\(^{13}\) CPMAS-NMR of the humic stock solutions and of selected filtrated solid are shown in Table 13. The filtration process did not alter the humic substances, as there is no change in NMR spectra. There is also no change in the ratio of carbon containing functional groups as ionic strength and size distribution is varied, an indication that the individual size fractions do not differ significantly in composition. There is however differences between SAHA and ESHA, especially with respect to the carbon functional groups that we do not associate with metal complexation. While the NMR data shown do not show any correlation between metal binding and carbon functional groups, more studies are needed to determine if any trends in coagulation and size distribution can be extrapolated from these types of studies.

This paper shows that a wide variety of analytical methods allowed to study the binding between Tc(IV) and humic acids of different sizes. We have observed that most metal binding occurred for the 50-1000 nm size fractions, with much less binding with the small 10-50 nm and large < 1000 nm size fractions. Spectroscopic data demonstrated that this is likely not due to a difference of composition of the different size fractions, but that the Tc binding is driven by surface charge. Zeta potential measurements show that the < 1000 nm humic size fraction has a
less negative zeta potential, and thus would not be expected to bind metal as efficiently as the more highly charged smaller size fractions. While we are currently not able to obtain zeta potential measurements for the 10-50 nm size fraction, it is likely that it has a similar zeta potential to the other colloidal sized particles. If such case, it would also have a much higher surface area (per mass unit) than the other size fractions and, at equal humic concentration, smaller sizes will bind more metal than larger humic size. However, if the fraction of humic of very small size is minimal, its metal binding may be negligible compared to the binding of humic of larger sizes. Competition for metal binding between the size fractions may also play a role, and the smaller colloidal size would have a surface area disadvantage if the surface charges are the same.

These studies also showed a trend in the metal binding between the colloidal humic acid moieties and Tc(IV), independent of the source of the humic acids. The trend is maintained over large increases in ionic strength, pH, and with multiple background electrolytes. This is important as such parameters may influence the humic acids functional group distributions as well as coagulation characteristics, and while the strength of the humic binding to Tc(IV) have been well documented in the literature, the binding constants were not influenced by pH and ionic strength. Future studies with more variation of zeta potential are needed to allow for greater accuracy in complexation modeling. Such analyses will aid in future evaluation of radio-contaminated areas, as well as in the planning of future storage sites and waste forms.

Acknowledgements

This work was supported by the Office of the Biological and Environmental Research, Office of Science, U.S. Department of Energy (DOE) under the grant DE-FG02-08ER64696 with Washington State University and by the U.S. Nuclear Regulatory Commission under the grant
3808953. The authors would also like to thank the NMR Center at Washington State University for their help with CPMAS NMR work.
References


List of figures:

**Figure 15.** Percentage of Tc(IV) (Red) or humic acid (Grey) associated with different size fractions (nm) with NaCl used to control ionic strength, determined after size discrimination performed via ultracentrifugation. 1-3 are SAHA at pH 4.5 and ionic strength 0.1, 0.5 and 1.0 respectively. 4-6 are ESHA at pH 7.0 and ionic strength 0.1, 0.5 and 1.0 respectively.

**Figure 16.** Zeta potentials, in mV, for different pH, ionic strength, and humic acid sources after selective sedimentation by ultracentrifugation. Errors are 2s, and all measurements were performed in at least duplicate.

**Figure 17.** ATR-FTIR spectra of selected humic acid dry filtrates (0.45 μm) at different pH and ionic strength.

**Table 12.** %Tc(IV) sorbed to humics-to-% humic acid ratio for ESHA and SAHA as a function of pH, ionic strength, and background electrolytes (BGE) after size discrimination performed via ultracentrifugation.

**Table 13.** Carbon functional group relative abundances from C\(^{13}\) CP-MAS NMR of selected humic acid dry filtrates (0.45 μm)
Figure 16: Zeta potentials, in mV, for different pH, ionic strength, and humic acid sources after selective sedimentation by ultracentrifugation. Errors are 2s, and all measurements were performed in at least duplicate
Figure 17: ATR-FTIR spectra of selected humic acid dry filtrates (0.45 μm) at different pH and ionic strength
<table>
<thead>
<tr>
<th>HA source</th>
<th>Ionic strength</th>
<th>pH</th>
<th>BGE</th>
<th>%HA</th>
<th>%Tc(IV)/%HA</th>
<th>%HA</th>
<th>%Tc(IV)/%HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESHA</td>
<td>0.1</td>
<td>4.5</td>
<td>NaCl</td>
<td>41 ± 4</td>
<td>0.4 ± 0.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>7</td>
<td>NaCl</td>
<td>22 ± 3</td>
<td>0.2 ± 0.3</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.5</td>
<td>NaCl</td>
<td>50 ± 4</td>
<td>0.4 ± 0.1</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>7</td>
<td>NaCl</td>
<td>37 ± 3</td>
<td>0.2 ± 0.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.5</td>
<td>NaCl</td>
<td>47 ± 5</td>
<td>0.7 ± 0.2</td>
<td>3 ± 3</td>
<td>0.1 ± 3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7</td>
<td>NaCl</td>
<td>36 ± 3</td>
<td>0.7 ± 0.3</td>
<td>14 ± 4</td>
<td>0.2 ± 3</td>
</tr>
<tr>
<td>SAHA</td>
<td>0.1</td>
<td>4.5</td>
<td>NaCl</td>
<td>40 ± 3</td>
<td>0.6 ± 0.2</td>
<td>12 ± 4</td>
<td>0 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>7</td>
<td>NaCl</td>
<td>17 ± 3</td>
<td>0.6 ± 0.1</td>
<td>11 ± 4</td>
<td>0.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.5</td>
<td>NaCl</td>
<td>40 ± 3</td>
<td>0.6 ± 0.1</td>
<td>24 ± 4</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>7</td>
<td>NaCl</td>
<td>29 ± 3</td>
<td>0.8 ± 0.2</td>
<td>9 ± 4</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.5</td>
<td>NaCl</td>
<td>17 ± 3</td>
<td>0.6 ± 0.3</td>
<td>63 ± 4</td>
<td>0.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7</td>
<td>NaCl</td>
<td>43 ± 4</td>
<td>0.5 ± 0.1</td>
<td>8 ± 4</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>4.5</td>
<td>NaNO₃</td>
<td>45 ± 4</td>
<td>0.6 ± 0.1</td>
<td>3 ± 3</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>7</td>
<td>NaNO₃</td>
<td>22 ± 2</td>
<td>0.8 ± 0.1</td>
<td>3 ± 2</td>
<td>0.5 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>4.5</td>
<td>NaClO₄</td>
<td>42 ± 3</td>
<td>0.6 ± 0.1</td>
<td>3 ± 2</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>7</td>
<td>NaClO₄</td>
<td>25 ± 4</td>
<td>0.5 ± 0.2</td>
<td>3 ± 2</td>
<td>0.5 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>4.5</td>
<td>MgCl₂</td>
<td>11 ± 2</td>
<td>0.7 ± 0.1</td>
<td>77 ± 4</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>7</td>
<td>MgCl₂</td>
<td>15 ± 2</td>
<td>0.7 ± 0.1</td>
<td>32 ± 3</td>
<td>0.5 ± 0.2</td>
</tr>
</tbody>
</table>

Table 12: %Tc(IV) sorbed to humics-to-% humic acid ratio for ESHA and SAHA as a function of pH, ionic strength, and background electrolytes (BGE) after size discrimination performed via ultracentrifugation
Table 13: Carbon functional group relative abundances from $^{13}\text{C}$ CP-MAS NMR of selected humic acid dry filtrates (0.45 μm).
Chapter 6

PREFACE

These studies were preformed out of our need to be able to determine the oxidations state of Tc that we were using. They were born out of necessity, but have evolved into an ongoing and larger study. This chapter is meant to show a proof of concept for the separation of Tc(VII) and Tc(IV) oxidation states.

One of the first problems that I ran into with my research was being able to prove that I had obtained a pure Tc(IV) solution. In the literature one method of determining oxidation states of Tc was widely used, but there had been no published studies characterizing it. Upon attempting to use this method as documented in the literature we obtained varying results, which were contradictory to other results, and were not reproducible. Thus we were left to believe that this method is not actually suitable for oxidation state determination, and another had to be found.

The literature did offer one example of separating Re oxidation states, as Re is a decent analog of Tc, we sought to use this method. This chapter shows that we were able to obtain full extraction of Tc(VII), with minimal influence of Tc(IV). We have not been able to fully explain the slight extraction of Tc(IV), but it is likely that the extractant used may degrade in solution, or have impurities present in it.

This is the full manuscript that will be submitted to the *Journal of Radioanalytical and Nuclear Chemistry*. 
Rapid Separation of IV/VII Technetium Oxidation States by Iodonitrotetrazolium Chloride by Solvent Extraction

Mark A. Boggs, Larissa C. Gribat, Cherilynn A. Boele, Nathalie A. Wall

Washington State University, Chemistry Department, Pullman, WA 99163. USA

Keywords: Technetium, Pertechnetate, Tc(IV), INT, Solvent extraction

Abstract:

Technetium\(^{99}\) poses a difficult problem to many Department of Energy sites, as there are multiple incidents of release into the environment due to large quantities that are held in storage tanks. Laboratory scale experiments with the lower oxidation states of Tc are difficult to perform as there is not a well characterized method of determining oxidation state of low concentration samples. These studies offer a solvent extraction system for rapid separation and oxidation state determination between the +7 and +4 oxidation states. Tc(VII) can be extracted by INT in chloroform, while Tc(IV) remains in aqueous solution.

Introduction

Technetium poses a particularly difficult problem at many United States Department of Energy (DOE) nuclear waste storage sites. At both the Hanford and Oak Ridge sites, in Washington state and Tennessee respectively, \(^{99}\)Tc has been released into the environment\(^{1,2}\). At Hanford, up to 30 Ci of \(^{99}\)Tc have been released into the vadose zone.

\(^{1}\) Corresponding author: nawall@wsu.edu
and are expected to reach the Columbia river in the near future; there is almost 30,000 Ci of \(^{99}\text{Tc}\) in underground storage currently at the Hanford site\(^3\).

Technetium can be found in oxidation states ranging from +1 to +7, with the +7 and +4 being the most common. \(\text{Tc(VII)}\) exists as the pertechnetate anion, \(\text{TcO}_4^-\), which is highly mobile in the environment, while \(\text{Tc(IV)}\) exists primarily as the sparingly soluble \(\text{TcO}_2\times\text{H}_2\text{O}\text{(am)}\) solid. Recent studies of waste stored at the Hanford site have found that up to 75% of the technetium waste in some tanks is not in the +7 oxidation state, with 50% of that being in the aqueous phase\(^4,5,6\). While specific oxidation state of Tc was not identified, \(\text{Tc(IV)}\) is the most likely form.

A method to separate \(\text{Tc(IV)}\) from \(\text{Tc(VII)}\) is through the use of tetraphenolphosphonium chloride\(^7,8,2\), but a specific understanding of the separation process is still missing. Because of a lack of knowledge of the limits of this method, a more robust well-characterized method for rapid analysis of Tc oxidation states +4 and +7 is sought after. Iodonitrotetrazolium chloride (INT) has been used to separate many different oxidation states of transition metals\(^9,10\). Studies of INT have shown that separations of Re(IV/VII) oxidation states are easily achievable\(^11\) and rhenium is generally considered a good analog of technetium, especially in the +7 oxidation state\(^12\). This work aims to create a fast and robust method to separate \(\text{Tc(VII)}\) from \(\text{Tc(IV)}\) using INT in a solvent extraction system.

**Procedure**

All salts and buffers used were reagent grade (Fisher) and were dissolved in DDIW. Iodonitrotetrazolium chloride (INT) solutions were stored in dark glassware and fresh solutions were prepared weekly. \(\text{Tc(VII)}\) was obtained from aliquots of \(\text{NH}_4\text{TcO}_4\) (Oak
Ridge), used without further purification. Tc(IV) was prepared from NH$_4$TcO$_4$, as previously described$^{13-15}$. Aqueous solution pH values were maintained with sodium acetate, 2-Morpholinoethanesulfonic acid Monohydrate(MES), and 3-(Tris(hydroxymethyl)methylamino)propane-1-sulphonic acid(TAPS) buffers were used for pH 3-4, 5-6, and 7-8 respectively. All extractions of Tc(IV) were performed in an atmospherically controlled glovebox (N$_2$, 99.999%). Separation extractions were performed by contacting 1 ml of an aqueous solution of 0.8 mM INT, ~1000 cpm Tc(VII) and/or ~1000 cpm Tc(IV), 10 mM NaCl, and 1.0 mM buffer, and 1.0 mM EDTA with 3 ml of chloroform for 15 minutes – EDTA is known to strongly complex Tc(IV) in aqueous solution, but not Tc(VII)$^{16}$. Upon equilibration, at least 500 ml of each phase were sampled and activities were determined by liquid scintillation counting (Beckman LS 6500); aqueous solution pH were determined. Sampling for liquid scintillation counting was for aqueous phase due to a slight quenching from the organic phase solvent. Solubility experiments were performed by contacting an aqueous phase of 0.8 mM INT and 10 mM NaCl with 3 ml of chloroform, and shaking to emulsion for 15 minutes. Post contact the aqueous phase concentration of INT was measured by UV-VIS at 250 nm with a Varian Carrie 5000 UV-Vis spectrophotometer.

**Results and Discussion**

In order to maximize extraction of Tc(VII), the concentration of INT in aqueous phase was varied from 0.1 to 1.0 mM in a system that contained Tc(VII) but no Tc(IV).

Results, presented with Figure 15, show that 0.8 mM of initial concentration of INT in aqueous solution is necessary to reach maximum extraction of 600-1400 cpm Tc(VII) in chloroform; the extraction is independent of pH between 3 and 8.
In subsequent tests, extraction of Tc(IV) was studied in absence of Tc(VII), using an initial 0.8 mM INT in aqueous phase and a varying Tc(IV) concentration. Tests consisted in samples containing increasing Tc(IV) activity, from 500 cpm/mL to 2000 cpm/mL. Upon equilibration, the chloroform phase consistently contained 120 ± 15 cpm/mL, regardless of the initial Tc concentration and the aqueous solution pH. Consequently, 120+/− 15 cpm/mL of Tc(IV) is soluble in the chloroform phase, in presence of 0.8 mM INT. No evidence of Tc(IV) in chloroform was observed in absence of INT. The percent Tc(IV) and Tc(VII) left remaining in the aqueous phase shows a consistent extraction of Tc(IV) into the chloroform from pH 3-8. (Figure 16) The percent Tc(IV) was corrected for the 120 ± 15 cpm/mL of Tc(IV) is soluble in the chloroform phase. The authors of a previous publication\textsuperscript{11}, in which Re(IV) was used, hypothesized that species extracted by INT to the chloroform phase would be anionic, thus likely ReCl\textsubscript{6}^{2−}. This should be the case at very low aqueous phase pH, but not at the higher pH used in these studies – Tc(IV) extraction remains unchanged over a pH range, while Tc speciation varies greatly over this pH range. In the current studies EDTA is used as a holdback agent for Tc(IV), and TcOEDTA\textsuperscript{2−} is expected to be the dominate species from pH 4 to 7.5\textsuperscript{16}. Complexation between INT and TcOEDTA\textsuperscript{2−} is possible, but again TcOEDTA\textsuperscript{2−} concentration varies in the pH range studied. Thus the authors believe that the extraction of Tc(IV) is controlled by INT-Tc(IV) species solubility in chloroform.

Further experiments were performed with both oxidation states of Tc present, using 0.8 mM INT, with different Tc(IV)/Tc(VII) ratios. Data (Table 12) show that almost all the equivalent of Tc(IV) activity alone remained in the aqueous phase, thus Tc(VII) was extracted in the chloroform phase, regardless of the Tc(IV)/Tc(VII) ratio. However, the
slight solubility of a Tc(IV)-INT complex in the chloroform phase discussed above, must be accounted for; we observe that the difference between the activities of the original Tc(IV) spike and in the post-extraction aqueous phase remains constant at 120 ± 15 cpm/mL.

Experiments performed to quantify the solubility of INT in chloroform showed that, in absence of Tc, 0.010 ± 1 mM INT is extracted into chloroform, over the range of pH used in this work. The percent INT remaining in the aqueous phase was 40 ± 5 % (Figure 17). INT solubility in chloroform may be due to impurities in the INT; formation of formazans are well documented, as well as quite strong complex with metals have been observed\textsuperscript{17}. This may also account for the relative high concentrations of INT (0.8 mM) needed to extract Tc(VII) as well. Furthermore, formazans have limited solubility in water, which may explain the solubility of the Tc(IV) species in the organic phase. Further studies are needed to determine the exact mechanism of Tc(IV) extraction, as direct observation of a formazan Tc(IV) complex has not been made.

Despite a low solubility of Tc(IV)-INT in the organic phase the system described here has shown to be fast, reproducible, and robust over a wide range of pH. This rapid method allows for laboratory scale experiments, especially those needing a rapid, well characterized, method for Tc oxidation state analysis.
References


List of Tables

Table 14: Separation of Tc VII/VI oxidation states (0.01 I) with 0.8 mM INT and vary concentrations of Tc(VII). Errors are 3σ of triplicates.

List of Figures

Figure 18: Extraction of ca. $2 \times 10^{-7}$ M Tc(VII) from an aqueous phase of 1 mM sodium acetate (pH 3.0) and 1 mM TAPS (pH 8.0) buffers into an organic phase chloroform. Results are from triplicate experiments; errors are reported as 3 sigma

Figure 19: Percent Tc Remaining in the Aqueous Phase as a function of pH (0.1 I) with 0.8 mM INT; errors are reported as 3σ. The Tc(IV) data is corrected for the small solubility of Tc(IV) into chloroform

Figure 20: UV-Vis Spectra of 0.02 mM INT in aqueous phase
Figure 21: Extraction of ca. $2 \cdot 10^{-7}$ M Tc(VII) from an aqueous phase of 1 mM sodium acetate (pH 3.0) and 1 mM TAPS (pH 8.0) buffers into an organic phase chloroform. Results are from triplicate experiments; errors are reported as 3 sigma.
Figure 22: Percent Tc Remaining in the Aqueous Phase as a function of pH (0.1 I) with 0.8 mM INT; errors are reported as 3σ. The Tc(IV) data is corrected for the small solubility of Tc(IV) into chloroform.
Figure 23: UV-Vis Spectra of 0.02 mM INT in aqueous phase.
<table>
<thead>
<tr>
<th></th>
<th>% Tc in Aqueous (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc(IV) initial</td>
<td>38 ± 1</td>
<td>45 ± 2</td>
</tr>
<tr>
<td>Tc(VII) initial</td>
<td>62 ± 1</td>
<td>55 ± 2</td>
</tr>
<tr>
<td>Tc Aq post extraction pH 3.0</td>
<td>32 ± 7</td>
<td>63 ± 3</td>
</tr>
<tr>
<td>Tc Aq post extraction pH 8.0</td>
<td>33 ± 2</td>
<td>63 ± 22</td>
</tr>
</tbody>
</table>

Table 15: Separation of Tc VII/VI oxidation states (0.01 I) with 0.8 mM INT and vary concentrations of Tc(VII). Errors are 3σ of triplicates.
Chapter 7

CONCLUSIONS

Summary

Technetium poses a particularly difficult problem at multiple DOE sites, as its long half-life and the vast quantities currently stored will have to be accounted for a very long time. This is compounded by the large amounts that have been released into the environment, due to the fact that Tc(VII), predominant in oxic environment, is highly mobile. While VII oxidation state is expected to account for the bulk of the Tc in the environment, recent studies suggest that Tc(IV) may be an important factor when considering environmental mobilities. The chemistry of lower oxidation states of Tc, specifically IV, was not well understood and very little information was available in the literature on their possible behavior in the environment.

The purpose of the work included in this thesis was to quantify and understand the interactions of Tc(IV) with organic complexing ligands and humic acids. Such work is important for determining solubility and speciation of Tc that has been released into the environment, as well as allow for greater understanding of the behavior of Tc currently stored at multiple DOE sites.

The complexation of Tc(IV) with acetate was investigated over a wide range of ionic strengths (NaCl) and the stability constant at zero ionic strength was modeled using SIT\textsuperscript{1}, Table 13. Using the stability constants determined for acetate and Tc(IV), the solubility of Tc(IV) was modeled, using the PHREEQC software. The results show that acetate
does not affect the solubility greatly, as expected due to the rather weak complexing capability of acetate. These studies showed that we were able to determine stability constants for Tc(IV) with carboxylic acids, and that complexation reactions with Tc(IV) have a potential to greatly affect Tc(IV) solubility.

Studies of the complexation of Tc(IV) with EDTA were performed, to further elucidate the influence of organic ligand complexation on Tc(IV) solubility. A much stronger complex was formed between Tc(IV) and EDTA, compared to that of Tc(IV) and acetate, as presented by Table 13. This was expected, as an increase in the number of carboxylic acid groups leads to an increased stability constant. EDTA also formed complexes with multiple Tc(IV) species, which implies that EDTA can affect Tc solubility over a wide pH range. The solubility of Tc(IV) in the presence of EDTA was modeled and calculations showed that the addition of 2.5 mM EDTA leads to an increase in Tc solubility by two orders of magnitude, in agreement with experimentally determined solubility data obtained by Gu. et al2.

The complexation studies described above allowed for highlighting the difficulty and the importance of understanding system speciations. Through these studies many different species of Tc(IV) were predicted to occur, based on previously published thermodynamic data, including cations (TcOOh⁺), anions (TcO(OH)₂⁻), and neutral (TcO(OH)₂₀) species. Each of these species must be accounted for to accurately describe Tc solubility and ultimately its migration in the environment. The cationic species are expected to be the least mobile, as there are many negatively charged mineral phases which can immobilize these species. Due to limited interactions with mineral phases, the neutral and anionic species can be expected to be very mobile in the environment. To further complicate
matters, the effect of complexing organic ligands on the solubility of Tc(IV) must also be included. The determination of stability constants provides a foundation for future investigations and for the creation of accurate environmental mobility models.

To accurately predict the environmental mobility of Tc(IV), complexation with humic substances must be included. Humic substances environmental ubiquity and ability to form strong complexes with metals implies that they will greatly influence the mobility of Tc(IV). The stability constants for a variety of humic and fulvic acids were determined, and quantifications are shown in Table 13. Strong complexation, with binding constants that are independent of source of humics, was observed for Tc(IV) and humic substances. The lack of a difference between complexation by humic and fulvic acid was not expected; in previously published work on humic and fulvic metal complexation there is roughly a one order of magnitude stronger complexation with humic acid. We have not yet been able to fully explain this discrepancy between this Tc work and previous work with other metals; however, our findings were confirmed by the solubility studies performed with humic and fulvic acids from the Field Research Center in Oak Ridge Tennessee.

To better understand the complexation of Tc(IV) with soil humic acid, a larger body of work was performed to study the influence of particle size and charge on complexation was investigated. These studies show a preferential complexation between Tc(IV) and humic acid particles in the 50 – 1000 nm range. Particles in the size ranges smaller and larger than this range did not bind to Tc(IV) as efficiently, which can be due to different reasons. Zeta potential measurements show that the larger particles sizes are less negatively charged than those of smaller size, and thus would lead to less metal binding.
However, the 10-50 nm particles have a zeta potential similar to that of the 50-1000 nm particles, despite binding less to Tc(IV). Thus, the lack of binding would likely be due to the fact that smaller size lead to decreased surface areas and, therefore, fewer binding sites. These same trends were observed as the background electrolyte was changed from NaCl to NaNO₃, NaClO₄, and MgCl₂. Within the 50 -1000 nm size range a somewhat constant fraction of bound Tc to humic acids was observed; this bound Tc fraction was found independent of pH, background electrolyte, and ionic strength. Trends such as these are important, as they can be used in future models of Tc(IV) complexation with humic acid under a wide variety of conditions.

Further analysis of humic acid solids by IR and solid state NMR show major differences in composition between the different sources of humic acids used. However, these differences were not observed within each source as size changed. This points towards the size fractions being similar in composition, and thus the binding mechanism being the same. Metal complexation could then be explained by changes in charge (zeta potential) of the different particles.

Complexation of Tc(IV), or any other metal, with humic substances is difficult to characterize, especially when only one or two variables are considered. In order to truly understand these processes the dynamic nature of humic substances needs to be considered (i.e. humic characteristic modifications with changes of solution conditions).

**Future work**

There are many paths that this present work could be expanded. Tc(IV) solution speciation data are still lacking. The low solubility of Tc(IV) limits the types of
techniques that can be used to investigate solution speciation. Measurements using EXAFS have been made with Tc(IV), but the concentrations of Tc(IV) needed for such experiments is so high (e.g. 1x10^-4 M or greater) that there is undoubtedly colloidal Tc(IV) present. The same problems hold true for potentiometric titrations as well. The lack of direct observation of many of the species thought to be present in solution is troublesome.

In many studies the presence of colloidal Tc(IV) is deemed to be an interference, and is avoided. Colloidal formation of other metals, such as Pu, has been shown to greatly alter their interaction with minerals, even at low concentrations of metal. There is little information in the literature on the colloidal properties of Tc(IV). Furthermore, there have been no studies to investigate Tc(IV) colloid formation under environmental or storage. If a greater understand the interaction of Tc(IV) with complexing agents in the environment is to be obtained, it is imperative to account for Tc colloids.

Further studies of the nature of humic substances are obviously needed. Humic substances are incredibly difficult to fully describe without using a litany of instruments and techniques. Yet, there may be simplified methods that can describe smaller attributes, like metal binding. These studies have shown that there are trends of complexation and that knowing with knowledge of only few parameters (i.e. zeta potential, size distribution, ionic strength), one can determine the amount of Tc(IV) bound to the organic matters. If this were to be expanded to cover more metals our ability to model the role that humic acids play in the transport of radio-contaminates would be greatly increased.
The use of advanced spectroscopic techniques, such as solid and liquid state NMR, allows for determining specific compositional make up of individual humic acids. Zeta potential determination may help predicting the amount of Tc(IV)-humic moeties, but there is currently no method to predict the coagulation characteristics of different humic acid sources in presence of metals or not. A combination of systematic analysis using NMR and IR of a variety of sources of humic substances would allow for developing trends in composition and coagulation to be determined and therefore developing vast simplifications in modeling of radio-contaminates binding to humic substances.
References


<table>
<thead>
<tr>
<th>Ligand</th>
<th>M,H,L</th>
<th>logβ (0.5 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>1,-1,1</td>
<td>2.46 ± 0.03</td>
</tr>
<tr>
<td>EDTA</td>
<td>1,0,1</td>
<td>17.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1,1,1</td>
<td>22.1 ± 0.5</td>
</tr>
<tr>
<td>Humic Acid</td>
<td>1,-1,1</td>
<td>6.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1,-2,1</td>
<td>4.3 ± 0.4</td>
</tr>
<tr>
<td>Fulvic Acid</td>
<td>1,-1,1</td>
<td>6.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>1,-2,1</td>
<td>3.9 ± 0.3</td>
</tr>
</tbody>
</table>

*Table 16* Stability constants with various ligands and Tc(IV) at 0.5 M (NaCl).
Appendix 1
Complexation of Tc(IV) with acetate at varying ionic strengths

By M. A. Boggs1, W. Dong2, B. Gu1 and N. A. Wall1,∗

1 Department of Chemistry, Washington State University, Pullman, WA 99164-4630, USA
2 Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

(Received September 30, 2009; accepted in revised form March 9, 2010)

Tc(IV) / Acetate stability constant / Solvent extraction / Specific ion interaction theory

Summary. In order to accurately model and predict the fate and transport of metals and radionuclides at multiple radio-contaminated sites, there is a need for an understanding on how metals such as technetium interact with their environment. Many contaminated sites are known to contain large amounts of organic ligands that can affect the solubility and mobility of metals. This study focuses on the effect of acetate on the complexation and dissolution of Tc(IV). Studies were performed at pH 4.5 (±0.3), at which TcOOH+ is the predominant species. The stability constants for the TcOOH-acetate complex were determined at ionic strengths varying from 0.5 to 3.0 M (NaCl), using a solvent extraction method. The stability constants showed the expected increasing trend over the range of ionic strengths, from 2.46 ± 0.03 (I = 0.5) to 3.09 ± 0.08 (I = 3.0). A stability constant of 2.8 ± 0.16 at zero ionic strength was determined by specific ion interaction theory. Geochemical modeling data suggest that the dissolution of TcO2·1.6H2O is not greatly affected by the presence of acetate, at concentrations equal or less than 20 mM.

1. Introduction

The chemical processes used to separate plutonium from uranium generated wastes containing actinides, fission products, and chelating agents. As a result, mixtures of complexing organic ligands and radioisotopes co-exist at a number of disposal sites within the US Department of Energy complex [1]. At the Field Research Center (FRC) at Oak Ridge (TN), 99Tc is present at concentrations as high as 31 000 pCi/L in groundwater and 95 pCi/g in sediments; while acetate concentrations can reach 26 mg/L [2]. The FRC is but one example of Tc contamination, there is thought to be about 500 Ci of Tc at the Hanford site that has entered the vadose zone and has the potential to enter the feeds of the Columbia River [3]. Tc can exist in several oxidation states; while Tc(VII) is predominant in the environment and has been shown to be highly mobile [4], Tc(IV) can be present under reductive conditions in soils rich in biogenic Fe(II), such as those found at the Oak Ridge FRC [5]. Although little is currently known about Tc(IV) mobility, it is thought that Tc(IV) will form the insoluble TcO2·1.6H2O and will remain relatively immobile [6]. There is currently little known about Tc(IV) behavior in presence of strong chelating agents, such as acetate, ubiquitous in the environment as well as in current storage sites [1]. Previous studies have shown that Tc(IV) can form strong complexes with oxalic acid [7] and it is expected to also form soluble complexes with acetate, although with weaker stability constants than the oxalate complexes. This paper describes the experimental data and modeling work performed to determine the stability constants of Tc(IV)/acetate complexes, using a solvent extraction method. Consequences for Tc(IV) solubility are drawn from the data obtained.

2. Experimental

All solutions were prepared from reagent-grade chemicals in de-ionized distilled water (DDIW). NaCl (Fisher) solutions were used as a background electrolyte to control the ionic strength, from 0.5 to 3.0 M, in all experiments. 0.5 M sodium acetate (Fisher) solutions were prepared at appropriate ionic strengths. NaCl and sodium acetate solutions were filtered over 0.22 µm pore size Nalgene filters. A 0.1 M bis-(2-ethylhexyl) phosphoric acid (HDEHP) (Sigma-Aldrich) in hexane (Fisher) solution, used as the organic phase for all extractions, was shielded from light for the duration of the experiments. A Tc(IV) stock solution was prepared according to Hess et al. [8]. Briefly, an aliquot of 0.29 M NH4TcO4 (Oak Ridge) was added to water and freshly prepared 0.195 M Na2S2O4 (Mallínckrodt); the solution pH was raised to 12 to form a TcO2·xH2O amorphous black slurry, which was then washed three times with 0.01 M Na2S2O4. The Tc(IV) precipitate was separated by centrifugation, after a 72 h equilibration period, and dissolved in concentrated HCl (Fisher). The Tc(IV) stock solution was authenticated using an Ocean Optics USB4000 UV-Vis spectrometer, showing the TcCl62− peak [8]. An aliquot of this solution was diluted to obtain 4000 cpm per 20 µL, in 1 M HCl. Tc reduction and all subsequent experiments were performed in an oxygen-free glove box (<1 ppmO2(g)), to maintain Tc in its reduced form. Solvent extraction experiments were performed by vigorously shaking 1.5 mL of NaCl solutions with varying amounts of acetate, 4000 cpm Tc(IV) and at pH adjusted to 4.5 (±0.2), with equal volume of the 0.1 M HDEHP solution for at least 4 h. All experiments were con-
ducted at room temperature (25 ± 1 °C). 1.0 mL aliquots were drawn from each phase and diluted with Eco-scint cocktail for liquid scintillation counting (LSC) (Beckman Coulter LS6500 liquid scintillation counter). Each aqueous phase pH was measured using a Denver Instruments combination glass electrode and a Thermo-Fisher pH-meter. The electrode was calibrated daily with pH 4.01 and 7.00 buffers (Fisher) and the pH-meter readings (i.e. pHR) were converted to pH values (i.e. −log[H⁺]) by the following equation, determined as explained elsewhere [9, 10]:

\[ \text{pH} - \text{pHr} = 0.301 + 0.04 \]  

where I is the ionic strength in M (NaCl).

Additionally, aliquots of the aqueous phase of selected samples were equilibrated with 0.001 M methyltrioctylammonium bromide in methylene chloride, which has been shown to extract Tc(VII) anionic species only, not Tc(IV) cationic species [11]. Results showed that Tc(IV) did not oxidize to Tc(VII) over the course of the experiments.

3. Data treatment

The metal-ligand complexation reactions are generally described as (charges omitted for simplicity):

\[ m\text{M} + n\text{H} + z\text{L} \rightleftharpoons \text{M}_m\text{H}_n\text{L}_z \]  

with the stability constant defined as:

\[ \beta_{m,n,z} = [\text{M}_m\text{H}_n\text{L}_z] / [\text{M}]^m [\text{H}]^n [\text{L}]^z \]  

where a negative \( n \) value indicates an hydroxo species. For the solvent extraction system in question the distribution ratio \( (D) \) is defined as:

\[ D = \sum [\text{M}_{aq}] / \sum [\text{M}_{org}] \]  

Labeling \( D \) as the distribution of metal without ligand, using known stability constants for the metal hydrolysis, considering the formation of only one ML complex, and the absence of CO₂(g) or any buffer in the system, Eq. (4) becomes:

\[ D_0 / D - 1 = \beta_{\text{MHL}} [\text{L}] / (1 + \text{OH}\beta_{1}[\text{OH}] + \text{OH}\beta_{2}[\text{OH}]^2) \]  

With, in the case of a monoprotic acid:

\[ [\text{L}] = [\text{L}] / (1 + 10^{\text{pK}_a - \text{pH}}) \]  

and

\[ \text{OH}\beta_{1} = [\text{MOH}] / ([\text{M}] [\text{OH}]) \]  

\[ \text{OH}\beta_{2} = [\text{M(OH)}_2] / ([\text{M}] [\text{OH}]^2) \]  

In the particular case of our work, the experiments were performed at pH 4.50 ± 0.2, to ensure the presence of deprotonated acetic acid. TcOOH⁺ and TcO(OH)₂ are the only species present at such pH, as shown on Fig. 1; TcO²⁺ is negligible. As a result, in the case of the formation of one MOHL complex, Eq. (5) is modified:

\[ D_0 / D - 1 = \beta_{\text{TcOOHL}} [\text{Ac}^-] / (1 + \text{OH}\beta_{1}[\text{OH}]) \]  

with

\[ \text{OH}\beta_{1}' = [\text{TcO(OH)}] / ([\text{TcOOH}⁺ · [\text{OH}]) \]  

Eq. (9) shows that \( \beta_{\text{TcOOHL}} \) values can be determined from the linear plot of \( D_0 / D - 1 \) as a function of [\text{Ac}⁻], which slope is \( \beta_{\text{TcOOHL}} / (1 + \text{OH}\beta_{1}[\text{OH}]) \). Values of acetic acid pKₐ and pKₜ at specific ionic strength are presented in Table 2. The value of \( \text{OH}\beta_{1}' \) (i.e. at zero ionic strength) was used for all calculations, because of the lack of information currently available for the determination of this parameter at higher ionic strengths; its value, calculated from Tables 1 and 2 data, is 10⁻⁰⁻⁰⁻¹.

Specific ion interaction theory (SIT) [12] was used to determine the stability constant of the TcO(OH)Ac complex at zero ionic strength, from the experimental data obtained

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \log K^a )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TcO²⁺ + H₂O ↔ TcOOH⁺ + H⁺</td>
<td>0.0072</td>
<td>[8]</td>
</tr>
<tr>
<td>TcO²⁺ + 2H₂O ↔ TcO(OH)₂ + 2H⁺</td>
<td>−4.00</td>
<td>[12]</td>
</tr>
<tr>
<td>TcO²⁺ + 3H₂O ↔ TcO(OH)₃ + 3H⁺</td>
<td>−14.9</td>
<td>[12]</td>
</tr>
<tr>
<td>TcO₂⁻·1.6H₂O ↔ TcO(OH)₂ + 1.6H₂O</td>
<td>−8.4 ± 0.5</td>
<td>[12]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( I_a )</th>
<th>( pK_a )</th>
<th>Acetate ( pK_t )</th>
<th>( \Delta Z^2D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>13.72</td>
<td>4.50</td>
<td>−0.349</td>
</tr>
<tr>
<td>1.02</td>
<td>13.70</td>
<td>4.52</td>
<td>−0.407</td>
</tr>
<tr>
<td>1.55</td>
<td>13.74</td>
<td>4.60</td>
<td>−0.439</td>
</tr>
<tr>
<td>2.09</td>
<td>13.78</td>
<td>4.65</td>
<td>−0.461</td>
</tr>
<tr>
<td>2.65</td>
<td>13.86</td>
<td>4.73</td>
<td>−0.477</td>
</tr>
<tr>
<td>3.20</td>
<td>13.93</td>
<td>4.96</td>
<td>−0.490</td>
</tr>
</tbody>
</table>

a: Ref. [13];  
b: Ref. [14].

Fig. 1. PHREEQC predicted Tc(IV) species distribution using Table 1 hydrolysis constants at \( I = 0 \) in the absence of ligand and assuming total [Tc(IV)] = 10⁻⁶ M under O₂⁻ and CO₂⁻ free conditions. Total [Tc(IV)] is over-saturated at pH ≥ 2 with regard to the solubility of TcO₂⁻·1.6H₂O."
within the 0.5–3.0 M ionic strength range. SIT modeling is expressed in the following way:

$$\log \beta_{i-1}^\circ = \log \beta_{i-1} - \Delta Z^2 D + \Delta \varepsilon I_m$$  \hspace{1cm} (11)

where \(I_m\) is the ionic strength expressed in molality. The stability constant of the TcOOHAc complex at zero ionic strength is \(\log \beta_{i-1}^\circ\) and \(\log \beta_{i-1}\) is the experimental stability constants at a non-zero ionic strength. \(\Delta Z^2\) is relative to the change in charge from the uncomplexed to complexed metal ligand couple and is defined as:

$$\Delta Z^2 = (Z_{m1}^2 - Z_{m2}^2)$$  \hspace{1cm} (12)

and \(D\) is the Debye–Hückel term with \(A\) and \(aB\) defined as 0.509 kg^{1/2} mol^{1/2} and 1.5 kg^{1/2} mol^{1/2}, respectively [12]:

$$D = AI_m^{1/2} / (1 + aBI_m^{1/2})$$  \hspace{1cm} (13)

The term \(\Delta \varepsilon\) is the ion interaction parameter for the cation anion pair in question; it is mostly independent of the ionic strength [12, 15]. The stability constant of the TcOOHAc complex at zero ionic strength is extrapolated from the fitting of the plot of \[\log \beta_{i-1} - \Delta Z^2 D\] as a function of \(I_m\). Predicted aqueous speciation and solubility were calculated from the SIT data using the publicly available geochemical equilibrium speciation code PHREEQC [16].

### 4. Results and discussion

Fig. 2 shows an example of a \(D_0 / D - 1\) as a function of \([\text{Ac}^-]\), for the system at 0.5 M (NaCl) ionic strength and \(p\text{H} 4.75 \pm 0.03\). The linear regression of the plot indicates the presence of a single TcOOHAc complex; supplementary experiments performed at \(p\text{H} 6.5\) showed no complexation between TcO(OH), and acetate. Table A1 of Appendix A presents data obtained for each ionic strength studied, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 M; only one set of data is presented for each ionic strength, for conciseness, but the experiments were performed in triplicate. Table 3 shows that the TcOOHAc complex logarithm of the stability constant varies from 2.46 (±0.06) to 3.1 (±0.2), from 0.5 to 3.0 M ionic strength, respectively. The value of \(\log \beta_{i-1}^\circ\) was determined to be 2.8 ± 0.3 with \(\Delta \varepsilon\) at −0.28 ± 0.08.

![Fig. 2. Experimental data of \((D_0 / D - 1)\) as a function of free acetate concentration and its linear regression. \((I = 0.5\ M \ (\text{NaCl}), 25^\circ \text{C}, \ p\text{H} 4.75 \pm 0.03\), and \(p_{\text{CO}_2} = p_{\text{O}_2} = 0\).](image)

![Fig. 3. PHREEQC modeled solubility of Tc(IV)O\(_2\).1.6H\(_2\)O in presence varying amount of acetate in the pH range 3.5–6.5 using Table 1 reaction constants and the stability constant of TcO(OH)Ac complex obtained in this work at \(I = 0\ M\).](image)

As previously mentioned, the value of \(\text{OH}^+ \beta_1^0\) was used for all calculations, because tools are not yet available to calculate it at non-zero ionic strengths. While stability constants vary with ionic strength, we can show that it does not significantly alter our final calculations. For instance, the decrease of the first and second hydrolysis logarithm of the stability constants from 3 M ionic strength to 0 M ionic strength for UO\(_2^{2+}\), a polyatomic oxo-cation of same charge as TcO\(_2^{2+}\), is only 3 and 1%, respectively, (17). Assuming that Tc(IV) hydrolysis constant undergoes a similar trend, the final logarithm of the stability constant of the acetate complex at 3 M ionic strength deviates by only 3% from our reported results, a difference that falls within the error reported for this work. It is more appropriate to compare the variation of Tc(IV)O\(_2^{2+}\) hydrolysis with that of U(VI)O\(_2^{2+}\), rather than with a tetravalent cation, such as U(IV)\(_{2+}\), because the cations bear the same charge and are both oxocations, which takes precedent over the fact that TcO\(_2^{2+}\) and U\(_{2+}\) have the same oxidation state.

The small stability constants observed in this work for TcOOHAc are indicative of relatively weak acetate complexes, as expected; acetate has only one carboxylic acid group and stability constants often increase with the number of carboxylic acid groups, as observed for the lanthanide and actinide series [17, 18]. This trend is also found with transition metal complexes; for example, \(\log \beta_{i-1}\) for Mn\(_{2+}\) increases from 0.8 for acetate to 3.8 for citrate [17]. The weak TcOOHAc complex has little effect on the dissolution of solids; the stability constants determined in this paper were used to model the dissolution of TcO\(_2\).1.6H\(_2\)O in the
Appendix A. Experimental data

Table A1. Examples of distribution data for Tc(IV) acetate extraction (0.1 M HDEHP) experiments.

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[Ac]_{\text{expt}} (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 0.5 M (NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>526</td>
<td>671</td>
<td>0.391</td>
<td>0.0183</td>
<td>4.78</td>
</tr>
<tr>
<td>551</td>
<td>758</td>
<td>0.363</td>
<td>0.0217</td>
<td>4.74</td>
</tr>
<tr>
<td>609</td>
<td>758</td>
<td>0.451</td>
<td>0.00667</td>
<td>4.93</td>
</tr>
<tr>
<td>674</td>
<td>802</td>
<td>0.420</td>
<td>0.0133</td>
<td>4.84</td>
</tr>
<tr>
<td>559</td>
<td>716</td>
<td>0.390</td>
<td>0.02</td>
<td>4.92</td>
</tr>
<tr>
<td>549</td>
<td>767</td>
<td>0.357</td>
<td>0.0267</td>
<td>4.92</td>
</tr>
<tr>
<td>494</td>
<td>741</td>
<td>0.333</td>
<td>0.033</td>
<td>4.92</td>
</tr>
</tbody>
</table>

| I = 1.5 M (NaCl) |
| 619 | 1171 | 0.528 | 0.0216 | 4.57 |
| 904 | 987 | 0.915 | 0.005 | 4.57 |
| 827 | 1104 | 0.749 | 0.00833 | 4.58 |
| 712 | 1030 | 0.691 | 0.0116 | 4.5 |
| 713 | 1120 | 0.636 | 0.015 | 4.48 |
| 728 | 1084 | 0.671 | 0.0166 | 4.59 |
| 634 | 1159 | 0.547 | 0.0183 | 4.7 |

| I = 2.0 M (NaCl) |
| 585 | 844 | 0.693 | 0.005 | 4.56 |
| 518 | 879 | 0.589 | 0.0083 | 4.63 |
| 448 | 806 | 0.555 | 0.015 | 4.48 |
| 466 | 875 | 0.532 | 0.018 | 4.57 |
| 441 | 847 | 0.520 | 0.01 | 4.57 |
| 438 | 853 | 0.513 | 0.016 | 4.58 |
| 400 | 935 | 0.427 | 0.023 | 4.54 |
| 380 | 920 | 0.413 | 0.03 | 4.55 |
| 372 | 924 | 0.402 | 0.033 | 4.5 |
| 356 | 883 | 0.403 | 0.036 | 4.53 |

| I = 2.5 M (NaCl) |
| 500 | 707 | 0.707 | 0.005 | 4.89 |
| 625 | 838 | 0.745 | 0.0083 | 4.88 |
| 502 | 761 | 0.659 | 0.011 | 4.85 |
| 435 | 826 | 0.526 | 0.018 | 4.83 |
| 432 | 854 | 0.505 | 0.021 | 4.83 |
| 382 | 859 | 0.444 | 0.025 | 4.77 |
| 626 | 733 | 0.854 | 0.005 | 4.71 |
| 547 | 916 | 0.597 | 0.015 | 4.72 |
| 514 | 856 | 0.600 | 0.018 | 4.73 |
| 439 | 891 | 0.492 | 0.021 | 4.74 |

Table A1. Continued.

<table>
<thead>
<tr>
<th>Organic (cpm)</th>
<th>Aqueous (cpm)</th>
<th>D</th>
<th>[Ac]_{\text{expt}} (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 3.0 M (NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>634</td>
<td>939</td>
<td>0.675</td>
<td>0.005</td>
<td>4.79</td>
</tr>
<tr>
<td>563</td>
<td>1017</td>
<td>0.553</td>
<td>0.00833</td>
<td>4.72</td>
</tr>
<tr>
<td>572</td>
<td>1112</td>
<td>0.514</td>
<td>0.0116</td>
<td>4.79</td>
</tr>
<tr>
<td>519</td>
<td>1152</td>
<td>0.450</td>
<td>0.015</td>
<td>4.76</td>
</tr>
<tr>
<td>545</td>
<td>1140</td>
<td>0.478</td>
<td>0.0166</td>
<td>4.81</td>
</tr>
<tr>
<td>517</td>
<td>1224</td>
<td>0.422</td>
<td>0.0183</td>
<td>4.86</td>
</tr>
<tr>
<td>378</td>
<td>1220</td>
<td>0.309</td>
<td>0.025</td>
<td>4.86</td>
</tr>
</tbody>
</table>

Acknowledgment. This work was supported by the Office of the Biological and Environmental Research, Office of Science, US Department of Energy under the grant DE-FG02-08ER64696 with Washington State University and under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, which is managed by UT-Battelle LLC.

References


Appendix 2
ABSTRACT: To understand the key processes affecting $^{99}$Tc mobility in the subsurface and help with the remediation of contaminated sites, the binding constants of several humic substances (humic and fulvic acids) with Tc(IV) were determined, using a solvent extraction technique. The novelty of this paper lies in the determination of the binding constants of the complexes formed with the individual species TcO(OH)$^-$ and TcO(OH)$_2^0$. Binding constants were found to be 6.8 and between 3.9 and 4.3, for log$\beta_{1-1.5}$ and log$\beta_{1-2.4}$, respectively; these values were little modified by a change of ionic strength, in most cases, between 0.1 and 1.0 M, nor were they by the nature and origin of the humic substances. Modeling calculations based on these show TcO(OH)$^-$$-$HA to be the predominant complex in a system containing 20 ppm HA and in the 4–6 pH range, whereas TcO(OH)$_2^0$ and TcO(OH)$_2^-$$-$HA are the major species, in the pH 6–8 range.

ATOMIC Number: 43

INTERACTION Tc(IV) with Humic Substances

Mark A. Boggs,* Travis Minton,† Wenming Dong,‡ Samuel Lomasney,‡ Mohammed R. Islam,* Baohua Gu,‡ and Nathalie A. Wall†,*

†Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, United States
‡Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Interactions of Tc(IV) with Humic Substances

$^{99}$Tc is a significant environmental contaminant, with a long half-life of $2.1 \times 10^9$ years, found in sites such as the U.S. Department of Energy (DOE) Oak Ridge Integrated Field Research Center (IFRC) and Hanford site. At Oak Ridge, $^{99}$Tc is present in groundwater and sediments at concentrations as high as 31 nCi/L and 95 pCi/g, respectively; the Hanford site shows four large $^{99}$Tc groundwater plumes 5— including one showing 90 pCi/L of $^{99}$Tc in the 200 area  — and 15 $\mu$Ci/kg. $^{99}$Tc has been found in the vadose zone, near underground tanks. 3 $^{99}$Tc presents a challenge for clean up because of its complex mobility in the environment.

Although Tc valence state can vary from VII to III, 4 Tc(VII) (in the form of pertechnetate oxyanion, TcO$_4^-$) is the most stable in natural oxidizing environments, rendering it highly mobile in environmentally relevant pH conditions, because of its high solubility in water and essentially nonadsorptive properties toward sediment minerals. However, Tc(VII) can be reduced in the environment, to produce relatively immobile and sparingly soluble Tc(IV) species. The biogenic Fe(II) reduction of TcO$_4^-$ has been observed in many instances; for example, in unamended soil, representative of a United Kingdom nuclear site 5,6 clay minerals; 7 subsurface materials from the U.S. Department of Energy’s Hanford and Oak Ridge sites 1,8,9 and core samples from a shallow sandy aquifer that contained Fe(II). 10 Tc(IV)O$_2$•$\times$H$_2$O(s) has a very low solubility of $10^{-8}$ M, under reducing conditions and in a pH ranging from 4 to 9.11,11 but Tc(IV) is more soluble at higher pH: $10^{-6}$ M at pH 14.12 and is especially soluble in acidic solution: $10^{-3}$ M at pH $\leq 1.13$ The species issued from the solubility of TcO$_2$.1.6 H$_2$O(am) were identified as the hydrolyzed species TcO$_2^{5+}$(aq), TcO(OH)$_2^{3+}$(aq), TcO$_2$(OH)$_2^{0}$(aq), and TcO(OH)$_2$$(aq)$, in absence of carbonate; Guillaumont et al. reported that the presence of carbonate leads to the formation of the species Tc(CO$_3$)$_2$(OH)$_2^{3+}$(aq) and Tc(CO$_3$)$_3$(OH)$_3^{2+}$(aq),14 however a more recent work demonstrates that at least 0.01 M carbonate must be present to induce the formation of Tc(IV) carbonate species. 14 Yet, Tc(IV) solubility can increase in the presence of complexing organic ligands; for example, Tc(IV) forms complexes with oxalate and acetate 15,16 and experiments showed that an increase of oxalate concentration from $10^{-6}$ M to $10^{-5}$ M increased Tc(IV) solubility from $10^{-8}$ M to $10^{-3}$ M, at pH 4. 17

Humic substances (HS), organic colloids derived from the degradation of natural organic matter, are traditionally segregated in three major groups, humic acids (HA) that precipitate at low pH, fulvic acids (FA) that are soluble at all pH, and humin that is insoluble at all pH. HS are known to strongly bind metals (e.g., refs 18–20). The past decade literature has shown evidence of Tc(IV)–humics species, using a combination of XANES and gel permeation chromatography 21 or by surface-enhanced Raman spectroscopy (SERS). 22 As predicted, such complexes affect Tc solubility; it was suggested that the presence of organic matter maintained Tc in a soluble form, in buried peat, in spite of an excess of Fe(II), 10 while a study showed that the 160 ppm of organic matter contained in Gorleben groundwater enhanced Tc dissolution by 2 orders of magnitudes, under neutral and alkaline anoxic conditions. 21 Studies also showed that HS increase Tc(IV) mobility. 23 While the formation of soluble Tc(IV)–HS species had been studied in terms of ligand–metal complexation, for solutions of low Tc(IV) concentrations (e.g., ref 24), a combination of XANES and EXAFS measurements implied an HS sorption onto Tc(IV) colloids, in suspensions containing near-to-millimolar amounts of Tc, under slightly basic pH and reducing conditions. 25 Trace levels of Tc(IV) interactions with Boom Clay HS samples in synthetic clay water of neutral pH.

Received: October 8, 2010
Accepted: February 4, 2011
Revised: January 19, 2011
Published: March 02, 2011


156

2718
were quantified using a modified Schubert method; the logarithm of the binding constants of the TcO(OH)$_2$–HS complexes was found to be 5.3 ± 0.3, in an HS equivalence/L basis, or 2.6–2.3. (±0.3), using a g HS/L basis. The experiments described in the literature presented above were performed with HS, without segregation of HA from FA; and, more importantly, the experiments have been performed only in pH regions where neutral and negative Tc(IV) species occur, but the binding constant to each individual species have not been determined. This paper present the experimental determination of the binding constant of several HA and one FA samples with TcO(OH)$_2$ and TcO(OH)$_3$ at different ionic strengths, using a solvent extraction method and modified Schubert calculations. Speciation calculations were also conducted based on these results.

**EXPERIMENTAL SECTION**

**Humic Solution Preparations.** All solutions were prepared from reagent-grade chemicals in deionized distilled water. The Oak Ridge IFRC HA (FRCHA) and FA (FRCFA) were obtained from a background toposoil at the U.S. Department of Energy’s Integrated Field Research Challenge (IFRC) site at the Y-12 National Security Complex in Oak Ridge, Tennessee. Details of the extraction procedures and characteristics of these humic materials were given elsewhere. Humic acids purchased from Sigma Aldrich HA were purified according to the literature; purified Sigma Aldrich HA will be referred to as SAHA for the continuation of this paper. The purified Elliot soil humic acids (ESHHA) were purchased from The International Humic Substances Society (IHSS) and used without further purification. All stock humic substances solutions were prepared in deionized water and were stored at 1–3 °C when not in use.

**Potentiometric Titration.** Potentiometric titrations were conducted with a Denver Instrument model 352 autotitrator, connected to a PHC2401–a Denver electrode and a TitraMaster 85 software Version 5.0.0 (Radiometer Analytical). All titrations were performed at 25 °C, in a jacketed vessel, and under a blanket of N$_2$ (g). The electrode was calibrated daily, by conducting a titration of standardized 0.5 M HCl (Fisher) with carbon-free standardized 0.5 M NaOH (Fisher), at the desired ionic strength (NaCl, Fisher). The daily electrode calibration also provided the equation for the potential expression, V, as a function of the calculated pcH (−log[H$^+$]), for each ionic strength studied, as presented in Table 1. HS potentiometric titrations were then carried out by measuring the weight of 0.02 g HS to the fourth decimal, to which a known amount of DDIW was added and enough 5.0 M NaCl to reach the appropriate ionic strength. Small aliquots of carbon-free standardized 0.1 M NaOH (Fisher) and set at the appropriate ionic strength (NaCl) were slowly added, under constant stirring, until pH was measure to be between 10.75 and 11.00; the total amount of added NaOH was recorded (the NaOH solution added was too small to modify the sample ionic strength). The HS solution was allowed to equilibrate for at least 20 min before titrated with standardized 0.05 M HCl (Fisher) set at the appropriate ionic strength (NaCl); the titrant was added at a maximum rate of 0.1 mL/min, allowing a next titrant addition only if the potential deviation between two consecutive measurements did not exceed 0.6 mV/min (a difference of 0.01 pH unit/min), after a 30 s measurement; when an inflection point was detected, the autotitrator automatically decreased the amount of titrant addition. The titration was set to be completed when the potential reached a value of 260 mV (pH 2.5). pK$_a$ values and carboxylic site capacities were determined graphically, from the titration curve first derivatives, as described elsewhere; carboxylic sites are responsible for HS metal binding at the pH values of this work. Each HS titration was performed in triplicates.

**Solvent Extraction.** A Tc(IV) stock solution was prepared according to the literature. Briefly, an aliquot of 0.29 M NH$_4$+$\text{H}_{2}$TcO$_4$ (Oak Ridge) was added to water and freshly prepared 0.195 M Na$_2$S$_2$O$_4$ (Mallinckrodt); the solution pH was raised to 12 to form a TcO$_2$·xH$_2$O(am) black slurry, which was then washed three times with 0.01 M Na$_2$S$_2$O$_4$. The Tc(IV) precipitate was separated by centrifugation, after a 72 h equilibration period, and dissolved in concentrated HCl (Fisher). The Tc(IV) stock solution was authenticated using an Ocean Optics USB4000 UV−vis spectrometer, showing the characteristic TcCl$_2^{2−}$ peak. For the extraction performed at ionic strengths equal or larger than 0.5 M, the Tc(IV) stock solution was prepared by diluting an aliquot of the previous Tc(IV) solution in 1 M HCl to obtain 4000 cpm per 20 μL. For extractions performed at 0.1 M ionic strength, a second Tc(IV) stock solution was prepared; 1 mL of the previous Tc(IV) stock solution prepared in concentrated HCl was evaporated to dryness, using acetone (Fisher) and redissolved in 5 mL of DDIW. Tc reduction and solvent extraction experiments were performed in an oxygen-free glovebox (<1 ppm O$_2$(g)), to maintain Tc in its reduced form. NaCl (Fisher) solutions were used as a background electrolyte to control the ionic strength, from 0.1 to 1.0 M, in all experiments. Sodium acetate (Fisher) or MES (Sigma-Aldrich) solutions were used to buffer NaCl solutions at pH 4.8 and 6.8, respectively. NaCl and sodium acetate solutions were filtered over 0.22 μm pore size Nalgene filters. A solution of 0.05 M Cyanex 272 (Cycltech Industries) with 0.05 M Tri-Octylphosphine oxide (TOPO) (Sigma-Aldrich − 99%) in hexane was used for the extractions at pH 6.8. A 0.1 M Bis-(2-ethylhexyl) phosphoric acid (HDEHP) (Sigma-Aldrich-97%) in hexane (Fisher) solution was used for the extractions at pH 4.8 and kept in the dark when not in use.

Solvent extraction experiments were performed by vigorously shaking, for 24 h and at room temperature (25 ± 1 °C), 1.5 mL of an aqueous solution with an equal volume of organic extractant solution (Cyanex+TOPO in hexane for extractions at pH 6.8 and HDEHP in hexane for experiments at pH 4.5); the NaCl aqueous solutions contained varying amounts of H$_5$, 6000 cpm Tc(IV), either 0.005 M sodium acetate or 0.01 M MES, and enough NaOH or HCl to adjust the pH to the desired value. Upon equilibration, 750 μL aliquots were drawn from each phase and diluted to 7.0 mL with Eco-scint cocktail for liquid scintillation counting (Beckman Coulter LS6500 liquid scintillation counter). Each aqueous phase pH was measured using a Denver Instruments combination glass electrode and a Thermo-Fisher pH-meter. The electrode was calibrated daily with pH 4.01 and 7.00 buffers (Fisher) and the pH-meter readings (i.e, pHr) were

<table>
<thead>
<tr>
<th>ionic strength (NaCl, M)</th>
<th>s</th>
<th>yo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>57.6 ± 0.02</td>
<td>370.2 ± 0.1</td>
</tr>
<tr>
<td>0.50</td>
<td>58.8 ± 0.02</td>
<td>381.4 ± 0.2</td>
</tr>
<tr>
<td>1.00</td>
<td>59.1 ± 0.02</td>
<td>386.5 ± 0.2</td>
</tr>
</tbody>
</table>

Table 1. Electrode Calibration As a Function of the Ionic Strength (NaCl): V = s·pH + yo, Where V is the Electrode Potential in mV and pH is −log[H$^+$]. Errors are 2σ of replicates.
converted to pH values (i.e., $\log[H+]$) by the following equation, determined as explained elsewhere:32,34

$$\text{pH} - \text{pH}_{R} = 0.30 \cdot I + 0.04$$  \hspace{2cm} (1)$$

where $I$ is the ionic strength in M (NaCl).

It was ensured that HS stayed in aqueous solution, by spectrophotometrically measuring their concentration in the aqueous phases, before and after extraction. Tables showing examples of extraction data are available as Supporting Information.

**Data Treatment.** At pH 6.8, TcO(OH)$_2$ is the dominant aqueous species according to previous calculations$^6$ since the experiments were performed in the presence of MES buffer, which does not complex metals. Therefore, the equilibria of concern at such pH are:

$$\text{TcO(OH)}_2^+ + \text{HS} \rightleftharpoons \text{TcO(OH)}_2^{-} \text{HS}$$  \hspace{2cm} (2)$$

and

$$\text{TcOOH}^+ + \text{OH}^- \rightleftharpoons \text{TcO(OH)}_2^0$$  \hspace{2cm} (3)$$

with the complex binding and stability constants defined as follow:

$$\beta_{i_1-2,1} = \frac{[\text{TcO(OH)}_2^0 - \text{HS}]}{[\text{TcO(OH)}_2^0]}$$  \hspace{2cm} (4)$$

$$\beta_{i_1-2,0} = \frac{[\text{TcO(OH)}_2^0]}{[\text{OH}^-][\text{TcOOH}^+]}$$  \hspace{2cm} (5)$$

The humic concentrations account for the carboxylic capacity, the humic $K_a$ values, and the pH at which the experiments are performed:

$$[\text{HS}] = C_{\text{HS}} \cdot \alpha_{\text{HS}} \cdot \text{capacity}_{\text{HS}}$$  \hspace{2cm} (6)$$

where $C_{\text{HS}}$ is the total HS concentration; $\alpha_{\text{HS}}$ the degree of ionization of HS at the experiment pH$_i$ and capacity$_{\text{HS}}$ the HS capacity determined in this paper by potentiometric titration.

The distribution coefficient ($D$) of Tc between the organic and aqueous phases is defined as the ratio between the sum of Tc species in the organic phase and the sum of Tc species in the aqueous phase:

$$D = \frac{\sum [\text{Tc}_{\text{org}}]}{\sum [\text{Tc}_{\text{aq}}]}$$  \hspace{2cm} (7)$$

Labeling $D_0$ as the distribution of metal without ligand, in absence of CO$_2$(g) or any metal complexing buffer in the system, the equation becomes:

$$D_0 = \frac{[\text{TcO(OH)}_2^0] + [\text{TcO(OH)}_2^{-} - \text{HS}]}{[\text{TcO(OH)}_2^0]}$$  \hspace{2cm} (7)$$

Therefore:

$$\frac{D_0}{D} - 1 = \beta_{i_1-2,1} [\text{HS}]$$  \hspace{2cm} (8)$$

The plot of $D_0/D-1$ as a function of $[\text{HS}]$ is a linear regression, which slope is $\beta_{i_1-2,1}$.

However, at pH 4.5, about 34% of Tc(IV) is present as TcOOH$^+$ species, and 66% as TcO(OH)$_2^0$ according to previous calculations.$^{16}$ Therefore, the following equilibrium is considered in addition to eq 2

$$\text{TcO(OH)}^+ + \text{HS} \rightleftharpoons \text{TcO(OH)} - \text{HS}$$  \hspace{2cm} (9)$$

| Table 2. Selected Tc(IV) Reactions and Associated Thermodynamic Constants at Zero Ionic Strength Considered in This Work |
|---|---|---|
| reactions | $\log K_0$ | ref |
| TcO$^{2+}$ + H$_2$O $\rightleftharpoons$ TcOOH$^+$ + H$^+$ | 0.0072 | 13 |
| TcO$^{2+}$ + 2 H$_2$O $\rightleftharpoons$ Tc(OH)O$_2^0$ + 2 H$^+$ | -4.00 | 11 |
| TcO$^{2+}$ + 3 H$_2$O $\rightleftharpoons$ Tc(OH)$_3$ + 3 H$^+$ | -14.9 | 11 |

| Table 3. Additional Data Necessary for $\beta_{i_1-1,1}$ Calculations |
|---|---|---|
| I (M, NaCl) | pK$_{Ac}^*$ | acetate pK$_{Ac}$ | log $\beta_{i_1-1,Ac}$ $^5$ |
| 0.1 | 13.83 | 4.56 | 2.74 $^*$ |
| 0.5 | 13.72 | 4.50 | 2.46 ± 0.06 |
| 1.0 | 13.70 | 4.52 | 2.7 ± 0.1 |

With the associated binding constant expressions:

$$\beta_{i_1-1,1} = \frac{[\text{TcOOH} - \text{HS}]}{[\text{TcOOH}^+][\text{HS}]}$$  \hspace{2cm} (10)$$

Considering Tc second hydrolysis, shown in eq 3 and Tc complexation with acetate, used to buffer pH:

$$\text{TcOOH}^+ + \text{Ac}^- \rightleftharpoons \text{TcOOH} - \text{Ac}$$  \hspace{2cm} (11)$$

and its respective stability constant:

$$\beta_{i_1-1,Ac} = \frac{[\text{TcOOH} - \text{Ac}]}{[\text{Ac}^-][\text{TcOOH}^+]}$$  \hspace{2cm} (12)$$

the ratio of Tc distribution coefficients, described in eqs 7–9 becomes:

$$\frac{D_0}{D} = \frac{[\text{TcOOH}^+] + [\text{TcO(OH)}_2^0] + [\text{TcO(OH)}_2^-] + [\text{TcO(OH)}_2^{-} - \text{HS}]}{[\text{TcOOH}^+] + [\text{TcO(OH)}_2^0] + [\text{TcO(OH)}_2^-] + [\text{TcO(OH)}_2^{-} - \text{HS}]}$$  \hspace{2cm} (13)$$

and:

$$\frac{D_0}{D} - 1 = \frac{(\beta_{i_1-1,1} + \beta_{i_1-2,1} \beta_{i_1-2,0}[\text{OH}^-])}{1 + \beta_{i_1-2,0}[\text{OH}^-] + \beta_{i_1-1,Ac}[\text{Ac}^-]} \times [\text{HS}]$$  \hspace{2cm} (14)$$

where $[\text{HS}]$ is defined by eq 6 and $[\text{Ac}^-]$ is the concentration of deprotonated acetate at the experiment pH and ionic strength. The plot of $D_0/D-1$ as a function of $[\text{HS}]$ provides a linear regression; the only unknown term of the slope expression is $\beta_{i_1-1,1}$, as $\beta_{i_1-2,1}$ was determined in this work, from the experiments conducted at pH 6.8, $\beta_{i_1-2,0}$ can be calculated from the literature.$^{11,13}$ $\beta_{i_1-1,Ac}$ was previously determined by this group.$^{16}$ The data necessary to calculate $\beta_{i_1-1,1}$ are presented in Tables 2 and 3. The value for $\log \beta_{i_1-1,Ac}$ at 0.1 M was extrapolated using the specific ion interaction theory (SIT) modeling and the parameters described by Boggs et al.$^{16}$

**RESULTS AND DISCUSSION**

**HS Potentiometric.** HS titration curves were similar to that presented in previous published work.$^{35}$ For each potentiometric titration, three inflection points were detected, corresponding to


158
two different carboxylic sites (the two first inflection points) and one phenolic site (the last inflection point, at higher pH), as explained elsewhere. The $pK_a$ values of each HS functional group (determined at the half equivalence points) and the total carboxylic capacities are presented in Table 4. The values of $pK_{a1}$ and $pK_{a2}$ are that of carboxylic groups and $pK_{a3}$ of phenolic groups. Table 4 results are in accordance with those presented elsewhere with other humic substances, including the fact that the ionic strength has little influence on most $pK_a$ values, except for SAHA within the ionic strength range 0.1–0.5 M. The deviation we would obtain, had we had access to nonzero ionic strength hydrolysis constants, would fall within the errors of our reported binding constants, as explained elsewhere.

Our results for the binding constants of humic and fulvic acids with $\text{TcO(OH)}^+$ (log$\beta_{1,-1,1}$) and $\text{TcO(OH)}_2^0$ (log$\beta_{1,-2,1}$) are presented in Table 4. The values of log$\beta_{1,-1,1}$ were determined at 0.1 M, 0.5 M, and 1.0 M ionic strengths, for FRCFA, FRCHA, and SAHA; the similarity of the results between each humic and at the three ionic strengths lead to conclude that log$\beta_{1,-1,1}$ would not significantly vary either between humics at a fixed ionic strength, or for one particular humic material between different ionic strengths. Therefore, log$\beta_{1,-2,1}$ were determined at only one ionic strength, 0.5 M, for all the humic substances studied. Similar stability constants between humic acids of different origin have been observed in the past, in particular for the binding of other humic acids with uranyl. However, Tc(IV) binding constants are unexpectedly similar between HA and FRCFA complexes, whereas previous works have shown a difference of at least 1 order of magnitude between HA and FA binding constants with actinides, with HA complexes being the strongest. The log$\beta_{1,-2,1}$ value of the Tc(IV) complex with the IHSS HA sample ESHA is again similar to those obtained with the other humics studied in this work. It is unsure at this point, if the similar strength of complexes between the HA samples and FRCFA is due to the nature of FRCFA, which may

Table 4. HS Potentiometric Titration Results and Binding Constants with $\text{TcO(OH)}^+$ (log$\beta_{1,-1,1}$) and $\text{TcO(OH)}_2^0$ (log$\beta_{1,-2,1}$)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Ionic strength (meq/g HS)</th>
<th>FRCFA</th>
<th>FRCHA</th>
<th>SAHA</th>
<th>ESHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>4.0 ± 0.4</td>
<td>3.3 ± 0.2</td>
<td>3.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>0.2 M</td>
<td>6.9 ± 0.3</td>
<td>6.4 ± 0.2</td>
<td>6.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.3 M</td>
<td>8.8 ± 0.3</td>
<td>8.8 ± 0.3</td>
<td>8.9 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Log $\beta_{1,-1,1}$</td>
<td>4.0 ± 0.8</td>
<td>4.8 ± 0.4</td>
<td>4.2 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Ionic strength (meq/g HS)</td>
<td>FRCFA</td>
<td>FRCHA</td>
<td>SAHA</td>
<td>ESHA</td>
</tr>
<tr>
<td>1.0 M</td>
<td>6.5 ± 0.3</td>
<td>6.2 ± 0.2</td>
<td>5.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Log $\beta_{1,-1,1}$</td>
<td>3.4 ± 0.2</td>
<td>3.4 ± 0.2</td>
<td>4.2 ± 0.2</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>Log $\beta_{1,-2,1}$</td>
<td>6.4 ± 0.1</td>
<td>6.5 ± 0.2</td>
<td>6.9 ± 0.3</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>Log $\beta_{1,-2,1}$</td>
<td>8.9 ± 0.1</td>
<td>8.9 ± 0.1</td>
<td>9.1 ± 0.1</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td>Log $\beta_{1,-2,1}$</td>
<td>4.2 ± 0.3</td>
<td>4.8 ± 0.3</td>
<td>2.4 ± 0.4</td>
<td>4.6 ± 0.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Errors are 2σ of replicates.

Figure 1. Tc(IV) speciation in the absence of HA. Total Tc concentration is $10^{-7}$ M. Calculations were performed using PHREEQC. (Note that the concentration of the species $\text{TcO}^{2+}$ and $\text{TcO(OH)}_3^-$ are negligible).
be a stronger complexant than other FA samples, or to a difference of humic interactions between actinides and transition metals. The data also showed that the binding constants of HS with the cationic Tc(IV) species are substantially larger (by 2 orders of magnitude) than with the neutral TcO(OH)$_2^0$, as would be expected.

Previous work showed a logarithm of the binding constant of Tc(IV)$^-\text{HA}$ complex of 5.3 ($\pm 0.3$, for tracer levels of Tc(IV) and at pH 8.0, where TcO(OH)$_2^0$ is the only species present (Figure 1). Maes’ studies were performed in synthetic clay water consisting of a mixture of background electrolytes, and HA and FA were not discriminated, rendering a difficult comparison with our results. However, our work lead to remarkably similar data; our results for log$\beta_{1-2,1}$ range from 3.9 $\pm$ 0.3, for FRCFA, to 4.6 $\pm$ 0.1, for ESHA, in solution of ionic strength of 0.5 M. The binding constant data we obtained, in conjunction with Tc(IV) thermodynamic data of Table 2, allowed performing speciation calculations, using the publicly available geochemical equilibrium speciation code PHREEQC. Figure 2 presents Tc(IV) speciation in presence of 20 ppm FRCHA. While TcO(OH)$_2^0$ and TcO(OH)$_3^-$ are the two major species in the 4–5 pH range in absence of HA (Figure 1), the addition of 20 ppm HA allows the complex TcO(OH)$^-\text{HA}$ to be predominant in the same pH array. Also, the presence of 20 ppm HA allows the species TcO(OH)$_2^-\text{HA}$ to be predominant at pH 7, whereas the neutral TcO(OH)$_3^-$ is in absence of HA. Figure 3 presents a compilation of data obtained from PHREEQC calculations, to show the maximum HA concentration necessary to obtain maximal Tc–(IV)$^-\text{HA}$ species concentration (i.e., the addition of TcO(OH)$_2^-\text{HA}$ and TcO(OH)$_3^-\text{HA}$ concentrations). In a solution containing $10^{-7}$ M Tc(IV), while less than 20 ppm HA is sufficient to obtain an absolute dominance of the soluble humic complexes at pH 4.5, 75 ppm HA is necessary to reach the maximum predominance of humic complexes at pH 6.8. Additionally, 100 ppm HA is still not quite enough for the humic complexes to be the absolute dominant species at pH 6.8, due to
the smaller binding constant of the neutral Tc(IV) species at this pH; a small amount of TcO(OH)₂⁺ is still present at this pH, as shown in Figure 2.

**ASSOCIATED CONTENT**

Supporting Information. Tables presenting examples of extraction data, including ⁹⁹Tc counting, D values, HS concentrations, and pH. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: nawall@wsu.edu.

**ACKNOWLEDGMENT**

This work was supported by the Office of the Biological and Environmental Research, Office of Science, U.S. Department of Energy (DOE) under the grant DE-FG02-08ER64696 with Washington State University and under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, which is managed by UT-Battelle LLC for DOE.

**REFERENCES**


