

The Speciation and Solvent Extraction of Zirconium and Hafnium: A Computational and Experimental Approach

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ABSTRACT

Zirconium and hafnium have important applications within the nuclear industry, where zirconium is used to clad the uranium fuel rod tubes that are used during nuclear reactions and hafnium is used in the control rods which moderate these reactions. Since zirconium and hafnium occur together in nature, these metals have to be separated prior to use in nuclear reactors. A promising technology that can be used to separate these metals is solvent extraction. However, when evaluating the literature on the solvent extraction of zirconium and hafnium, it becomes apparent that these studies often entailed choosing a set experimental parameters on a trail-and-error basis and optimising those parameters, without paying attention to understanding the mechanisms which underpins these solvent extraction reactions. One of the reasons why these extraction mechanism is not understood is the lack of data pertaining to the speciation of zirconium and hafnium in aqueous phases.

It this project, the mechanisms that underpin the solvent extraction of ZrF_4 and HfF_4 with phosphorus based extractants were investigated. Molecular modelling was used to investigate the aqueous speciation of ZrF_4 and HfF_4 , and a combined molecular modelling and experimental approach was used to investigate the bonding and reactivity of the reactions between ZrF_4 and HfF_4 complexes and phosphorus based extractants.

Concerning the modelling of the speciation, it was predicted that for pH ranges below 0, which is of interest in solvent extraction, the aqueous speciations of ZrF_4 and HfF_4 are dominated by $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. For pH ranges above 0, these complexes are hydrolysed to yield $[\text{Zr}(\text{H}_2\text{O})\text{F}_4(\text{OH})]^-$ and $[\text{Hf}(\text{H}_2\text{O})\text{F}_4(\text{OH})]^-$. As the pH continues to increase, complexes which are further hydrolysed start to appear. Furthermore, it was predicted that the F^- ligands do not dissociate.

Concerning the investigations of the bonding and reactivity between the aqueous ZrF_4 and HfF_4 complexes and phosphorus based extractants, it was proposed that the extraction mechanisms involved the formation of hydrogen bonds between the extractants, which had to be protonated, and the aqueous zirconium and hafnium complexes. Furthermore, it was proposed that for these extractants to bind preferentially to either zirconium or hafnium, and therefore extract one of these metals selectively, the metals have to be coordinated to an acid anion, in such a way that the extractants can form hydrogen bonds to this acid anion. It was observed that when HClO_4 was present in the aqueous phase, hafnium was extracted selectively; while aqueous phases for which HNO_3 was present resulted in the selective extraction of zirconium or hafnium, depending on how many oxygen

atoms were present on the extractants. Aqueous phases for which HCl was present did not result in selective extraction at all. Furthermore, phosphorus acid based extractants resulted in greater overall extraction compared to phosphorus oxide extractants. Overall, the greatest selectivity (30 %) that was observed involve the selective extraction of hafnium from an 8.0 M HClO₄ medium.

Keywords: molecular modelling, density functional theory, conceptual density functional theory, solvent extraction, speciation, zirconium, hafnium

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CHAPTER 1 INTRODUCTION

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1.1 Topic Introduction

Zirconium and hafnium have important applications within the nuclear industry, due to their specific nuclear properties.¹ Since free neutrons cross through the zirconium nucleus unaffected², while hafnium nuclei absorb free neutrons², zirconium or hafnium can be used to construct materials that will either admit or shield against free neutrons. Therefore, high purity zirconium is used to clad the fuel rod tubes that are used during neutron induced nuclear reactions, such as the uranium nuclear reaction.¹ Conversely, control rods, which are used to moderate the rate of such nuclear reactions, often contain high purity hafnium.¹

The most abundant source of zirconium and hafnium is zircon, a mineral which consists mainly of ZrO_2 , HfO_2 , and SiO_2 .³ Since zirconium and hafnium have conflicting neutron capturing properties, the two metals have to be separated prior to use in nuclear reactors. Furthermore, zircon crystals are chemically inert³, and therefore difficult to dissolve into an aqueous phase. A plasma based technology, by which naturally occurring zircon crystals are heated to the plasma phase leading to the formation of so called Plasma Dissociated Zircon, has been developed by researchers at the Nuclear Energy Corporation of South Africa SOC limited (NECSA).⁴ This Plasma Dissociated Zircon can be treated with gaseous HF to produce a mixture of ZrF_4 and HfF_4 .⁴ If a hydrometallurgical separation process is envisaged for the separation of ZrF_4 and HfF_4 , as was attempted in this study, the mixture of ZrF_4 and HfF_4 can be dissolved into an aqueous phase and used as a feed solution for this separation process.

Conventional methods for the separation of zirconium and hafnium are based on solvent extraction, sometimes called liquid-liquid extraction, which is a chemical separation technique wherein a species is selectively transferred from one liquid to another. For the solvent extraction of zirconium and hafnium, mixtures of ZrF_4 and HfF_4 can be dissolved into an aqueous phase, which could then be brought into contact with an organic phase. Organic ligands, called extractants, which are dissolved in the organic phase, form organometallic complexes more preferentially with either of the two metals. These organometallic complexes favour dissolution in the organic phase, and therefore the metal that reacts with the extractants to form organometallic complexes is extracted into the organic phase.

Two commercial processes for the solvent extraction of zirconium and hafnium are currently in use: the MIBK process and the TBP process.⁵ During the MIBK process, thiocyanide complexes of zirconium and hafnium are formed. The higher solubility of the hafnium thiocyanide complexes, compared to the zirconium thiocyanide complexes, in methyl isobutyl ketone (MIBK) results in the preferential extraction of hafnium.⁵ Therefore, the MIBK process has the drawback of producing

waste streams that contain cyanides and thiocyanides. During the TBP process, a mixture of ZrOCl_2 and HfOCl_2 are dissolved into an aqueous phase containing 3.5 M nitric acid. This aqueous phase is contacted with an organic phase containing tributyl phosphate (TBP), and the zirconium is preferentially extracted into the organic phase.⁵ Since mixtures of nitric acid and TBP are explosive⁶, the TBP process is associated with significant health hazards.

1.2 Problem Statement

Much research has been done, during the past few decades, on the solvent extraction of zirconium and hafnium. However, when evaluating the literature⁵, it becomes apparent that these studies often entailed choosing a set of acids and extractants on a trial-and-error basis, followed by a series of solvent extraction experiments across concentration ranges for the chosen acids or extractants. In these studies, little attention has been paid to understanding the mechanisms that underpin the solvent extraction of zirconium and hafnium. While this kind of screening approach has advantages, it does not necessarily lead to insight into the mechanisms of the extractions.

Understanding these mechanisms could support a rational design approach towards the study of the solvent extraction of ZrF_4 and HfF_4 , making it possible to rationalise known solvent extraction trends and even predict future trends. However, there is limited literature on the mechanisms underpinning the solvent extraction of zirconium and hafnium. One of the reasons for this limitation is, amongst other, the lack of speciation data for ZrF_4 and HfF_4 in the aqueous phase.

1.3 Aim of Research

The aim of the research presented in this dissertation was to investigate the mechanism of the extraction of ZrF_4 and HfF_4 mixtures with phosphorus based extractants. The project therefore had two objectives:

to use a molecular modelling approach to investigate the speciation of ZrF_4 and HfF_4 in aqueous environments; and

to use a combined molecular modelling and experimental approach to investigate the bonding and reactivity of the reactions between ZrF_4 and HfF_4 complexes and phosphorus based extractants.

Concerning the first objective, there were two reasons to study the speciation of zirconium and hafnium. Firstly, knowing what kind of zirconium and hafnium complexes are present in the aqueous phase could help in the elucidation of the extraction mechanism. Secondly, the separation of

zirconium and hafnium might further benefit from the exploitation of differences between the speciation of the two metals. For instance, zirconium is known to hydrolyse to a greater extent than hafnium.⁷ Hence, an extractant that binds more selectively to a hydrolysed species would therefore preferentially extract zirconium.

For the purposes of the research presented in this dissertation, it was decided to use a molecular modelling approach to investigate the speciation of ZrF_4 and HfF_4 . Had an experimental approach been used, it would have been necessary to use an in situ analysis technique; since other techniques, like x-ray diffraction or titration, can potentially disturb the system in such a way that an incorrect picture of the speciation is inferred. In situ analysis techniques, like UV-vis (ultra violet and visible light spectroscopy), requires data about which spectral peaks correspond to which species in solution. Such published data could not be found in the literature. On the other hand, recent publications on the use of ab initio molecular dynamics for the study of the hydrolysis of aluminium^{8,9}, plutonium¹⁰ and uranium¹¹ ions have shown that accurate predictions about the speciation of metals can be made with this technique.

Concerning the second objective, understanding the bonding and reactivity in the solvent extraction of zirconium and hafnium allows insights to be gained into the mechanism that underpins these reactions. Investigating the reactivity between ZrF_4 and HfF_4 complexes and phosphorus based extractants allows insights to be gained about the overall ability of these extractants to transfer zirconium and hafnium into the organic phase, as well as the ability of a given extractant to transfer either zirconium or hafnium more preferentially into the organic phase. Investigating the bonding between ZrF_4 and HfF_4 complexes and phosphorus based extractants allows these reactivity trends to be related to the trends in the structures of the zirconium and hafnium complexes and the extractants.

For the purposes of the research presented in this dissertation, a combined experimental and molecular modelling approach was used in pursuit of the second objective. Experimental work allowed real world observations to be made in a laboratory, while the molecular modelling work complemented these observations. Molecular modelling uses various classical and quantum chemical methods to model chemical phenomena. It can, for example, be used to calculate binding energies and the hardnesses (in the Pearson sense) of atoms. Therefore, molecular modelling was an apt tool for the investigation of bonding and reactivity.

The scope of this study was limited as follows. Concerning the first objective, the possibility of polymerization of the metal complexes and the effect of acid counter ions (Cl^- , NO_3^- and SO_4^{2-}) were not investigated. The reason for this limitation is computational cost. For the method used in this study (ab initio molecular dynamics), the computational time of the calculations go as N^3 , where N is

related to the number of atomic orbitals in the system being modelled.¹² Modelling ZrF₄ or HfF₄ together with other metal complexes or acid counter ions, would have meant adding a dozen additional water molecules. Adding these extra molecules would have required an increase in the number of atomic orbitals in the system by a few hundred, which would have meant that the calculations would have taken a few million times longer ($100^3 = 1,000,000$). The computational time that would have been needed to include these investigations to the scope of this study would have extended the study beyond the allotted time. For the second objective, the solvent extraction study was limited by using only phosphorus based extractants, since a large body of published work exists for this class of extractants. Focusing on phosphorus based extractants allowed comparisons to be made between of the ZrF₄ and HfF₄ mixture, as used in this study, and the solvent extraction of zirconium and hafnium reported in the literature.

This work was initiated by the South African Department of Science and Technology (DST), that launched the Advanced Metals Initiative (AMI). The South African Nuclear Energy Corporation SOC Limited (NECSA), due to existing expertise and infrastructure, was entrusted to investigate the manufacturing of zirconium, hafnium, tantalum and niobium, thereby establishing the Nuclear Metals Development Network (NMDN) Hub of the AMI.

1.4 Layout of this Dissertation

This dissertation is made up of five chapters. In Chapter 1, the study is introduced. After a problem statement, the objectives of the project are presented together with the limitations applied to these objectives.

The literature chapter, Chapter 2, is divided into five sections: Introduction, Molecular Modelling, Aqueous Speciation, Solvent Extraction and Conclusions. A separated section on molecular modelling was added, since both of the objectives of this study involved extensive use of molecular modelling. The sections on aqueous speciation and solvent extraction give background and relevant literature pertaining to the two objectives of this study.

Chapters 3 and 4 present the work done in pursuit of the first and second objectives. Both chapters are divided into the following sections: Introduction, Methods, Results & Discussion, and Conclusion. In Chapter 3 the modelling of the aqueous speciation of ZrF₄ and HfF₄ is presented, while the focus in Chapter 4 was on the modelling and experimental work on the solvent extraction of ZrF₄ and HfF₄ with phosphorus based extractants.

Lastly, Chapter 5 presents the evaluation of this study and recommendations for future studies.

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CHAPTER 2 LITERATURE REVIEW

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2.1 Introduction

In this chapter, which is divided into five sections, the literature review that was done for this M.Sc. project, is presented. The background on molecular modelling, which is presented in Section 2.2, is presented separately because both objectives of this study involved extensive use of molecular modelling and the same kinds of calculations were used in pursuit of both objectives.

In the section on molecular modelling, Section 2.2, background on density functional theory (DFT), modelling of solvent environments and molecular dynamics is presented. DFT is a method that can be used to calculate Gibbs reaction energies and various descriptors of bonding and reactivity. Concerning this study, there were two reasons for modelling of solvent environments: the aqueous speciation of ZrF_4 and HfF_4 involves interaction between these complexes and the aqueous environment; and solvent environments could have important effects on bonding and reactivity, which should therefore be taken into account when modelling the bonding and reactivity of ZrF_4 and HfF_4 complexes and phosphorus based extractants. Since aqueous speciation depends on temperature, molecular dynamics is discussed as a way to account for the effects of temperature on aqueous speciation.

In Section 2.3 relevant background theory and literature on aqueous speciation that pertains to the first objective of this study, is presented. Aqueous speciation is described as being a set of equilibrium reactions between the various species that form part of the speciation. Therefore, a thermodynamic description of speciation is presented. Additionally, relevant literature on the aqueous speciation of zirconium and hafnium is also presented.

In Section 2.4 relevant background theory and literature on solvent extraction that pertains to the second objective of this study, is presented. The principles of solvent extraction are presented, including the three basic kinds of extraction mechanisms, into which all extraction mechanisms can be categorised. A review of the three major commercial processes for the production of nuclear grade zirconium and hafnium is presented.

In the last section of this chapter, Section 2.5, the conclusions that were drawn regarding the relevance of the literature to the objectives of this study, are presented.

2.2 Molecular Modelling

Molecular modelling is a branch of chemistry that uses numerical computational methods to model various chemical phenomena. In molecular modelling, the quantities being modelled are calculated

directly from atomistic parameters. Therefore, molecular modelling allows investigations into speciation, bonding and reactivity to be done at the atomistic level; a feat which is difficult to achieve by experimental work alone.

A key area of molecular modelling is electronic structure theory that aims to model various properties of a system's electronic structure, such as bond energy and Gibbs reaction energy. Ultimately, all chemical properties depend on electronic structure. It was therefore vital that an accurate description of electronic structure was used for the modelling done during this study.

There are three broad approaches to modelling a system's electronic structure: ab initio, semi-empirical, and empirical (see Figure 2-1). These approaches vary in computational expense, accuracy and the system size for which they are suited.

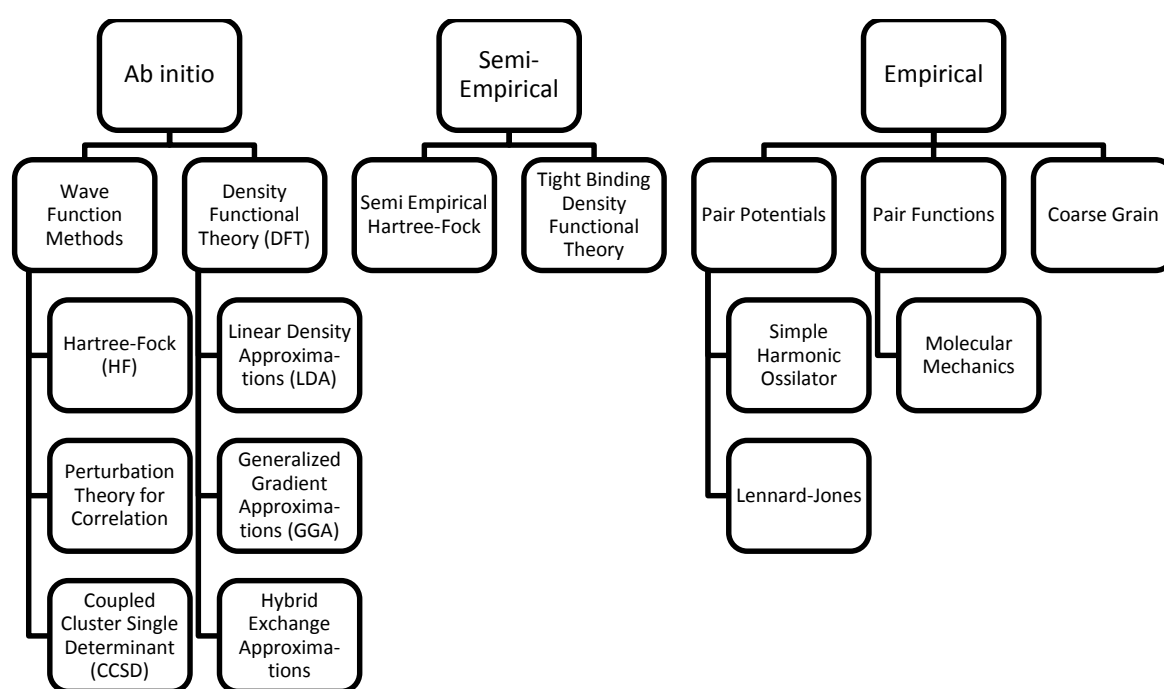


Figure 2-1. The three main classes, and various subclasses, of electronic structure theory

In the ab initio approach an expression for the system's electronic energy is derived from first principles. That is, in the ab initio approach chemical quantities are calculated by assuming only the fundamental constants of nature and the postulates of quantum mechanics to be true. In the semi-empirical approach the expression for the system's electronic energy is also derived from first principles, but some of the terms are replaced by fitted parameters. In the empirical approach the expression for the system's electronic energy is assumed to have some form, which does not have to be related to first principles. Energy expressions in the empirical approach involve parameters that are fitted to experimental data or highly accurate ab initio calculations.

In Section 2.2.1 DFT is presented as a kind of ab initio electronic structure theory (see Figure 2-1). Compared to other electronic structure theories, DFT boasts a very useful accuracy-to-computational-cost ratio¹, which makes it well suited to modelling large systems, which is necessary to do when modelling aqueous speciation. Furthermore, many concepts related to bonding and reactivity, like electronegativity and hardness, have been grounded in DFT, in an area called conceptual DFT.² Conceptual DFT is therefore an ideal framework in which to model bonding and reactivity.

The modelling of aqueous speciation and bonding has to account for interactions between the solute and the solvent environment. A discussion of the two basic methods that can be used to model a solvent environment is presented in Section 2.2.2. The so-called explicit solvent method is the most appropriate method for modelling aqueous speciation, while the so-called implicit solvent method is appropriate for modelling bonding and reactivity. The method of periodically repeating unit cells is also presented. This method allows bulk solutions to be modelled, which is desirable when modelling aqueous speciation.

Molecular dynamics is a method that can be used to model the effects of kinetic energy on a system's particles, and therefore the system's temperature. Since aqueous speciation depends on temperature, the so called ab initio molecular dynamics method, which models the time evolution of a system in a quantum mechanical way is presented in Section 2.2.3. Ensembles and thermostats are presented as a way to control the modelled temperature during a molecular dynamics calculation. Constrained ab initio molecular dynamics is introduced as a way to model chemical reactions. Lastly, a few case studies are presented that illustrate the accuracy with which constrained ab initio molecular dynamics can be used to make predictions about hydrolysis reactions.

2.2.1 Density Functional Theory

2.2.1.1 Fundamentals of Density Functional Theory

The hallmark feature of DFT is that a system's properties are calculated from the system's electron density, $\rho(\mathbf{r})$, rather than the system's wave function.¹ In 1964 Hohenberg and Kohn showed³ that there exists, in principle, a functional that uniquely maps a system's ground-state electron density onto the ground-state electronic energy, E_0 , of that system. The exact expression of this functional is unknown.¹ However, much of the work done on DFT has been dedicated to finding accurate approximations to this functional.¹ In general, the functional can be resolved into three terms:

$$E_0 = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + E_{eN}[\rho(\mathbf{r})],$$

where $T[\rho(\mathbf{r})]$ is a functional that represents the kinetic energy of the electrons, $E_{ee}[\rho(\mathbf{r})]$ is a functional that represents the electron-electron repulsion energy, and $E_{eN}[\rho(\mathbf{r})]$ is a functional that represents the electron-nuclei attraction energy.

The functional $E_{ee}[\rho(\mathbf{r})]$ can be written as the sum of a Coulombic energy functional

$$J[\rho(\mathbf{r})] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}',$$

and an exchange energy functional

$$E_X[\rho(\mathbf{r})],$$

which has to be approximated since its exact expression is unknown.

The functional $E_{eN}[\rho(\mathbf{r})]$ is given by

$$-\sum_A^M \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r},$$

where M is the total number of nuclei in the system, Z_A is the charge on the A-th nucleus, and $\mathbf{R}_A$ is the position of the A-th nucleus.

In 1965 Kohn and Sham suggested⁴ that the kinetic energy functional, $T[\rho(\mathbf{r})]$, can be given as the sum of two terms. The first term describes a system of non-interacting electrons

$$-\frac{1}{2} \sum_i^N \int \phi_i^* \nabla^2 \phi_i d\mathbf{r}_i,$$

where ϕ_i is the system's i-th orbital. The second term, called the correlation energy functional,

$$E_C[\rho(\mathbf{r})],$$

corrects for the non-interaction idealization. $E_C[\rho(\mathbf{r})]$ also has to be approximated since its exact expression is unknown.

The total Kohn-Sham DFT energy expression for a system's ground state electronic energy is therefore given by

$$E_0 = -\frac{1}{2} \sum_i^N \int \phi_i^*(\mathbf{x}_i) \nabla^2 \phi_i(\mathbf{x}_i) d\mathbf{x}_i + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \sum_A^M \int \frac{Z_A \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r} + E_{XC}[\rho(\mathbf{r})],$$

where the unknown term, E_{XC} , is the so-called exchange-correlation functional, which is the sum of the exchange and correlation functionals. There are many approximations for the exchange-correlation functional.¹ These different approximations give rise to the various classes of modern day

DFT, such as the linear density approximations, the generalised gradient approximations and the hybrid exchange approximations (see Figure 2-1).

2.2.1.2 Conceptual Density Functional Theory

Conceptual DFT is an area of DFT in which many of the principle notions of chemical reactivity, like electronegativity, hardness and regioselectivity, are expressed in terms of changes in a molecule's electron density. In solvent extraction, an extractant's ability to extract a given metal, and the preferentiality with which it does so, are underpinned by the extractant's reactivity toward that metal.

In 1977, Robert Parr and co-workers proposed⁵ the notion of global chemical potential, μ_{global} , as the rate at which a molecule's energy, E , changes with respect to a change in the number of electrons, N ,

$$\mu_{global} = \left(\frac{\partial E}{\partial N} \right)_v,$$

where v , the positions of the nuclei, is held constant. The local chemical potential⁵, μ_{local} , is the rate at which E changes with regard to the electron density, $\rho(\mathbf{r})$, at a specific position $\mathbf{r}$,

$$\mu_{local}(\mathbf{r}) = \left(\frac{\partial E}{\partial \rho(\mathbf{r})} \right)_v.$$

An important observation is that while μ_{global} is a property of the entire molecule, $\mu_{local}(\mathbf{r})$ is a function of position, $\mathbf{r}$. Furthermore, the definition of μ_{local} has important consequences. If $\mu_{local} < 0$, at some point $\mathbf{r}$, then the molecule will have electron donating characteristics at $\mathbf{r}$. Conversely, if $\mu_{local} > 0$, at some point $\mathbf{r}$, then the molecule will have electron accepting characteristics at $\mathbf{r}$.

In 1983, Robert Parr and Ralph Pearson defined⁶ global hardness, η_{global} , as the rate at which μ_{global} changes with respect to a change in the number of electrons

$$\eta_{global} = \left(\frac{\partial \mu_{global}}{\partial N} \right)_v = \left(\frac{\partial^2 E}{\partial N^2} \right)_v.$$

Analogous to before, local hardness, $\eta_{local}(\mathbf{r})$, is given by

$$\eta_{local}(\mathbf{r}) = \left(\frac{\partial \mu_{local}}{\partial \rho(\mathbf{r})} \right)_v = \left(\frac{\partial^2 E}{\partial \rho(\mathbf{r})^2} \right)_v.$$

In words, $\eta_{local}(\mathbf{r})$ is a measure of how much electron density is donated/accepted during the formation of a bond. That is, a molecule, call it molecule A, will continue to donate electron density to another molecule, molecule B, until $\mu_{local,A} = \mu_{local,B}$. If $\eta_{local,A}$ is small (i.e. the rate at which

$\mu_{local,A}$ changes is small), then molecule A has the capacity to donate a lot of electron density, since a lot of electron density has to be donated before $\mu_{local,A} = \mu_{local,B}$. These definitions of hardness form a theoretical justification of Pearson's Hard Acid Soft Base (HASB) principle⁷. A hard acid/base is a species which accepts/donates few electrons, while a soft acid/base is a species that accepts/donates many electrons.

While an intuitive understanding is helpful, it does not answer the question of how η_{global} and η_{local} can be calculated in practice. A useful approximation is

$$\eta_{global} \cong E_{ionization} - E_{affinity},$$

where $E_{ionization}$ is the ionization energy and $E_{affinity}$ is the electron affinity of the molecule.² According to Koopmans' theorem²,

$$E_{ionization} = -E_{HOMO}$$

and

$$E_{affinity} = -E_{LUMO},$$

where E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively.

η_{local} can be calculated with the use of Fukui functions. Fukui functions⁸ describe how the electron density changes as the number of electrons in the molecule change

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v,$$

where the nuclei are held fixed. Application of the chain rule of calculus reveals

$$\eta_{local}(\mathbf{r}) = \left(\frac{\partial \mu}{\partial \rho(\mathbf{r})} \right)_v = \left(\frac{\partial \mu}{\partial N} \right)_v \left(\frac{\partial N}{\partial \rho(\mathbf{r})} \right)_v = \eta_{global} f(\mathbf{r}).$$

Therefore the local hardness, at point $\mathbf{r}$, is simply the Fukui function, at $\mathbf{r}$, multiplied by the global hardness.

Fukui functions are more than just a means to calculate local hardness – Fukui functions are descriptors of regioselectivity. To see why, consider two specific kinds of Fukui functions: f_+ and f_- . The f_+ Fukui function is the change in electron density upon adding an electron to a molecule:

$$f_+(\mathbf{r}) = (\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}))_v.$$

The f_+ function represents the slice of electron density that is added to a molecule's electron density when the molecule gains an electron. Therefore, f_+ represents the region on a substrate where a nucleophile is likely to attack.

The f_- Fukui function is the change in electron density upon removing an electron from a molecule:

$$f_-(\mathbf{r}) = (\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}))_v.$$

Conversely, the f_- function represents the slice of electron density that a molecule loses due to the loss of an electron. Therefore, f_- represents the region on a substrate where an electrophile is likely to attack. See Figure 2-2 for examples of Fukui functions.

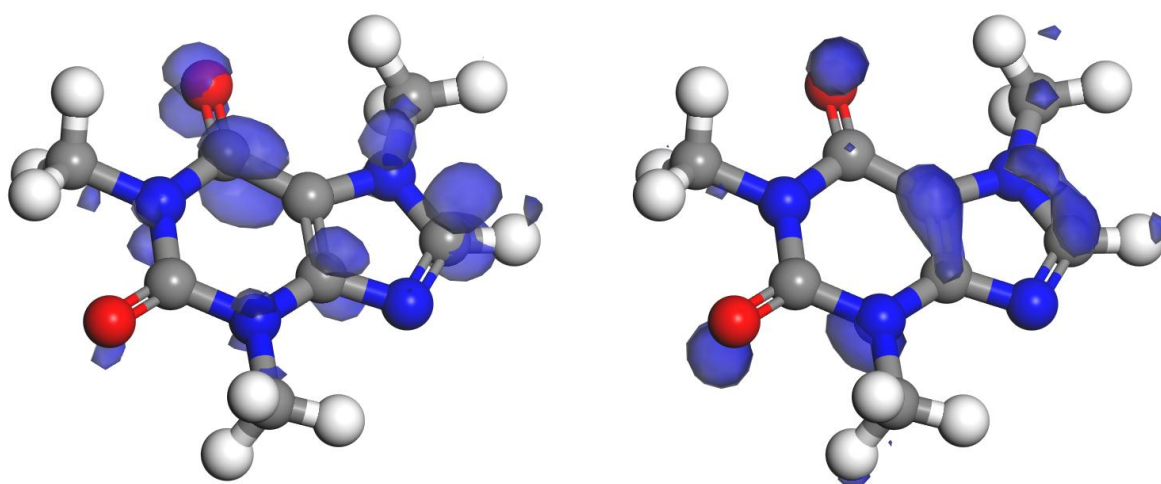


Figure 2-2. Fukui functions on a caffeine molecule drawn using Materials Studio's (v 6) Visualizer. The f_+ function is shown on the left, and the f_- function is shown on the right.

2.2.2 Solvent Environments

2.2.2.1 Fundamentals of Solvent Environment Modelling

Broadly speaking, there are two methods that can be used to model the effects of the solvent environment on a solute: the explicit and implicit methods. In the explicit method, the solute and solvent molecules are modelled as a single self-consistent system (see Figure 2-3). In the implicit method only the solute molecules are modelled self-consistently; the effects due to the solvent environment are accounted for by adding a correction term to the energy expression for the solute molecules.

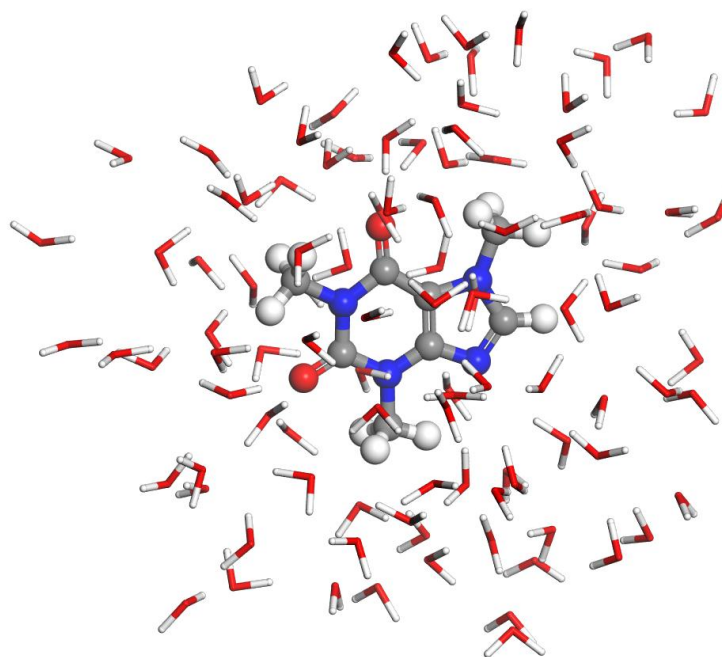


Figure 2-3. An example of explicit solvent environment modelling. A caffeine molecule surrounded by water molecules, drawn using Materials Studio's (v 6) Visualizer.

During implicit solvent environment modelling, the correction term that accounts for the effects of the solvent, is calculated by approximating the solvent environment as a dielectric continuum (i.e. a material that is polarisable by an external electric field) and 'placing' the solute inside a cavity within this dielectric continuum (see Figure 2-4). This cavity is determined by the solute's solvent-accessible surface. A molecule's solvent-accessible surface is calculated, in principle, by rolling a probing sphere around the van der Waals radii of the molecule's atoms, where the probing sphere's center sweeps out the solvent-accessible surface (see Figure 2-5).⁹ Solvent-accessible surfaces are sometimes called Connolly surfaces, after Micheal Connolly who contributed¹⁰ a generalised computational method for determining the solvent-accessible surface for any given molecule.

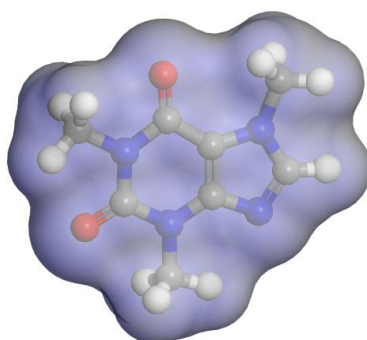


Figure 2-4. An example of implicit solvent environment modelling. A caffeine molecule surrounded by a Connolly surface, drawn using Materials Studio's (v 6) Visualizer.

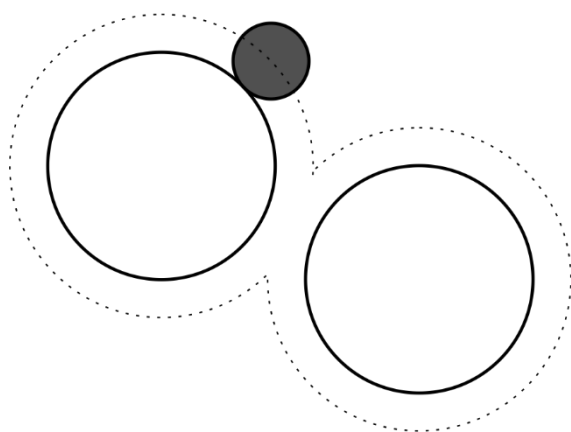


Figure 2-5. An illustration of how a solvent-accessible surface is determined. The two light spheres each represent the van der Waals radii of atoms, the dark sphere represents a probing sphere and the dotted line represents the solvent-accessible surface.

The explicit solvent environment method is generally more accurate than the implicit solvation method, at the cost of being more computationally expensive. Both methods can account for ionic bonding between the solute and solvent molecules. However, since the dielectric continuum approach averages out the positions of charges, the implicit method is less accurate at accounting for ionic bonding than the explicit method. Furthermore, only the explicit method can model the formation of covalent bonds between the solute and solvent molecules.

2.2.2.2 Periodically Repeating Unit Cells

Periodically repeating unit cells is a method that can be used to model bulk environments, such as aqueous phases. Although the interactions between a solute and its nearest surrounding solvent molecules can be modelled accurately by the explicit solvent environment method, it would be too computationally expensive to model a bulk solution in this way. Periodically repeating unit cells can be used to avoid this problem.

During such calculations a unit cell, called the original unit cell, is subjected to periodic boundary conditions (see Figure 2-6), such that the original unit cell is infinitely repeated in all directions. The atoms in each cell “see” the atoms in adjacent cells. The result is a bulk system made up of periodically repeating motifs.

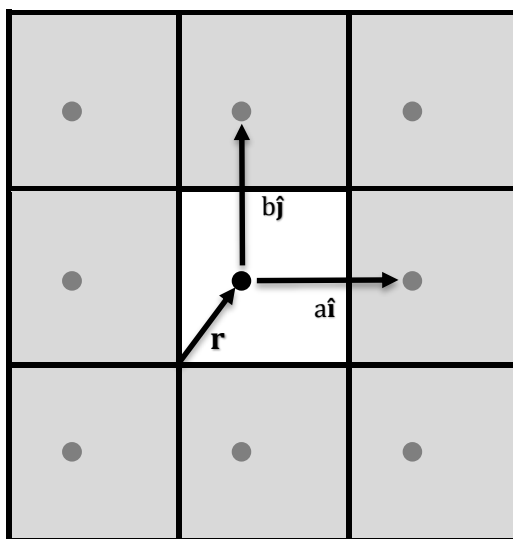


Figure 2-6. A two dimensional representation of a periodically repeating unit cell. The light square represents the original unit cell and the dark squares represent periodic images of the unit cell. The black sphere represents an atom in the original unit cell, and the grey spheres represents atoms in the periodic images of the unit cell.

Although the effects of a bulk environment are modelled, the computational expense of such a calculation is only that which is needed to model the original cell. This is because the image cells are computed by symmetry operations (i.e. translation along the x, y and z axes) on the original cell, and the energy of the total system is expressed as a converging series.

2.2.3 Molecular Dynamics

2.2.3.1 Fundamentals of Ab Initio Molecular Dynamics

Molecular dynamics (MD) is a method that can be used to model the time evolution of a system. During such calculations, the motion of the system's nuclei is treated using classical mechanics. Ab initio molecular dynamics (AIMD) is a kind of MD calculation in which the electronic structure of the system is treated using an ab initio electronic structure method.¹¹ Therefore, in AIMD the forces between the nuclei and electrons are determined quantum mechanically.

There are various different types of AIMD methods. In this study, the so-call Born-Oppenheimer molecular dynamics method was used. During a Born-Oppenheimer MD calculation, the motion of the system's nuclei is treated classically and the motion of the system's electrons is treated quantum mechanically. The calculation starts by randomly assigning initial velocities to the system's nuclei in such a way that these velocities match a Maxwell-Boltzmann velocity distribution. The procedure then enters a loop in which the system's electronic structure is calculated, the forces on the nuclei are calculated, and the nuclei are moved to new positions (see Figure 2-7). The calculation continues until a targeted number of steps, which is based on the desired simulation time, has been achieved.

Given contemporary high performance computing resources, Born-Oppenheimer MD calculations are suited to the modelling of systems made up of a few hundred atoms for a simulation time of less than 10 ps.¹¹

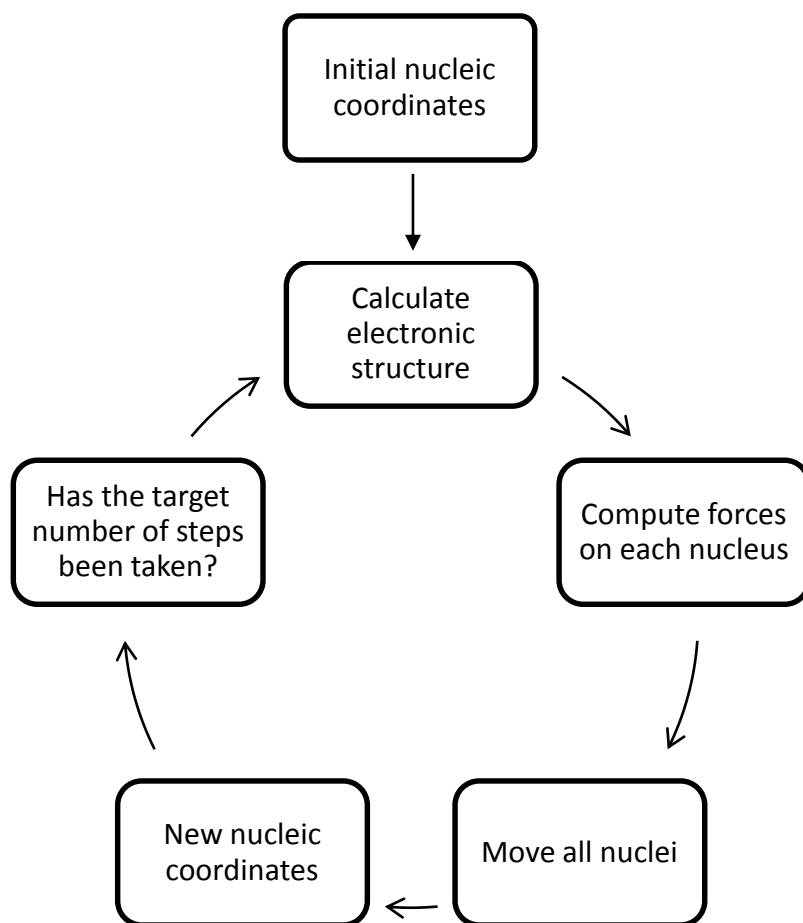


Figure 2-7. A flow diagram illustrating the steps of a typical Born-Oppenheimer molecular dynamics calculation

2.2.3.2 Ensembles and Thermostats

Ensembles are a way to enforce the desired thermodynamic behaviour during MD calculations; for instance, whether the system of interest should behave as though it is isothermally connected to the environment or adiabatically isolated. Failing to enforce such thermodynamic behaviour leads to results that are unphysical. Thermostats can be used to control the modelled system's temperature.

An ensemble is a set of states, or configurations, where each state has a certain probability of describing the system. Systems that are in thermal equilibrium with their environments are described by canonical ensembles, also called NVT ensembles.¹² Systems that behave canonically have, on average, a fixed number of particles (N), volume (V) and temperature (T). If N, V and T are not held fixed during MD calculations, the system could be predicted to evolve in a way that is

inconsistent with the known laws of thermodynamics. During solvent extraction experiments, the aqueous phases are in thermal equilibrium with the environment. Therefore, aqueous speciation was modelled in this study in such a way that canonical behaviour was enforced.

Thermostats are used during MD calculations to ensure that the modelled system behaves canonically. That is, thermostats emulate the natural flux of energy between the system and the environment in such a way that the system's average temperature is held fixed while still allowing for natural fluctuations in the system's temperature. The system's average temperature is held fixed by scaling the kinetic energy of the particles. Natural fluctuations in the systems temperature is modelled by controlling the rate at which the kinetic energy of the particles is scaled.

One of the great conclusions of statistical mechanics is the so-called equipartition theorem¹², which relates a system's temperature to the average kinetic energy of the system's particles

$$\sum_{i=1}^N \langle \frac{1}{2} m_i v_i^2 \rangle = (3N - N_c) \frac{k_B T}{2},$$

where m_i is the mass of the i -th particle, v_i the velocity of the i -th particle, N the number of particles, N_c the number of constraints, k_B Boltzmann's constant and T the temperature. The notation $\langle \ \rangle$ refers to the fact that the average of the quantity inside the brackets is taken.

In practice, the system's total kinetic energy is approximated as being equal to the sum of the particles' average kinetic energies

$$\sum_{i=1}^N \frac{1}{2} m_i v_i^2 = \sum_{i=1}^N \langle \frac{1}{2} m_i v_i^2 \rangle.$$

Using the two equations above, the system's temperature can be solved for:

$$T = \left(\sum_{i=1}^N \frac{1}{2} m_i v_i^2 \right) \frac{2}{k_B (3N - N_c)}.$$

Since only the time evolution of the nuclei are solved for in MD, it is assumed, within the context of thermostating, that the system is made up of only nuclei. That is, the equations above pertain only to the constraints, masses and velocities associated with the nuclei.

The system's temperature can be controlled by multiplying the velocity of each nucleus by a scaling factor. If the system's temperature, $T(t)$, at some time, t , is not equal to the desired temperature, T_o , then the temperature change needed to bring the system back to the desired temperature is

$$\Delta T = T_o - T(t).$$

An expression for the scaling factor, λ , can be obtained by substitution:

$$\Delta T = \left(\sum_{i=1}^N \frac{1}{2} m_i (\lambda v_i)^2 \right) \frac{2}{k_B(3N-N_c)} - \left(\sum_{i=1}^N \frac{1}{2} m_i v_i^2 \right) \frac{2}{k_B(3N-N_c)},$$

followed by factorization:

$$\Delta T = (\lambda^2 - 1) \left(\sum_{i=1}^N \frac{1}{2} m_i v_i^2 \right) \frac{2}{k_B(3N-N_c)},$$

and then resubstitution:

$$T_o - T(t) = (\lambda^2 - 1)T(t),$$

where the last equation can be rewritten as

$$\lambda = \sqrt{\frac{T_o}{T(t)}}.$$

Therefore the system's temperature can be controlled, rather elegantly, by multiplying the velocity of each nucleus by λ .

Besides for scaling the kinetic energy of the system's particles, it is also important that the rate at which the kinetic energy is scaled is not too fast. The reason for this is to allow for natural fluctuations in the system's temperature. There are various techniques used to control the rate at which the scaling occurs, many of which are complicated. These different techniques give rise to different thermostats such as the Gaussian¹³, Berendsen¹⁴ and Nose-Hoover^{15,16} thermostats.

2.2.3.3 Constrained Ab Initio Molecular Dynamics

Constrained AIMD is a method which can be used to model chemical reactions. Whereas AIMD (i.e. non-constrained AIMD) is suited to modelling systems for simulation times of a few picoseconds, constrained AIMD can be used to model chemical reactions that occur over a matter of seconds or even minutes.¹¹

When modelling reactions with constrained AIMD, the Gibbs reaction energy can be calculated by using a method called thermodynamic integration.¹⁷ The change in Gibbs energy of the system is given by

$$\Delta G = \int_a^b \langle f(\xi) \rangle d\xi,$$

where $\langle f(\mathbf{r}) \rangle$ to the average of the forces within the system as a function of reaction coordinate ξ .

Constrained AIMD has been used to study the hydrolysis of various aluminium(Al^{3+})¹⁸, plutonium(Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+})¹⁹ and uranium(U^{4+} and UO_2^{2+})²⁰ species. All three studies used constrained AIMD to predict the values for the first hydrolysis constants (i.e. pK_a values). These studies used an explicit solvation method, along with periodically repeating unit cells, to model bulk aqueous solutions. Note that because these studies used an explicit solvation method, aqua ligands were ‘allowed’ to coordinate to the species. For instance, Al^{3+} was predicted to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in an aqueous solution.²¹

In these studies, constraints were placed on the metal and aqua ligands’ proton such that the distance between these two nuclei were elongated in a step-wise fashion. Thermodynamic integration was used to calculate the Gibbs reaction energies for these step-wise dissociation reactions. Once the Gibbs reaction energies were known, it was possible to calculate the pK_a values (see Section 2.3.1). Overall, these predicted pK_a values are in good agreement with experimental values, as can be seen in Figure 2-8.

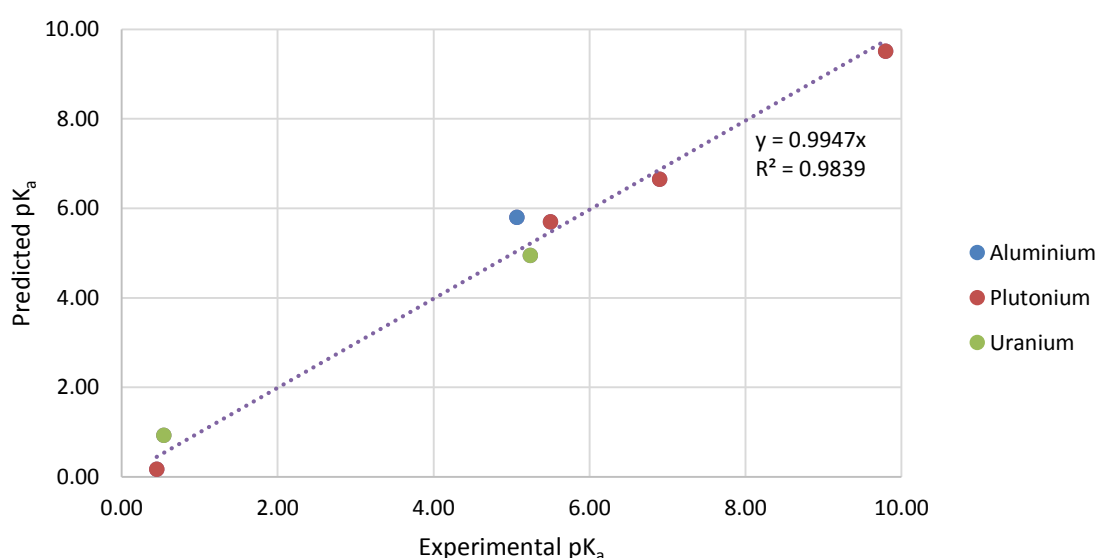


Figure 2-8. Comparison of predicted pK_a values to experimental pK_a values for various aluminium¹⁸, plutonium¹⁹ and uranium²⁰ species. All the predicted values were calculated using constrained AIMD. All data points were taken into account when computing the linear fit.

2.3 Aqueous Speciation

The aqueous speciation of a given element refers to the set of all chemically distinct species, in the aqueous phase, that contain that element. Although this set could, in principle, contain a large number of species, it is usually dominated by a few highly stable species. Furthermore, the exact composition of this distribution depends on temperature as well as the concentrations of the various species involved, such as metal or acid concentration.

As mentioned in Chapter 1, there were two reasons to study the aqueous speciation of zirconium and hafnium: elucidation of the extraction mechanism and the potential enhancement of the separation by exploiting differences in the speciation.

Section 2.3, which is the section on aqueous speciation, is divided into two parts. In the first part, Section 2.3.1, the principles of aqueous speciation are presented. Speciation can be thought of as being the result of a set of equilibrium reactions between the various species that form part of the speciation. Therefore, the aqueous speciation of a metal can be described by knowing the values of the corresponding equilibrium constants. In Section 2.3.1.1, this thermodynamic description of aqueous speciation is presented. A method, called Bjerrum's method, that can be used to systematically account for all species which could potentially form part of the speciation is presented in Section 2.3.1.2.

In Section 2.3.2 a review of the relevant literature on the aqueous speciation of zirconium and hafnium is presented. Zirconium and hafnium form stable hydroxo-bridged polymers in the absence of strongly coordinating ligands. In the presence of fluoride ligands, zirconium and hafnium usually form monomeric fluoride complexes. It is worthwhile to consider analogous systems. To this end, published works on titanium are also discussed, as titanium is in the same chemical group as zirconium and hafnium, on the periodic table.

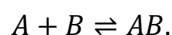
2.3.1 Principles of Aqueous Speciation

2.3.1.1 Thermodynamic Description of Speciation

The distribution of species that results from dissolving a metal in an aqueous phase can be thought of as a set of equilibria between the various species, where each equilibrium corresponds to an equilibrium constant. Describing the aqueous speciation of a given metal therefore amounts to finding this set of equilibrium constants.

In practice, the speciation of the metal can be described by knowing three things: the total concentration of the metal, which metal species exist in solution, and the relative concentrations of these metal species. The total concentration of the metal can easily be determined by quantitative analytical methods such as inductively coupled plasma spectroscopy. The question of which metal species exist in solution can be addressed by Bjerrum's method, which is described in Section 2.3.1.2. Determining the relative concentrations of the species in solution is the same as determining the equilibrium constants for the equilibria between the species. Thermodynamically, the equilibrium constant for a given equilibrium reaction is related to the Gibbs reaction energy.

Consider a general chemical reaction



This reaction corresponds to a number, called the equilibrium constant, given by

$$K = \frac{[AB]}{[A][B]}.$$

It can be shown¹² that if the above reaction is at equilibrium, K remains constant, even if the concentrations of A , B and AB change. In fact, K depends only on temperature and the Gibbs reaction energy¹²:

$$K = e^{\frac{-\Delta G}{k_B T}},$$

where ΔG is the Gibbs reaction energy in Joule, k_B is Boltzmann's constant in J/K, and T is the temperature in K.

As a specific case, consider hydrolysis reactions. The equilibrium reaction is given by

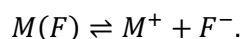


Rewriting the corresponding expression for the equilibrium constant yields

$$\frac{[M(OH)^-]}{[M(H_2O)]} = K \frac{1}{[H^+]}.$$

In words, as the concentration of H^+ decreases, the fraction of hydrolysed species increases. The exact ratio of hydrolysed to non-hydrolysed species, as a function of pH, can be completely determined if K is known. In turn, K can be determined if the Gibbs reaction energy for the hydrolysis reaction is known.

The equilibrium reaction for the dissociation of an F^- ligand is given by



Analogous to before, the exact ratio of dissociated species to non-dissociated species, as a function of pF (i.e. $-\log([F])$), can be completely determined if K or ΔG , is known.

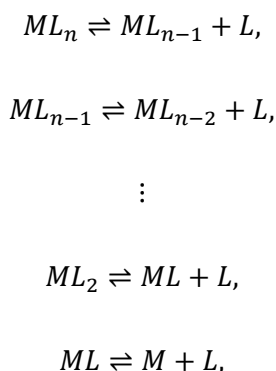
In general, metals can be coordinated, not only to more than one ligand, but also to more than one kind of ligand. Furthermore, any number of these ligands can dissociate to some extent, depending on the solution's free ligand concentration. The resulting distribution of species could therefore

consist of a large number of different metal complexes. Bjerrum's method can be used to treat such complicated systems in a systematic way.

2.3.1.2 Bjerrum's Method of Step-Wise Dissociation

The uncertainty of knowing which complexes form part of a metal's speciation can be resolved by considering, in principle, all complexes which could possibly exist. This can be done, as was suggested by the Danish chemist Jannik Bjerrum (1909 - 1992), by describing the speciation as a set of equilibria between a series of step-wise dissociation reactions, and rewriting the expressions for the equilibrium constants in such a way that the relative concentration of each complex is given as a function of the free ligand concentration.²²

The discussion begins by considering a set of step-wise reactions:



each of which is at equilibrium and corresponds to an equilibrium constant $K_1, K_2, \dots, K_n$.

The concentration of each complex formed in the step-wise dissociation can be written in terms of $[ML_n]$. To see how this is done, consider the expression for the equilibrium constants for the first and second dissociation reactions

$$[ML_{n-1}] = K_1 \frac{[ML_n]}{[L]},$$

and

$$[ML_{n-2}] = K_2 \frac{[ML_{n-1}]}{[L]}.$$

Substitution of the latter equation into the former gives

$$[ML_{n-2}] = K_1 K_2 \frac{[ML_n]}{[L]^2},$$

which can be tidied up by introducing so-called dissociation constants, $\beta_i = K_1 K_2 \dots K_i$, to give

$$[ML_{n-2}] = \beta_2 \frac{[ML_n]}{[L]^2}.$$

Doing similar substitutions for each dissociation reaction in the set of equilibria gives the following set of equations:

$$[ML_{n-1}] = \beta_1 \frac{[ML_n]}{[L]},$$

$$[ML_{n-2}] = \beta_2 \frac{[ML_n]}{[L]^2},$$

⋮

$$[ML] = \beta_{n-1} \frac{[ML_n]}{[L]^{n-1}},$$

$$[M] = \beta_n \frac{[ML_n]}{[L]^n}.$$

The next step in Bjerrum's method is to express the concentration of each complex as a fraction of the total metal concentration. The total metal concentration, c_m , is the sum of the concentrations of all the complexes which contain the metal:

$$c_m = [ML_n] + [ML_{n-1}] + \cdots + [ML] + [M].$$

Each term in the last equation can be written in terms of $[ML_n]$ to give

$$c_m = [ML_n] \left(1 + \frac{\beta_1}{[L]} + \frac{\beta_2}{[L]^2} + \cdots + \frac{\beta_{n-1}}{[L]^{n-1}} + \frac{\beta_n}{[L]^n} \right).$$

The concentration of metal atoms which exist in the form of ML_n , as a fraction of the total metal concentration is

$$\alpha_n = \frac{[ML_n]}{c_m}.$$

Substituting the expression for c_m in to the expression for α_n gives

$$\alpha_n = \frac{[ML_n]}{c_m} = \frac{[ML_n]}{[ML_n] \left(1 + \frac{\beta_1}{[L]} + \frac{\beta_2}{[L]^2} + \cdots + \frac{\beta_{n-1}}{[L]^{n-1}} + \frac{\beta_n}{[L]^n} \right)} = \frac{1}{\left(1 + \frac{\beta_1}{[L]} + \frac{\beta_2}{[L]^2} + \cdots + \frac{\beta_{n-1}}{[L]^{n-1}} + \frac{\beta_n}{[L]^n} \right)}.$$

The concentration of metal atoms which exist in the form of ML_{n-1} , as a fraction of the total metal concentration is

$$\alpha_{n-1} = \frac{[ML_{n-1}]}{c_m} = \frac{\beta_1 \frac{[ML_n]}{[L]}}{c_m} = \frac{\beta_1}{[L]} \alpha_n.$$

It is possible to express the concentrations of each complex as a fraction of the total metal concentration. Doing so gives the following set of equations:

$$\alpha_n = \frac{1}{\left(\frac{\beta_1}{[L]} + \frac{\beta_2}{[L]^2} + \dots + \frac{\beta_{n-1}}{[L]^{n-1}} + \frac{\beta_n}{[L]^n}\right)}$$

$$\alpha_{n-1} = \frac{\beta_1}{[L]} \alpha_n,$$

⋮

$$\alpha_2 = \frac{\beta_{n-1}}{[L]^{n-1}} \alpha_n,$$

$$\alpha_1 = \frac{\beta_n}{[L]^n} \alpha_n.$$

This last set of equations gives the relative concentration of every possible complex as a function of the dissociation constants and free ligand concentration. Therefore, if the values of the dissociation constants are known, then the relative concentration of each complex can be plotted as a function of the free ligand concentration. This diagram, called a distribution of species diagram, shows which species exist and what their relative concentrations are at a given free ligand concentration. The dissociation constants, or equivalently the equilibrium constants, can be calculated from the Gibbs reaction energies for the step-wise dissociation reactions by the relation

$$K = e^{\frac{-\Delta G}{k_B T}}.$$

2.3.2 Aqueous Speciation of Zirconium and Hafnium

2.3.2.1 Hydroxo-Bridged Polymers of Zirconium and Hafnium

In aqueous solutions, zirconium and hafnium form stable hydroxo-bridged polymers in such a way that the distribution of species for these two metals typically consists of polymeric species.²³ In highly acidic environments, the distribution is dominated by tetrameric species.^{23d} As the solution becomes more basic, larger polymeric species dominate.^{23d} It is only when certain strongly coordinating anions, like F^- or SO_4^{2-} , are added that monomeric species are observed.^{23f}

Mass spectroscopy^{23e} analysis of solutions of $ZrOCl_2$ in $HClO_4$ found that while tetrameric species, which are illustrated in Figure 2-9, dominate for solutions with a pH below 1.5, octameric species dominate for solutions with a pH above 1.5. For solutions with a pH below 0, the concentration of the Zr^{4+} monomer is in the order of 10^{-4} M.^{23d}

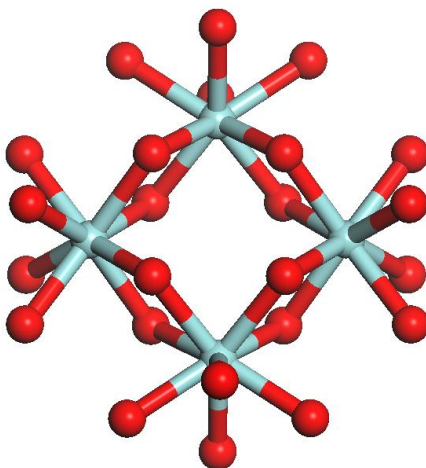


Figure 2-9. An illustration of a hydroxo-bridged zirconium tetramer drawn using Materials Studio's (v6) Visualizer. The light blue spheres represent zirconium atoms and the dark red spheres represent oxygen atoms. Hydrogen atoms have been omitted for clarity.

NMR analysis²⁴ on solutions containing the zirconium tetramer have found that each zirconium atom is bonded to four bridging hydroxo groups. Furthermore, each zirconium is also bonded to four other terminal ligands, which are either aqua or hydroxo groups depending on the pH of the solution. Mass spectroscopy studies^{23e} have shown that, for solutions with a pH below 0, all of these terminal groups are aqua ligands. In situations where all four terminal groups on each zirconium are aqua ligands, two of the aqua ligands appear to be inert while the other two are fast exchanging.²⁴ Adding low concentrations of HNO_3 to the solutions resulted in the substitution of the fast exchanging aqua ligands by NO_3^- , without dissociation of the tetrameric structure.²⁴

The stability of the tetramer is not affected by the presence of low concentrations of strongly coordinating anions. Small angle X-ray scattering experiments^{23c} found that solutions of ZrCl_4 , ZrOCl_2 , $\text{Zr}(\text{NO}_3)_4$, and $\text{Zr}(\text{SO}_4)_2$ all result in almost the same tetrameric structure, where the only difference is that the Zr-Zr distance is 3.38 Å for solutions prepared from $\text{Zr}(\text{NO}_3)_2$ and ZrOCl_2 , whereas it is 3.25 Å for solutions prepared from $\text{Zr}(\text{SO}_4)_2$.^{23c} No confirmed reason for this disparity was given.

Higher concentrations of H_2SO_4 do however break up the tetramer. Small angle X-ray scattering analysis on solutions of ZrOCl_2 has shown that for solutions at 0.5 M H_2SO_4 only dimeric structures of zirconium^{23f} or hafnium^{23g} exist; while only monomeric structures exist for solutions at 2.0 M H_2SO_4 .

As a matter of interest, UV-Vis spectroscopy²⁵ studies of solutions containing titanium did not reveal any evidence for the existence of monomeric titanium species. Rather dimers started to form when H_2SO_4 was added.²⁵ However, at high H_2SO_4 concentrations, FTIR spectroscopy²⁶ found only monomeric species.

2.3.2.2 Zirconium and Hafnium Fluorides

An extensive literature survey did not find any experimental work that has been done to determine which species are present in aqueous solutions of ZrF_4 or HfF_4 . However, as discussed below, work has been done on similar complexes.

Molecular modelling calculations²⁷ of the enthalpy of formation of ZrF_4 , ZrF_5^- , ZrF_6^{2-} and ZrF_7^{3-} in the gas phase predicted that ZrF_6^{2-} is the most stable zirconium fluoride. This prediction has partly been confirmed by NMR spectroscopy²⁸ of K_2ZrF_6 in aqueous solutions, where only peaks corresponding to ZrF_6^{2-} were observed. The authors of the NMR study specifically concluded that it did not seem as if ZrF_5^- was present. It should be noted that these NMR experiments²⁸ did not involve adding fluoride salts or HF to the solution; therefore nothing can be said about the possible formation of ZrF_7^{3-} . Furthermore, the NMR study²⁴ also involved analysis of K_2HfF_6 . The results were analogous to those of K_2ZrF_6 , i.e. only peaks corresponding to HfF_6^{2-} were observed.

Molecular modelling calculations²⁹ of the enthalpy of formation of monomeric ZrF_6^{2-} and dimeric $\text{Zr}_2\text{F}_{12}^{4-}$ in the gas phase, predicted that ZrF_6^{2-} should dimerise. NMR work²⁸ has found that this is not the case. Solutions of K_2ZrF_6 show no trace of the dimerised species. It is possible that $\text{Zr}_2\text{F}_{12}^{4-}$ is intrinsically stable, but that the solvent environment affects the dimer in such a way that ZrF_6^{2-} is more stable in aqueous solutions. This could explain the apparent discrepancy between the prediction that ZrF_6^{2-} would dimerise in the gas phase and the experimental observation that ZrF_6^{2-} is stable in aqueous solutions.

It has been concluded that ZrF_6^{2-} is not bound to any aqua ligands. Thermogravimetric studies³⁰ of MgZrF_6 , precipitated from solutions of ZrO_2 in 40% HF, found that aqua ligands are not coordinated to the zirconium metal. Since hydrolysis involves dissociation of an aqua ligand proton, the observation that ZrF_6^{2-} is not bound to aqua ligand implies that ZrF_6^{2-} will not hydrolyse.

For titanium the following was observed. Calculations of the energy of formation of TiF_4 and Ti_2F_8 in the gas phase have predicted that the dimer is more stable by about 10 kcal/mol.³¹ NMR studies³² of solutions of TiF_4 in pure aqua and in aqueous hydrofluoric acid have only found monomeric species. As before, it is possible that the dimer, Ti_2F_8 , is stable in gas phase, but that TiF_4 is stable in aqueous solutions. In contrast to the NMR experiments on K_2ZrF_6 , the NMR experiments³² on TiF_4 have found TiO^{2+} , TiOF^+ , TiOF_2 , TiF^{3+} , TiF_4 , TiF_5^- and TiF_6^{2-} species in solution. For solutions containing six or more fluoride atoms per titanium atom, TiF_6^{2-} dominates, even for solutions containing up to thirty-four fluoride atoms per titanium atom.

2.4 Solvent Extraction

Solvent extraction, or liquid-liquid extraction, is a separation technique by which solutes are selectively extracted from one liquid phase into another immiscible liquid phase. In the context of hydrometallurgy, one or more metals are preferentially extracted, from a mixture of metals, from an aqueous phase into an immiscible organic phase. Such hydrometallurgical extractions are often facilitated by extractants – organic ligands which preferentially bind to certain metals to form organometallic complexes that favour dissolution in the organic phase.

Solvent extraction is widely used in hydrometallurgical processes for the separation and purification of metals from ores and other sources (see Figure 2-10).³³ The initial step in such hydrometallurgical processes, called leaching, is the dissolution of metal ores into an aqueous phase. Leaching is traditionally done by dissolving the crushed ores in strong acids such as HCl, HNO₃, H₂SO₄, or even HF. The next step is the solvent extraction step, in which certain metals are preferentially transferred into the organic phase. The following step, called stripping, involves the transfer of metals from the organic phase into another aqueous phase. It may be desirable to reduce the metals to their solid state, in which case a reduction step can be added to the tail end of the process. It should be noted that each of the four steps mentioned can, in principle, facilitate the overall separation and purification of the initial metal mixture. Furthermore, real-world hydrometallurgical processes involve multiple extraction, stripping and/or reduction steps.³³

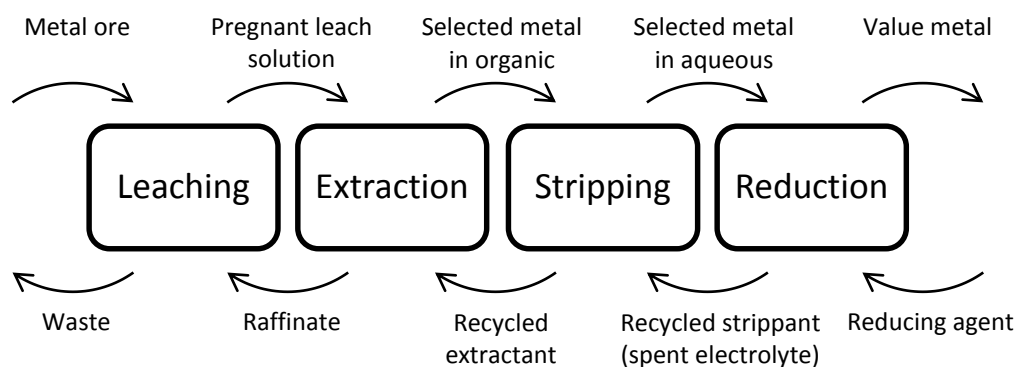


Figure 2-10. An idealised representation of a solvent extraction based hydrometallurgical process for the separation and purification of metals from their ores. Adapted from references 39 and 42.

During extraction, the aqueous phase (i.e. the leach solution) consists of a mixture of metals dissolved in strong acids. This aqueous phase is contacted with an organic phase that typically consists of high boiling point hydrocarbons, chosen on the basis of safety and cost effectiveness. The organic phase can also contain so-called modifiers. Modifiers are organic molecules that aid in phase disengagement, the transfer of metals into the organic phase, and solubility of the metals in the

organic phase.³³ A contemporary alternative to phase disengagement modifiers is the use of hollow-fibre membranes as contactors for the aqueous and organic phases.³⁴

Once the selected metals have been transferred to the organic phase, these metals are stripped into another aqueous phase. Doing so allows the recycling of the extractant molecules. Therefore, the organic phase is effectively a closed loop: the extractant molecules bind to metals from the leach solution, then transfer these metals into the strippant, before binding to new metals from the leach solution. In fact, all the steps in the hydrometallurgical process represented in Figure 2-10 are closed loops. Metal ore enters the process and the purified value metal, along with waste, exits the process. Since each step in the process is a closed loop, solvent extraction has excellent materials and energy balances.

Due to the increasing demand for metals, diminishing of high grade ores (i.e. ores which can be processed by pyrometallurgical methods) and drives for more environmentally friendly industrial processes, solvent extraction based hydrometallurgical processes are attractive technologies with which to separate and purify metals from their ores.³³ The high selectivity of these processes allows separation and purification of metals from low grade ores and secondary sources, such as spent catalysts and electronics. Furthermore, due to the continuous mode of operation, solvent extraction based processes have lower labour costs compared to other technologies.³⁵ The high selectivity that can be obtained by solvent extraction, makes it an ideal candidate technology for the separation of zirconium and hafnium.³⁵

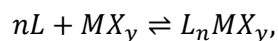
Section 2.4, which is the section on solvent extraction, is divided into two parts. In the first part, Section 2.4.1, the principles of solvent extraction are presented. From a chemistry perspective, the mechanisms which underpin solvent extraction reactions can be categorised into one of three classes, depending on whether the metal complex that binds to the extractant is a neutral complex, a cationic complex, or an anionic complex. Each class of mechanism has certain consequences in terms of how the extraction is affected by the pH of the solution and which strategy is suited for the stripping of the metal(s). If the mechanism by which ZrF_4 and HfF_4 is extracted can be identified, then knowing these consequences might aid in the future design of a solvent extraction based separation process.

In Section 2.4.2 the three major commercial processes for the production of nuclear grade zirconium and hafnium are presented: the TBP process, the MIBK process and the CEZUS process.

2.4.1 Principles of Solvent Extraction

2.4.1.1 Extraction of Neutral Complexes

Neutral complexes, MX_y , are transferred into the organic phase by binding to a neutral extractant. The extraction reaction can be given as:

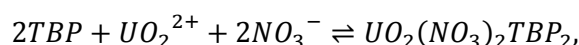


where L is the extractant and L_nMX_y is the extracted organometallic complex. The number of extractant molecules that bind to the metal complex, n , can be determined experimentally by the slope analysis method (see Section 2.4.1.4). Aqueous phases that are dominated by neutral complexes are often the result of leaching processes that involve moderate concentrations of strongly coordinating anions, such as Cl^- and NO_3^- .³³

It should be noted that although H^+ does not explicitly appear in the extraction reaction above, the extraction could still be indirectly influenced by the pH of the aqueous phase. For instance, complexes which contain aqua ligands form hydrolysis species depending on the pH of the solution. Furthermore, extractants which have lone electron pairs on oxygen or nitrogen atoms can be protonated in low pH solutions, which could therefore change the charge and chemical behaviour of the extractant.

Metallurgists often refer to this kind of extraction mechanism as a “solvation mechanism”. It has been suggested^{33,36} that this terminology is potentially misleading, since it might be interpreted to mean that the extractant binds to the complex exclusively through intramolecular interactions, i.e. that the extractant apparently solvates the complex. This is not the case. In this kind of mechanism, extractants can bind to the complex either by binding to the metal’s inner sphere, outer sphere or both.³⁶

A famous example of an extraction in which a neutrally charged complex is transported into the organic phase by binding to a neutrally charged extractant is the PUREX³⁷ process, which is used for the purification of uranium and plutonium from nitrate mediums. The extraction reaction for uranium is given by



where TBP (tri-n-butylphosphate) is the extractant. Single crystal X-ray diffraction spectroscopy³⁸ of the extracted complex suggests that the NO_3^- groups and extractant molecules are coordinated to the metal’s inner sphere, as shown in Figure 2-11.

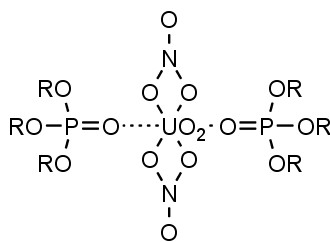
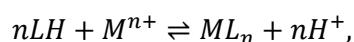


Figure 2-11. Representation of the extracted complex formed during the PUREX process. R is a n-butyl group. The structure was elucidated by X-ray diffraction.³⁸

2.4.1.2 Extraction of Cationic Complexes

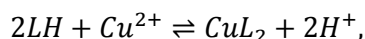
Cationic complexes, M^{n+} , bind to the extractants by substituting a proton on the extractant molecule. The extraction reaction can be given as:



where LH is a protonated extractant molecule. In this mechanism, the extractants are typically organic acids, such as carboxylic acids or phosphorus acids.³³ Aqueous phases that are dominated by cationic complexes are often the result of leaching processes that involve weakly coordinating anions, such as SO_4^{2-} .³³

In this kind of extraction mechanism there is a competition between M^{n+} and H^+ to coordinate to the deprotonated ligand. Therefore, these kinds of extractions are enhanced by low H^+ concentrations in the aqueous phase. On the other hand, stripping of the metals can be achieved by having a high H^+ concentration in the stripping solution. This method of controlling the extraction and stripping by adjusting the pH of the aqueous phases is sometimes called the pH-swing mechanism.^{33,36}

An example of this kind of mechanism is the extraction of copper by phenolic oximes, which depicted in Figure 2-12.³⁹ The extraction reaction is given by:



where LH is the protonated phenolic oxime. Phenolic oximes bind preferentially to copper because of the goodness-of-fit of the copper cation inside the cavity of the pseudo ring that is formed by dimerised phenolic oxime. Phenolic oximes can be fine-tuned to bind more preferentially to other metals by varying the groups next to the position of the phenol group (i.e. group X in Figure 2-12). When halogens are placed next to the position of the phenol group, steric hindrance between these halogens and the phenolic proton causes changes in the size of the cavity.

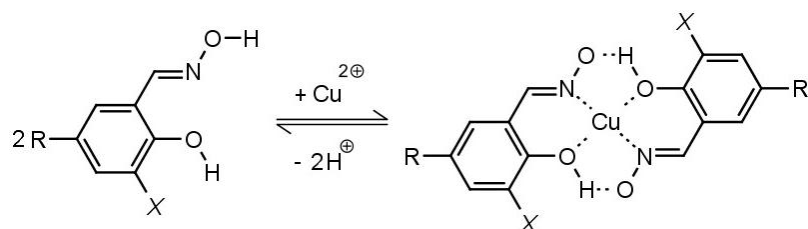


Figure 2-12. An illustration of the extraction of copper by phenolic oximes.³⁹ R is an alkyl group. X is a hydrogen or halogen groups.

It should be noted that the number of extractant molecules that coordinate to the metal complex is not necessarily equal to the charge of the cationic complex. For instance, phosphorus acids are known to form dimers in non-polar solvents, such as hydrocarbons.⁴⁰ In such cases the metal substitutes one of the hydrogens in the dimeric extractant molecule, as depicted in Figure 2-13. The extraction reaction is given by:

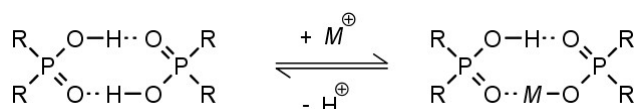
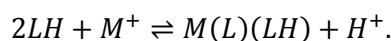


Figure 2-13. An illustration of the extraction of a cationic complex by phosphoric acid based extractants. Adapted from reference 42.

As mentioned before, the slope analysis method (see Section 2.4.1.4) can be used to determine the number of extractant molecules which form part of the extracted organometallic complex experimentally.

Furthermore, it is also possible that four extractant molecules coordinate to a single metal molecule, as depicted in Figure 2-14. In this case, the extraction reaction is given by:

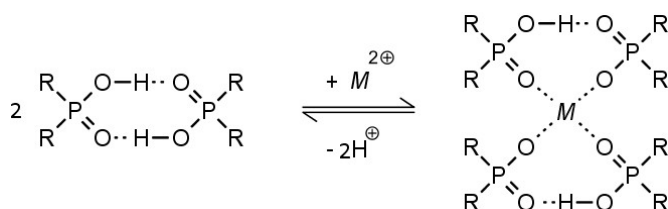
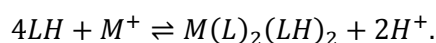
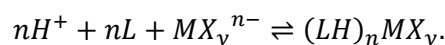


Figure 2-14. An illustration of the extraction of a cationic complex by phosphoric acid based extractants. Adapted from reference 42.

2.4.1.3 Extraction of Anionic Complexes

Anionic complexes, MX_y^{n-} , can be transferred into the organic phase by binding to an extractant that has been protonated. The extraction reaction can be given by:

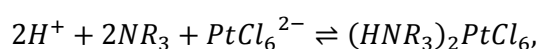


Aqueous phases that are dominated by anionic complexes are often the result of leaching processes in which high concentrations of strongly coordinating anions are present.³³

Since the extractant molecules have to be protonated to bind to the anionic metal complex, these kinds of extractions are enhanced by high H^+ concentrations in the aqueous phase. Subsequently, the stripping of the metals can be achieved by having a low H^+ concentration in the stripping solution.

When anionic complexes are present in the aqueous phase, the extractant molecules most often binds to the metal's outer sphere.^{33,36} In such cases, the metal's intrinsic preference for the hardness/softness of the binding atom cannot be exploited to enhance the selectivity. Selectivity has to be achieved on the basis of intramolecular interactions.

An example of this kind of extraction is the extraction of platinum from chloride mediums.⁴¹ The extraction reaction is given by:



where the extractant, NR_3 , is a trialkyl amine. During this extraction the extractants bind to the $PtCl_6^{2-}$ by hydrogen bonds, as shown in Figure 2-15.

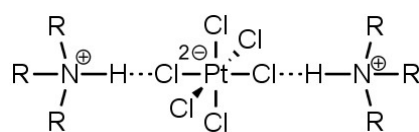
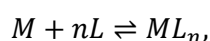


Figure 2-15. A representation of the extracted complexes formed during the extraction of platinum by amines. Adapted from reference 42. R can be a hydrogen or alkyl group.

2.4.1.4 Slope Analysis Method for Determining the Extractant Stoichiometry

It is possible to experimentally determine the number of extractant molecules that form part of an extracted complex, by simply repeating a solvent extraction experiment for different concentrations of the extractant. To see how this works, consider the following equilibrium:



which corresponds to the equilibrium expression

$$K = \frac{[ML_n]}{[M][L]^n}.$$

Taking the logarithm on both sides of the equilibrium expression gives

$$\log K = \log \left(\frac{[ML_n]}{[M][L]^n} \right).$$

Rewriting this equation gives

$$\log K = \log \left(\frac{[ML_n]}{[M]} \right) - n \log [L].$$

The quantity $\frac{[ML_n]}{[M]}$ is simply the distribution constant, D , the value of which is typically determined by ICP. Rewriting of the above equation gives

$$\log D = n \log [L] + \log K.$$

The slope of the graph of $\log D$ vs $\log [L]$ is the number n , which is the stoichiometric coefficient for the number of extractant molecules in the extracted organometallic complex.

2.4.2 Current Industrial Processes for the Separation of Zirconium and Hafnium

2.4.2.1 MIBK Process

In the MIBK³⁵ process, a mixture of $ZrOCl_2$ and $HfOCl_2$ is leached into a 2.0 M HCl solution. NH_4SCN is added to this solution to give an aqueous phase that consists of zirconium and hafnium thiocyanate complexes. When the aqueous solution is contacted to an organic solution that consists of pure methyl isobutyl ketone (i.e. MIBK), the hafnium thiocyanate complexes are preferentially extracted into the organic solution.

The MIBK process suffers from environmental, safety and economic drawbacks. The use of NH_4SCN results in the production of waste streams which contain cyanides and thiocyanides. Another hazard is the low flash point (14 °C) of methyl isobutyl ketone.⁴² Furthermore, methyl isobutyl ketone has solubility in water of almost 2 g/l, leading to loss of extractant from the organic phase.⁴³

2.4.2.2 TBP Process

In the TBP³⁵ process, a mixture of Na_2ZrO_3 and Na_2HfO_3 is leached into an aqueous phase that consists of 3.0 M HNO_3 and 3.5 M $NaNO_3$. The aqueous phase is contacted to an organic phase that consists of

60% tributylphosphate (i.e. TBP) in kerosene. Zirconium is selectively extracted into the organic phase.

The TBP process also suffers from safety and economical drawbacks. Mixtures of tributyl phosphate and highly concentrated HNO_3 form an explosive called red-oil.⁴⁴ At the same time, the use of 60% tributyl phosphate results in high chemical costs. Furthermore, since zirconium, which is the major component in naturally occurring zircon, is extracted, the TBP process is not efficient at producing high purity hafnium.

2.4.2.3 CEZUS Process

The CEZUS³⁵ process is an extractive distillation process. A mixture of molten KCl and AlCl_3 is poured counter-current into a mixture of rising ZrCl_4 and HfCl_4 vapour. The zirconium is extracted preferentially into the KCl/AlCl_3 mixture.

Since the KCl and AlCl_3 have to be heated to very high temperatures, the CEZUS process has the economic drawback of being energy intensive.

2.5 Conclusions

Recall that this project had two objectives: to model the aqueous speciation of ZrF_4 and HfF_4 , and to use of a combined molecular modelling and experimental approach to investigate the bonding and reactivity of ZrF_4 and HfF_4 with phosphorus based extractants.

Concerning the first objective, the thermodynamic description of aqueous speciation, as presented in Section 2.3, provides a suitable framework from which to investigate the aqueous speciation of ZrF_4 and HfF_4 . Accordingly, Bjerrum's method, which was presented in Section 2.3.1.2, can be used to derive the distribution of species for aqueous ZrF_4 and HfF_4 , as a function of pF and pH , given that the Gibbs reaction energies corresponding to the step-wise dissociations of F^- and H^+ are known. The reason why the dissociation of H^+ has to be considered is that water molecules could coordinate to ZrF_4 and HfF_4 , and therefore these complexes could form hydrolysis species.

Therefore, the Gibbs reaction energies that corresponds to all the equilibria which could result from the fluoride dissociation and hydrolysis, would have to be known. As presented in Section 2.2, these Gibbs reaction energies can be predicted by constrained AIMD calculations. DFT, which was introduced in Section 2.2.1, provides a suitable molecular modelling method with which aqueous speciation can be modelled. The use of an explicit solvation model, together with periodically repeating unit cells, can be used to model a bulk aqueous environment. As shown in Section 2.2.3.3,

it is well documented that the method of AIMD can yield accurate predictions for dissociation constants.

Concerning the second objective, conceptual DFT, which was presented in Section 2.2.1.2, provides a suitable framework from which to model the bonding and reactivity between the aqueous ZrF_4 and HfF_4 complexes and the phosphorus based extractants. By using Fukui functions predictions can be made about the regioselectivity with which extractants could bind to the ZrF_4 and HfF_4 complexes. The calculating of local hardnesses allows predictions to be made about the preferentiality which with a given extractant would bind to either ZrF_4 or HfF_4 . Furthermore, experimental investigating the overall ability of a given extractant to extractant ZrF_4 and HfF_4 , and the preferentiality with which it does so, compliments the molecular modelling, since this combined approach might make it possible to identify which one of the basic classes of extraction mechanisms, as presented in 2.4.1, best suits the extraction of ZrF_4 and HfF_4 .

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CHAPTER 3 AQUEOUS SPECIATION

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3.1 Introduction

In this chapter the work that was done in pursuit of the first objective of this study, namely the molecular modelling of the aqueous speciation of ZrF_4 and HfF_4 , is presented. Recall from Chapter 2 that aqueous speciation of ZrF_4 and HfF_4 can be described as a set of equilibria, and that the distribution of species for zirconium and hafnium can be determined if the species which contribute to these equilibria, as well as the values of the corresponding equilibrium constants, are known. The problem of knowing which species are part of the equilibria can be solved by Bjerrum's method.¹ The values of the corresponding equilibrium constants, K , can be calculated from the Gibbs reaction energy, ΔG , by the relation

$$K = e^{\frac{-\Delta G}{k_B T}},$$

where k_B is Boltzmann's constant and T is temperature.²

Gibbs reaction energies can be predicted by means of ab initio molecular dynamics (AIMD). During the past two decades AIMD has become a standard computational tool for predicting the microscopic structure of molecules and ions solvated in condensed phases.³ AIMD has been applied to the study of pure water, solvated ions and solvated complexes.³ During molecular dynamic calculations the motion of a system's atoms is solved classically given the forces between the atoms of the system. AIMD is a kind of molecular dynamic calculation in which the system's electronic structure is calculated quantum mechanically; therefore the forces between the atomic nuclei and the system's electronic structure are calculated accurately. Due to its relatively low computational cost and reasonable accuracy, density functional theory is well suited for treating a system's electronic structure during AIMD calculations for systems containing up to about 300 atoms, as is necessary when modelling aqueous speciation (see Section 2.2).

Thermostats are used during molecular dynamic calculations to ensure that the average of the modelled system's temperature is kept at a desired value and that the system behaves canonically (see Section 2.3.1). Since it is difficult to know beforehand which thermostat to use for a particular AIMD calculation, it is necessary to compare various thermostats. To that end, all thermostats available in DMol³, the software code which was used for the work presented in this chapter, were compared to determine which one is best suited to use when modeling the aqueous speciation of ZrF_4 and HfF_4 .

As mentioned in the introductory paragraph, Bjerrum's method can be used to determine which species contribute to the aqueous speciation of ZrF_4 and HfF_4 . However, to use Bjerrum's method it is necessary to know how many ligands can, at most, be coordinated to either zirconium or hafnium

(see Section 2.2). For instance, four F^- groups are bound to each metal atom in ZrF_4 and HfF_4 , which implies that for each metal there can exist, in principle, five products as a result of the step-wise dissociation of F^- . Similarly, to determine how many hydrolysis species can exist, it is necessary to know how many aqua ligands are coordinated to ZrF_4 and HfF_4 . Therefore, AIMD equilibration calculations were done on periodically repeating cells, populated with water molecules and either ZrF_4 or HfF_4 , to determine how many aqua ligands are bound to each complex in aqueous solutions.

After it had been determined how many ligands are coordinated to aqueous ZrF_4 and HfF_4 , the step-wise dissociation of F^- and step-wise hydrolysis reactions of aqueous ZrF_4 and HfF_4 were modelled by calculating the corresponding Gibbs reaction energies using thermodynamic integration (see Chapter 2). Finally, the distribution of the aqueous ZrF_4 and HfF_4 species as a function of pH were plotted. As will become clear later in this chapter, there was no reason to plot the distributions of the species as a function of pF.

The rest of this chapter is presented as follows. In Section 3.2 the molecular modelling method which was used is presented, including the comparison of thermostats, the equilibration of the periodic cells to determine how many aqua ligands are bound to each complex, and the method which was used to study the F^- dissociation and hydrolysis reactions. In section 3.3 the results and the discussion thereof are presented, followed by conclusions on the work done on the aqueous speciation of ZrF_4 and HfF_4 in Section 3.4.

3.2 Methods

The molecular modelling presented in this chapter was done using the DMol³ code⁴⁻⁵ as implemented in Accelrys' Materials Studio (v 6) molecular modelling software package. The calculations were done within the framework of density functional theory, where the PW91 functional⁶ was used to calculate the electron correlation and exchange terms of the Kohn-Sham energy expression⁷. Dispersion corrections were accounted for using the OBS scheme.⁸ All electron relativistic double numerical polarised plus diffusive basis sets (DNP+) were used to represent the electron density for each element.⁴⁻⁵ Since the modelling presented was done on various periodic systems, the values for the electron density function cut-off was half the size of the cubic periodic cell used in each instance. An orbital smearing of 0.005 Ha was allowed for all calculations to aid in the convergence of the self-consistent field calculations.

3.2.1 Comparison of Thermostats

All six thermostats available in the DMol³ code were investigated in this study. These thermostats are: 1) the Simple Nosè-Hoover thermostat (NH)⁹⁻¹⁰, 2) the Nosè-Hoover Chain thermostat (NHC)⁹⁻¹⁰, 3) the Massive Nose-Hoover Chain thermostat (MNHC)¹¹, 4) the Gaussian thermostat¹², 5) the Generalised Gaussian Moments thermostat (GGM)¹², and 6) the Massive Generalised Gaussian Moments thermostat (MGGM)¹¹.

These thermostats were investigated by running AIMD calculations on periodic cells containing water molecules, and comparing the average of the systems' temperatures and the standard deviations on those temperatures. An initial periodic cell, containing ten water molecules and having sides of 6.687 Å, was prepared by doing geometrically optimisation calculations on this cell. Subsequently, this initial periodic cell was used to do six AIMD calculations, where each calculation was done with a different thermostat while reusing the same initial periodic cell. A time step of 1.0 fs, for a total of 5000 steps, was used for each AIMD calculation. The desired temperature was set at 298.0 K for each thermostat.

The wall time (i.e. the total time it took the calculation to complete) is also reported for each thermostat. To facilitate the comparison, all six AIMD calculations were done on an Intel i7-3770 CPU (3.40 GHz) with 8.00 GB of primary memory. Since hyper threading was enabled on this CPU, all calculations were run in parallel using eight logical processors.

3.2.2 Equilibration of Cells

The maximum number of aqua ligands coordinated to either ZrF₄ and HfF₄ were determined by equilibrating two cubic periodic cells, each containing fifty-two water molecules and either ZrF₄ or HfF₄. The reason for adding fifty-two water molecules is that such a configuration corresponds to a 1 M solution. These two periodic cells, having sides of 11.740 Å, were each equilibrated by first doing geometrical optimisation calculations to minimise their potential energies and then doing 3.0 ps AIMD runs to introduce kinetic energy into these systems. These AIMD calculations were subjected to an NVT ensemble, using the Simple Nose-Hoover thermostat.⁹⁻¹⁰

For the purpose of this study, the intention was to model the systems at 298.0 K. However, generalised gradient functionals, such as the PW91 functional, are known to produce over-structured oxygen-oxygen radial distribution functions due to the absence of calculations which treat quantum proton effects.¹³ This problem can be avoided by setting the thermostat to control the system's temperature at a value higher than what is desired, specifically about 130 K higher.¹³ Subsequently, the thermostat was used to control the temperature at 430.0 K.

3.2.3 Step-wise Dissociation of Fluoride

These two equilibrated periodic cells, which were prepared as explained in Section 3.2.2, were used as initial configurations for the modelling of the F^- dissociation.

The step-wise dissociation of F^- was modelled using AIMD calculations, and the corresponding Gibbs reaction energies were calculated using the method of thermodynamic integration (see Section 2.2). Starting from equilibrated periodic cells (see Section 3.2.2), the metal-fluoride bonds were each elongated by 4.0 Å in a step-wise fashion.

First, the longest metal-fluoride bond was elongated. This was followed by doing geometry optimisation calculations on the periodic cells, followed by a 1.0 ps AIMD calculation. Then the second longest metal-fluoride bond was elongated, followed again by geometry optimisation and a 1.0 ps AIMD calculation. This process was repeated until no more F^- atoms were coordinated to the metals.

The temperature of the system was controlled as explained in Section 3.2.2.

3.2.4 Step-wise Hydrolysis

These two equilibrated periodic cells, which were prepared as explained in Section 3.2.2, were used as initial configurations for the modelling of the hydrolysis.

The step-wise hydrolysis was modelled using AIMD calculations and the corresponding Gibbs reaction energies were calculated using the method of thermodynamic integration (see Section 2.2). Starting from equilibrated cells (see Section 3.2.2), the distances between the metal atoms and the protons that were bound to the aqua or hydroxo ligands were each elongated by 4.0 Å in a step-wise fashion.

The procedure was analogous to the one used to model the F^- dissociation (see Section 3.3.3), where the longest metal-proton distance was elongated, followed by geometry optimisations and a 1.0 ps AIMD calculation.

A major difference between the modelling of the hydrolysis and the F^- dissociation reactions was that in the case of the hydrolysis reactions, the complex could be reprotonated by protons from the environment, which would defeat the purpose of the modelling. Therefore, distance constraints were set for all calculations between the coordinated oxygen atoms and all surrounding protons that were less than 3.5 Å away.

The temperature of the system was controlled in the way explained in Section 3.2.2.

3.3 Results and Discussion

3.3.1 Comparison of Thermostats

The Nosè-Hoover thermostats (i.e. the NH, NHC and MNHC thermostats) are discussed first, followed by the Gaussian thermostats (i.e. the Gaussian, GGM and MGGM thermostats). Since the purpose of a thermostat is to keep the modelled system's average temperature as close as possible to the desired temperature, the thermostats investigated in this study are discussed in view of the proximity of the average temperature to the desired temperature, as well as the magnitude of the standard deviation on those average temperatures. It is beyond the scope of this work to discuss the mathematical foundations of these thermostats.

The NH, NHC and MNHC thermostats kept the system's temperature close to the desired value of 298.0 K as shown in Figure 3-1, Figure 3-2 and Figure 3-3, respectively. Correspondingly, the kinetic energy was kept at approximately 8.0 kcal/mol for all three thermostats.

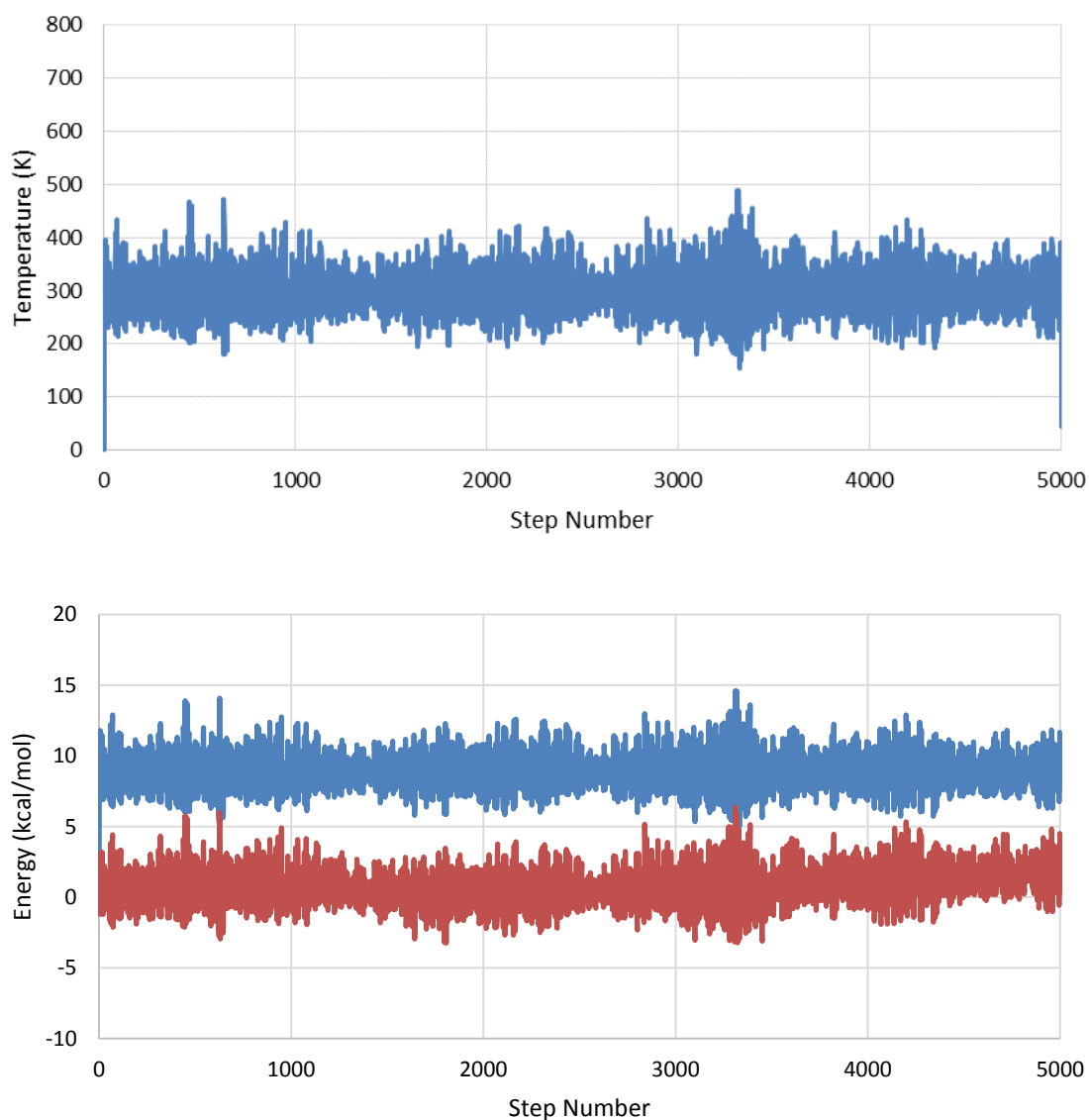


Figure 3-1. System parameters as modelled by the Simple Nosè-Hoover thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

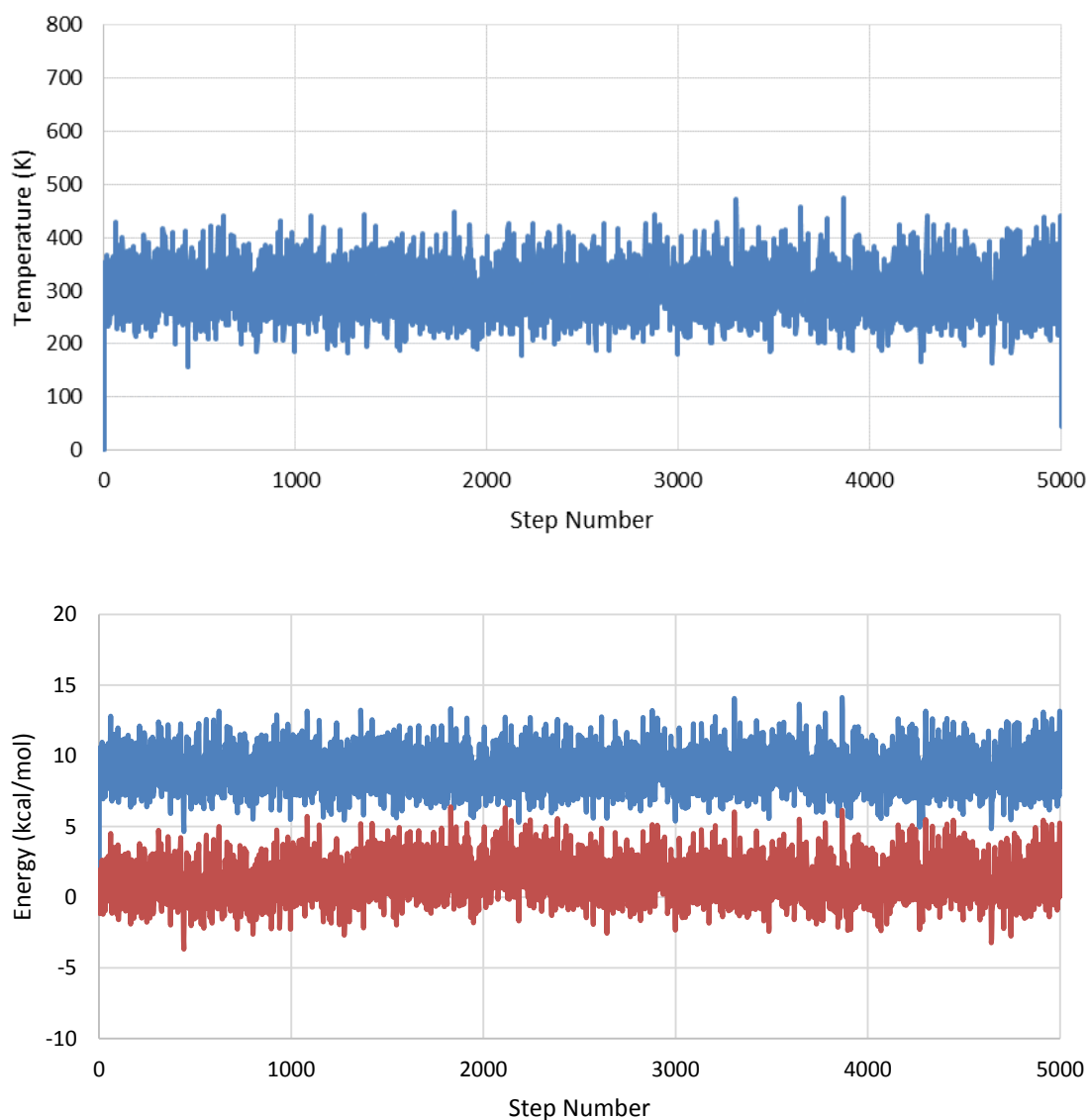


Figure 3-2. System parameters as modelled by the Nosè-Hoover Chain thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

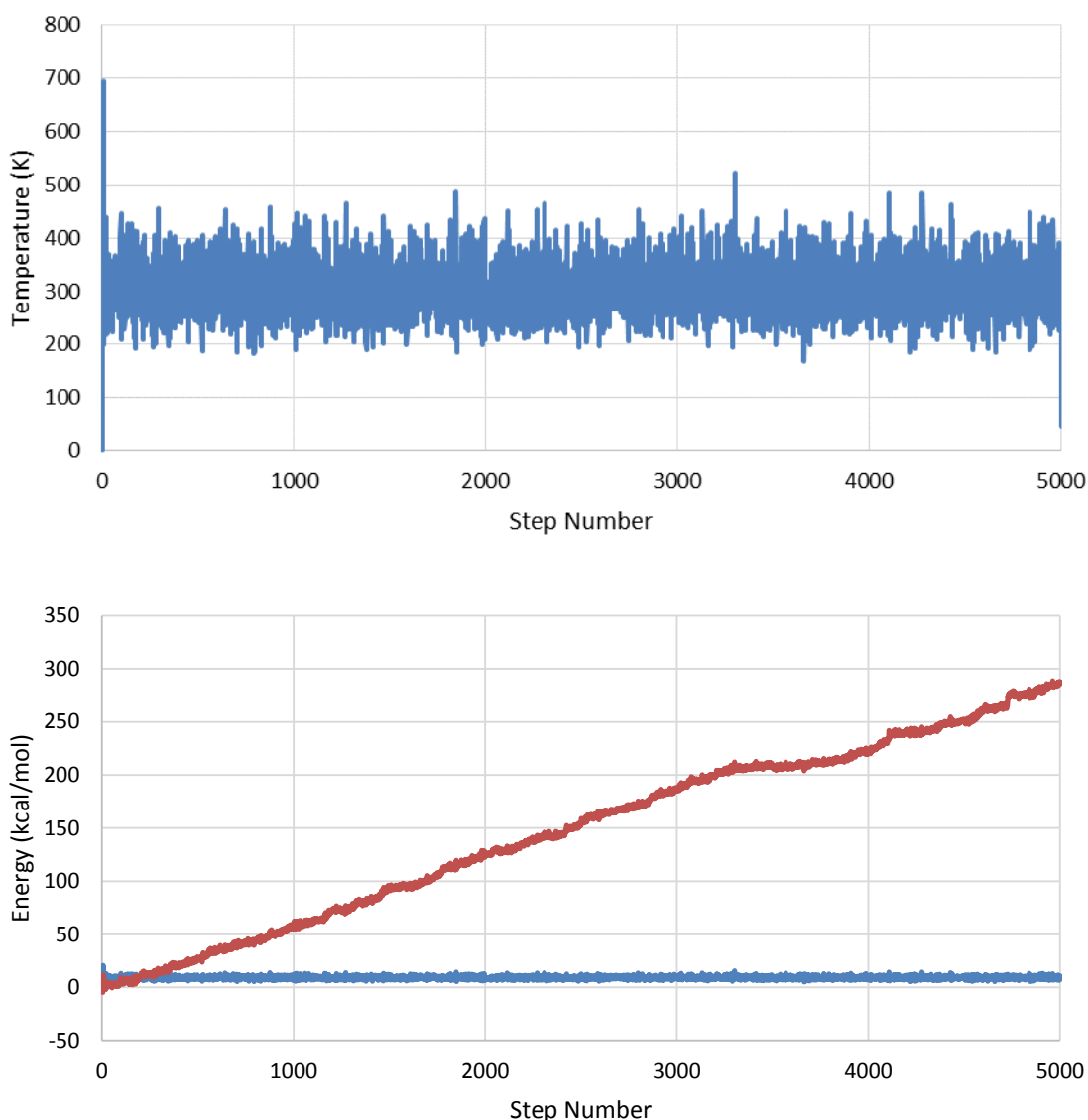


Figure 3-3. System parameters as modelled by the Massive Nosé-Hoover Chain thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

In order to produce accurate predictions, the systems that are being modelled should behave canonically (see Section 2.2). That is, the systems that were investigated should have behaved as if they were in thermodynamic equilibrium with an environment which was at 298.0 K, that entails, amongst other things, that the total energy of these systems should have remained constant. Since the NH and NHC thermostats held the relative total energy close to 0.0 kcal/mol (see Figure 3-1 and Figure 3-2), these thermostats produced the correct behaviour. However, for the MNHC thermostat the relative total energy of the system increased during the course of the AIMD calculation (see Figure 3-3). Since the kinetic energy of the MNHC thermostat remained close to 8.0 kcal/mol, the increase in relative total energy must have been due to an increase in the relative potential energy of the

system. Such an increase in relative potential energy is inconsistent with what would have been expected of a system that is in thermodynamic equilibrium with its environment.

Of the two Nosè-Hoover thermostats that resulted in acceptable behaviour (i.e. the NH and NHC thermostats), the NH showed superior modelling ability. The NH thermostat kept the average of the system's temperature closer to the desired value of 298.0 K, as shown in Table 3-1, compared to the NHC thermostat. Furthermore, the standard deviation on the system's temperature was smaller for the NH thermostat (43.2 K) than for to the NHC thermostat (45.2 K).

As a last remark, note that the wall time for the Nosè-Hoover thermostats were approximately the same (29.5 hours) for each of the thermostats. Since there is only a small difference between the wall times of these three thermostats, distinctions between the performances of the thermostats cannot be made on the basis of which thermostat resulted in less computational time.

Table 3-1. The systems' average temperatures, standard deviations on the systems' temperatures and the wall time for the 5000 step AIMD calculations

Thermostat	Temperature (K)		Wall time (m)
	Average	Standard Deviation	
Simple Nosè-Hoover	298.0	43.2	1763.32
Nosè-Hoover Chain	298.9	45.2	1769.68
Massive Nosè-Hoover Chain	306.1	46.7	1771.69
Gaussian	11.9	24.4	1802.13
Generalised Gaussian Moments	298.0	45.2	1700.86
Massive Generalised Gaussian Moments	6359.5	296.5	1139.26

When considering the Gaussian, GGM and MGGM thermostats, it became clear that only the GGM thermostat kept the system's average temperature close to the desired value of 298.0 K, as shown in Figure 3-5. For the Gaussian thermostat, the system's temperature fell to 0.0 K, as shown in Figure 3-4. For the MGGM thermostat, the system's temperature increased to 6350.0 K, as shown in Figure 3-6. Therefore, both the Gaussian and MGGM thermostats produced incorrect behaviour.

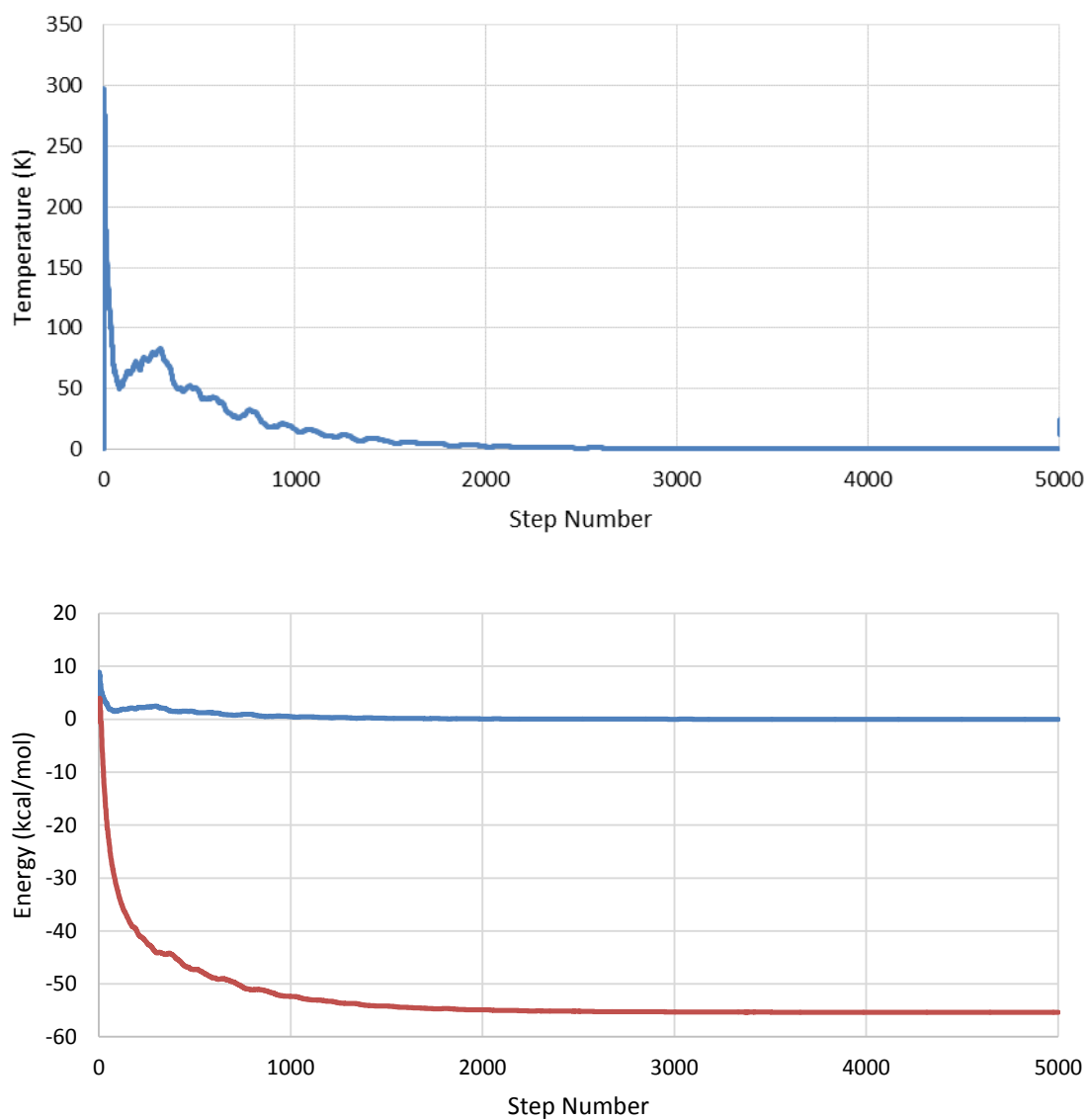


Figure 3-4. System parameters as modelled by the Gaussian thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

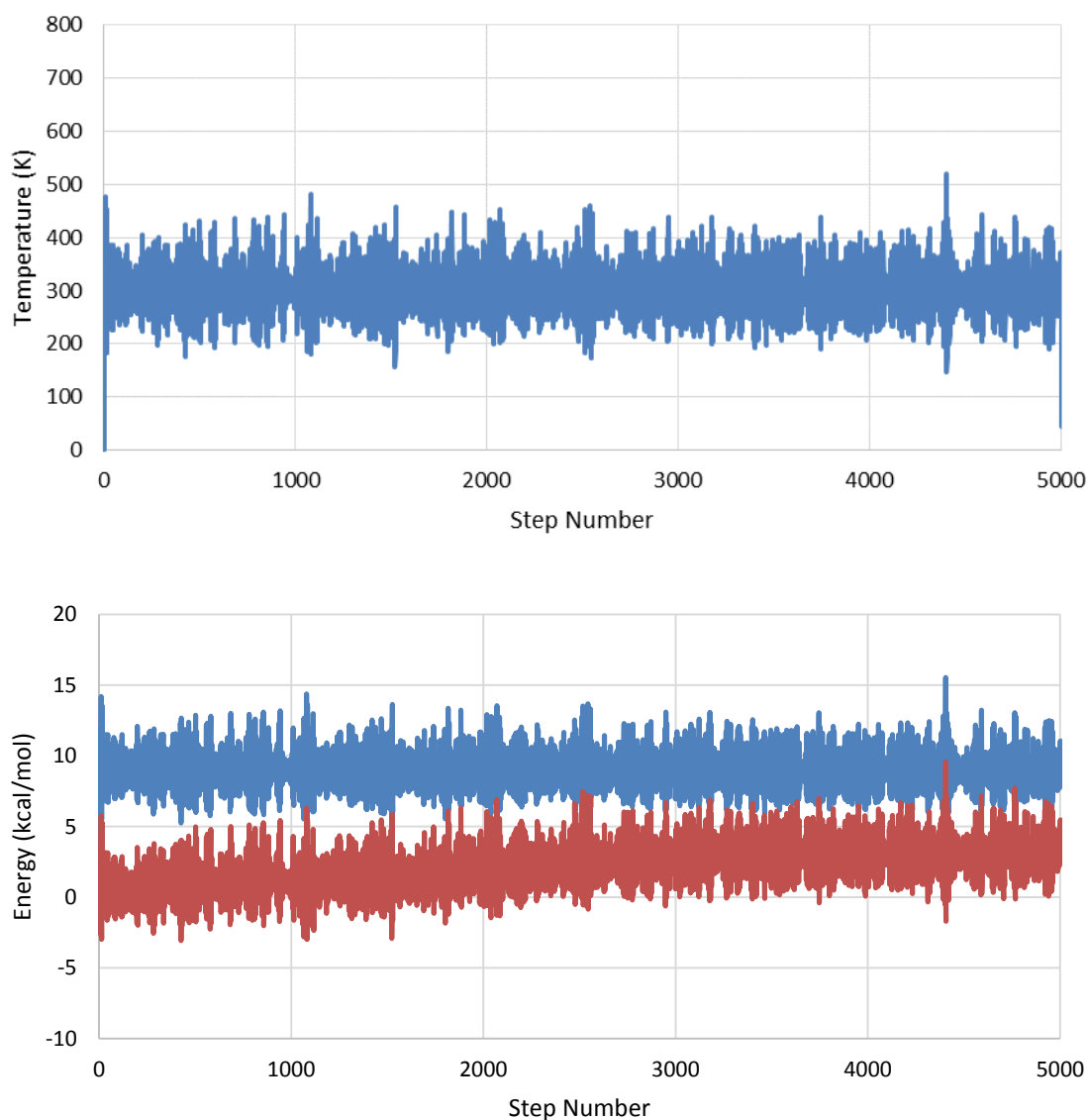


Figure 3-5. System parameters as modelled by the Generalised Gaussian Moments thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

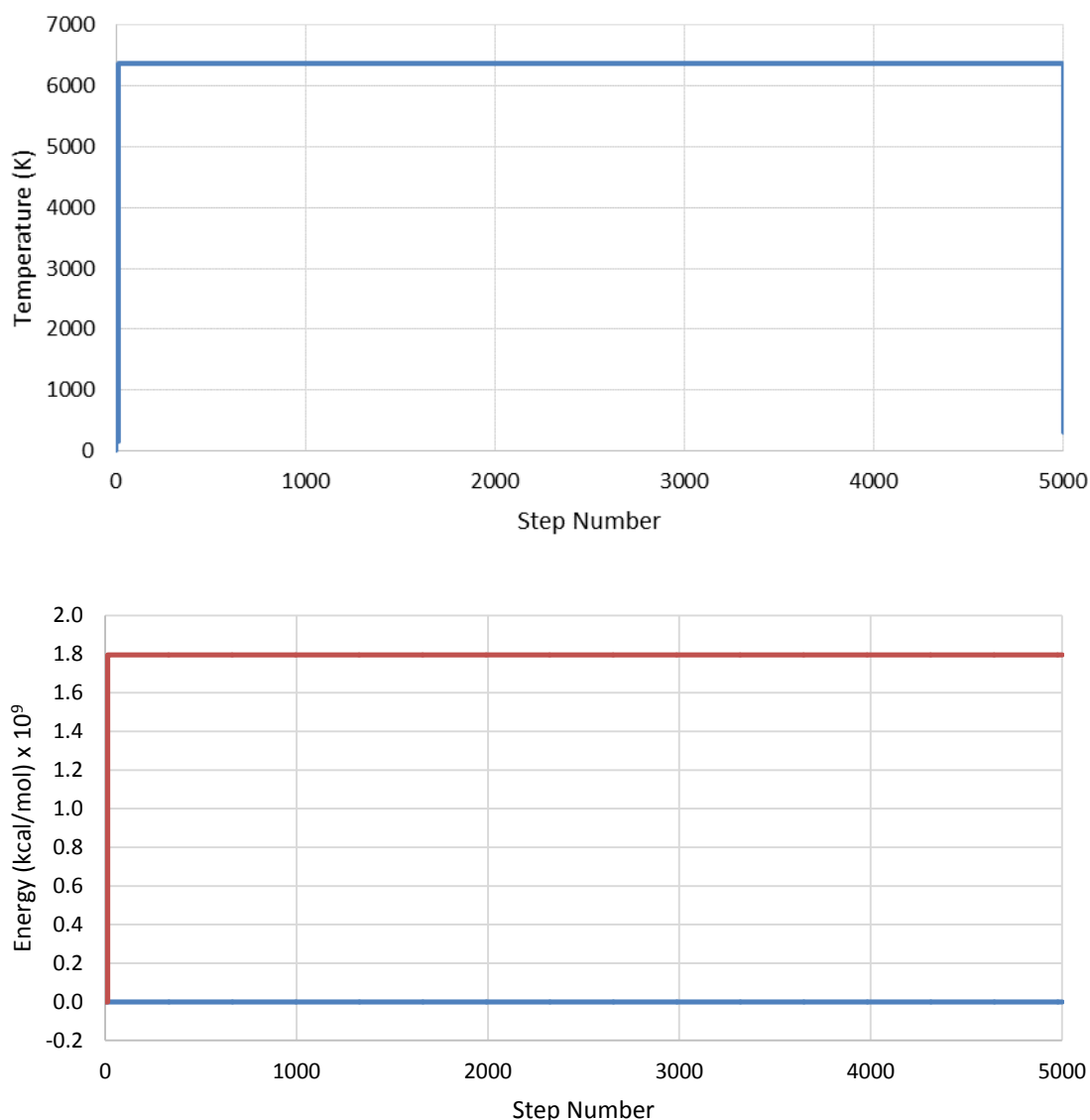


Figure 3-6. System parameters as modelled by the Massive Generalised Gaussian Moments thermostat during an AIMD calculation. Top: System temperature as a function of step number. Bottom: Relative system energy (red plot) and kinetic energy (blue plot) as a function of step number.

For the Gaussian thermostat, the relative total energy fell by about 55.0 kcal/mol during the course of the AIMD calculation. Since the kinetic energy fell by only 8.0 kcal/mol, the relative potential energy must have fallen by about 47.0 kcal/mol. Such an decrease in relative potential energy of the system is inconsistent with canonical behaviour.

The wall time for the Gaussian and GGM thermostats were also about 29.5 hours, which were similar to those of the Nosè-Hoover thermostats. The wall time for the MGGM thermostat was 19 hours, which was the shortest wall time of all the thermostats. However, since the MGGM produced temperatures and energies which are unphysical, this thermostat is unsuitable for the AIMD application. The fact that this thermostat had the smallest wall time is therefore of no consequence.

To summarise, six thermostats were compared for their ability to model systems' temperatures in such a way that the average of these temperatures are kept close to the desired temperature of 298.0 K. The NH, NHC and GGM thermostats were the only thermostats that produced results which are consistent with the behaviour that is expected of systems that are in thermodynamic equilibrium with their environments. Of these thermostats, the NH performed the best, since this thermostat produced an average temperature equal to that of the desired temperature and the smallest standard deviation on the temperature.

3.3.2 Equilibration of Cells

Two cells, each containing fifty-two water molecules and either ZrF_4 or HfF_4 , were equilibrated with the goal of predicting how many aqua ligands would coordinate to each complex. Knowing how many ligands are coordinated to each metal is necessary to be able to apply Bjerrum's method. The equilibrated cells for zirconium and hafnium are shown in Figure 3-7 and Figure 3-8.

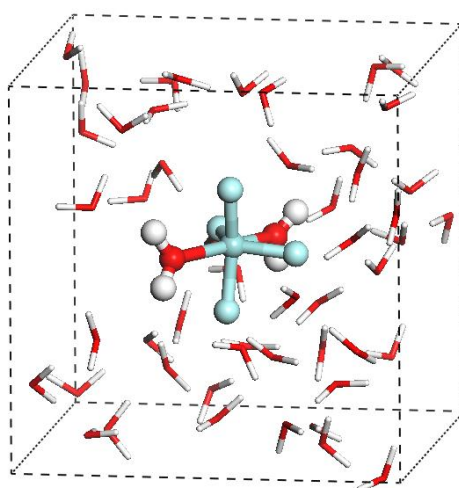


Figure 3-7. The equilibrated aqueous ZrF_4 periodic cell. The zirconium is coordinated to four F^- ligands and two aqua ligands.

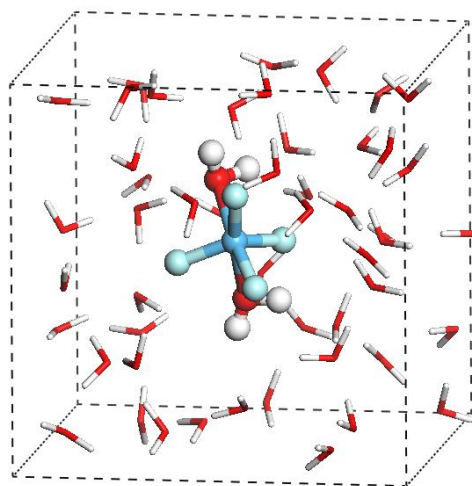


Figure 3-8. The equilibrated aqueous HfF_4 periodic cell. The hafnium is coordinated to four F^- ligands and two aqua ligands.

For both metals, it was predicted that four F^- ligands and two aqua ligands were coordinated to each of the metals. Since each metal is bound to four F^- ligands, it was predicted that five species can, in principle, exist as a result of the step-wise F^- dissociation: $\text{M}(\text{H}_2\text{O})_2\text{F}_4$, $[\text{M}(\text{H}_2\text{O})_3\text{F}_3]^+$, $[\text{M}(\text{H}_2\text{O})_4\text{F}_2]^{2+}$, $[\text{M}(\text{H}_2\text{O})_5\text{F}]^{3+}$, and $[\text{M}(\text{H}_2\text{O})_6]^{4+}$. Furthermore, since each metal is bound to two aqua ligands, and each aqua ligand contains two protons, it was predicted that five species can, in principle, exist as a result of the step-wise hydrolysis: $\text{M}(\text{H}_2\text{O})_2\text{F}_4$, $[\text{M}(\text{H}_2\text{O})\text{F}_4(\text{OH})]^-$, $[\text{MF}_4(\text{OH})_2]^{2-}$, $[\text{MF}_4(\text{OH})(\text{O})]^{3-}$, and $[\text{MF}_4(\text{O})_2]^{4-}$.

It should be noted that although the equilibration calculations produced results regarding the geometry, and therefore the stability, of the aqueous zirconium and hafnium complexes, such discussions are deferred to Chapter 4. The reason for this postponement is that the geometries of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ were modelled as part of the work done in pursuit of the second objective, as will be presented in Chapter 4. However a more accurate method was used for the work presented in Chapter 4 than was used for the work presented in Chapter 3. Therefore the results on the geometries of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ presented in Chapter 4 are more reliable than those presented in Chapter 3. Furthermore, additional types of calculations were done, as presented in Chapter 4 that complements the discussion of the geometries of these complexes.

3.3.3 Step-wise Dissociation of Fluoride

The Gibbs reaction energies for the step-wise dissociation of F^- ligands are shown in Figure 3-9. It is clear that as the step-wise dissociation of F^- continued, the Gibbs reaction energy for each subsequent F^- dissociation increased. The Gibbs reaction energy that was associated with the

dissociation of the first F^- ligand from zirconium or hafnium was about 25.0 kcal/mol, while the Gibbs energy necessary to dissociate the F^- ligands was 200.0 – 250.0 kcal/mol.

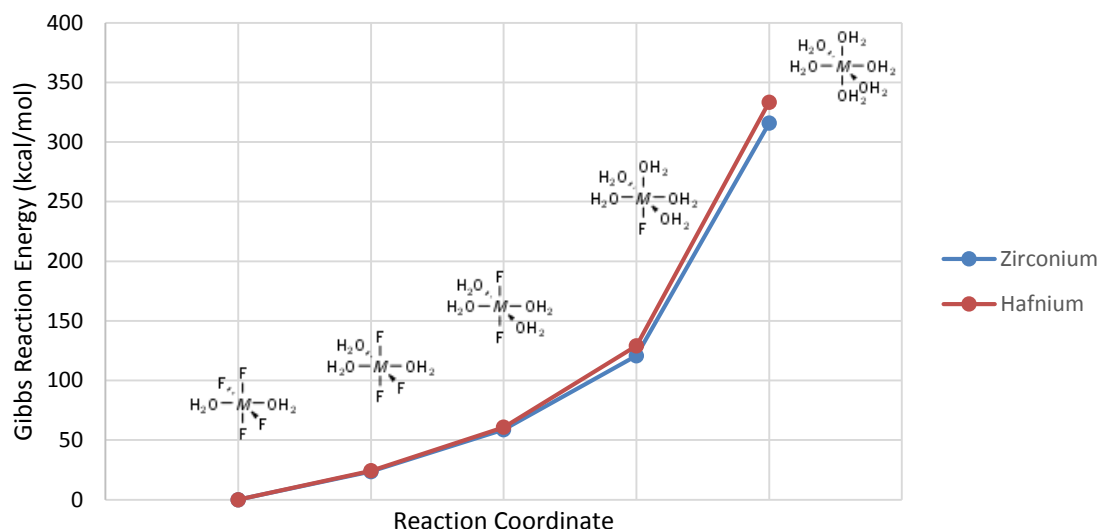


Figure 3-9. Gibbs reaction energy for the step-wise dissociation of F^- from the zirconium and hafnium complexes. All values are given relative to the initial tetrafluoro complexes. The charges on the complexes have been omitted for clarity.

The prediction that the Gibbs reaction energies for the step-wise dissociation of F^- are large (i.e. greater than 20 kcal/mol) can be rationalised by three possible explanations; two of these explanations can also explain the increase in Gibbs reaction energies for each subsequent F^- dissociation. Firstly, while F^- is a hard Lewis base, aqua is a borderline Lewis base.¹ Since zirconium(IV) and hafnium(IV) are hard Lewis acids, these metal atoms would form stronger coordination bonds to F^- than to aqua. Therefore, replacing a F^- ligand by an aqua ligand, would have resulted in an increase in Gibbs energy.

Secondly, as the dissociation of F^- continues, the charge of the resulting complex increases to the point where it is 4+. Localisation of such large charges on a single molecule would significantly increase the energy of the molecule. Therefore, as more F^- ligands dissociated, the charges on the resulting zirconium and hafnium complexes increased, which increased the Gibbs reaction energy for each subsequent dissociation step.

Thirdly, the electronegativity of the zirconium and hafnium atoms could have decreased as F^- ligands dissociated from these atoms. Since the strength of chemical bonds are related to the differences in electronegativity between the two participating atoms, dissociation of F^- ligands would have led to increases in the strengths of the remaining metal-fluoride bonds. Therefore, as more F^- ligands dissociated, the electronegativity of the zirconium and hafnium atoms changed,

which would have resulted in an increase in the Gibbs reaction energy for each subsequent dissociation step.

It is also clear that the Gibbs reaction energies for the dissociation of F^- ligands was predicted to be greater for hafnium than for zirconium (see Figure 3-9). This prediction is consistent with the suggestion that hafnium(IV) is a harder Lewis acid than zirconium(IV), and that F^- , which is a hard Lewis base, would therefore form stronger bonds to hafnium than to zirconium.

Since the Gibbs reaction energies for the dissociation of a F^- ligand from zirconium or hafnium were large (> 20.0 kcal/mol), the equilibrium constants were such that F^- would not dissociate. Therefore, the distribution of species is predicted to be dominated by zirconium and hafnium complexes containing four F^- ligands. None the less, a few remarks can be made about the distribution of species. $Zr(H_2O)_2F_4$ and $Hf(H_2O)_2F_4$ are neutrally charged complexes. It is only by the dissociation of F^- that these complexes can become positively charged, since the only other moieties which are likely to dissociate are a proton or aqua ligand, in which case the resulting complex would be negatively charged or neutral. Given that F^- forms stable coordination bonds with zirconium and hafnium and that dissociation of F^- ligands is the only way to form positively charged complexes, the complexes formed in solution will be either neutral or negatively charged.

3.3.4 Step-wise Hydrolysis

The Gibbs reaction energies for the step-wise hydrolysis of $Zr(H_2O)_2F_4$ and $Hf(H_2O)_2F_4$ are shown in Figure 3-10. Analogous to the F^- dissociation (see Section 3.3.3), the Gibbs reaction energy for each subsequent hydrolysis step increased as the step-wise hydrolysis proceeded. As before, this increase in the subsequent Gibbs reaction energy can be explained as being due to an increase in the charge of the resulting complex. As the step-wise hydrolysis reaction proceeded the complex became more negatively charged, up to the point where it had a charge of 4-, which would have resulted in an increase in the Gibbs reaction energies.

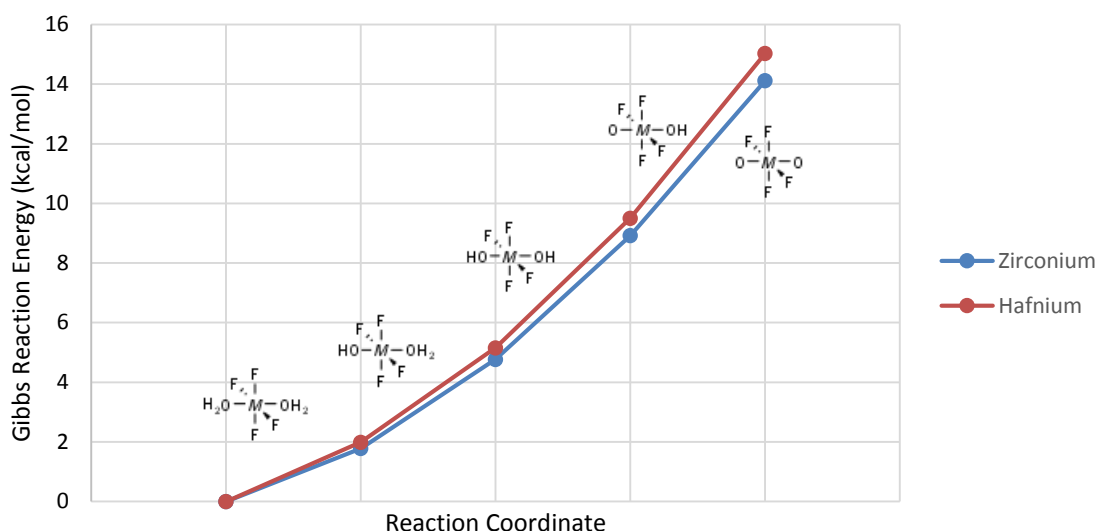


Figure 3-10. Gibbs reaction energy for the step-wise hydrolysis of the zirconium and hafnium complexes. All values are given relative to the initial diaqua complexes. The charges on the complexes have been omitted for clarity.

A noticeable difference between the step-wise F^- dissociation and the step-wise hydrolysis is that the Gibbs reaction energy for the hydrolysis is much less than for the F^- dissociation (14 - 15 kcal/mol vs > 300 kcal/mol for the F^- dissociation). There are two explanations which could be used to interpret this prediction. First, since zirconium and hafnium contained four F^- ligands, the negative charge that would have resulted due to the hydrolysis steps could be stabilised by the highly electronegative F^- ligands. Secondly, since aqua, hydroxo and oxo ligands are all considered borderline bases, the step-wise hydrolysis would not result in the replacement of a strong ligand by a borderline ligand, but rather a weak ligand by a borderline ligand.

Since the Gibbs reaction energies for the step-wise hydrolysis of ZrF_4 and HfF_4 were predicted to be relatively small (2.0 - 4.0 kcal/mol), the equilibrium constants were such that the distribution of ZrF_4 and HfF_4 hydrolysis species as a function of pH contained a number of species as shown for the distribution of hydrolysis species of ZrF_4 and HfF_4 in Figure 3-11 and Figure 3-12, respectively.

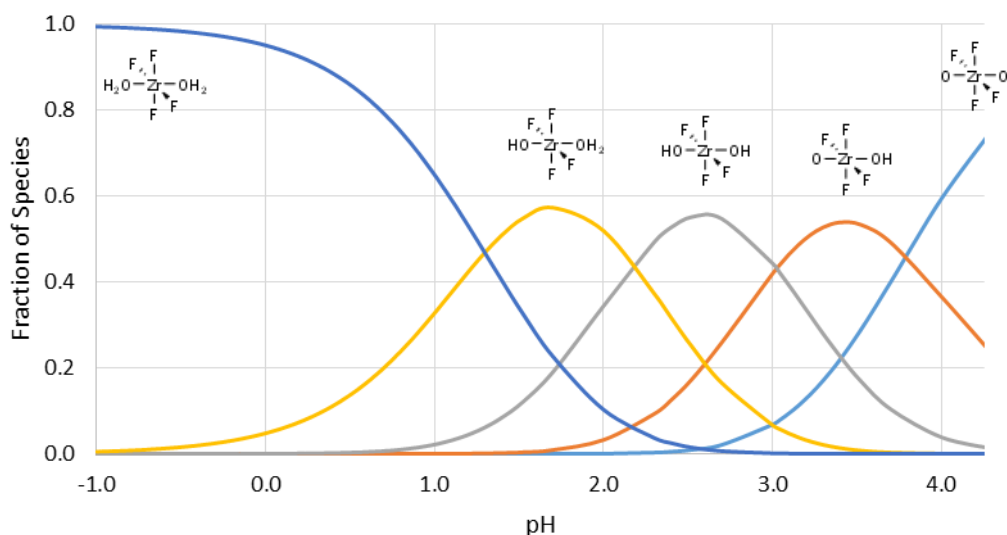


Figure 3-11. The distribution of species for the hydrolysis of ZrF_4

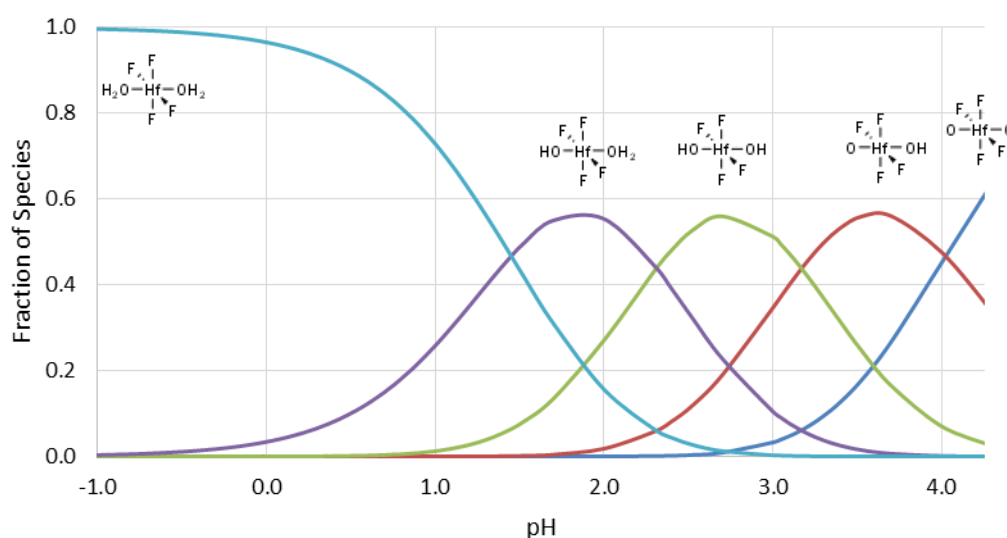


Figure 3-12. The distribution of species for the hydrolysis of HfF_4

Below a pH of 1.0, the distribution of hydrolysis species, for both ZrF_4 and HfF_4 was dominated by fully protonated, neutral complexes. This prediction is consistent with experimental observations made for the zirconium hydroxo-bridged tetramer that below a pH of 0.0 there are not terminal hydroxo ligands coordinated to the zirconium atoms.¹⁴

Comparison of Figure 3-11 and Figure 3-12 reveals that it was predicted that zirconium hydrolyses more readily than hafnium. For instance, at a pH of 1.0, the ZrF_4 distribution consisted of about 60% $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$, and 40% $[\text{Zr}(\text{H}_2\text{O})\text{F}_4(\text{OH})]^-$, while for HfF_4 the distribution consisted of about 65% $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$, and 35% $[\text{Hf}(\text{H}_2\text{O})\text{F}_4(\text{OH})]^-$. This prediction agrees with the experimental results from literature, as discussed in Section 2.3.2.

3.4 Conclusions

Recall that the first objective of this study was to use a molecular modelling approach to investigate the speciation of ZrF_4 and HfF_4 in aqueous environments. In this study, six thermostats were compared for their ability to control the temperature of an aqueous system during AIMD calculations. Of these thermostats, the Simple Nosè-Hoover thermostat gave the best results, since the use of this thermostat resulted in a system which behaved canonically and for which the standard deviation on the temperature was the smallest. Subsequently, predictions were made about how many aqua ligands would coordinate to ZrF_4 and HfF_4 by equilibrating periodic cells that contained water molecules and either ZrF_4 or HfF_4 . It was predicted that each metal would coordinate to two aqua ligands, resulting in $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. This was followed by the modelling of the F^- dissociation and hydrolysis of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$, where the Gibbs reaction energies of these reactions were predicted. Since it was predicted that the Gibbs reaction energies corresponding to the F^- dissociation are greater than 20 kcal/mol, the distribution of species would be dominated by tetrafluoro complexes. Given the Gibbs reaction energies for the step-wise hydrolyses reactions, distribution of species diagrams were plotted for the aqueous ZrF_4 and HfF_4 complexes as a function of pH.

Recall from Section 2.4 that solvent extraction mechanisms can be categorised into one of three classes: extraction of cationic complexes, extraction of anionic complexes and extraction of neutral complexes. Since F^- ligands do not dissociate, and since the dissociation of F^- ligands are the only way in which cationic complexes will be produced, the extraction of ZrF_4 and HfF_4 cannot occur by a mechanism where these complexes are extracted as cationic complexes. Therefore, the extraction of ZrF_4 and HfF_4 will not occur through the substitution of acidic protons on extractants.

The extraction of ZrF_4 and HfF_4 can however occur by either a mechanism where these complexes are extracted as anionic or neutral complexes. If the pH of the aqueous solution is less than 0.0, then the zirconium and hafnium complexes will be fully protonated and therefore be neutral. Therefore, if the pH of the aqueous phase is less than 0.0, and if there are no acid anions present that would coordinate to the metal atoms, then the extraction of ZrF_4 and HfF_4 will occur by a mechanism where these complexes are extracted as neutral complexes. Therefore, the extraction of ZrF_4 and HfF_4 could occur by binding to an extractant which exists as a neutral molecule in solution; or if the extractant exists as a positive molecules in solution, then an acid anionic will form part of the extracted complex in order to satisfy the requirement that the extracted organometallic complex, which dissolves in the organic phase, be neutral.

If the pH of the aqueous solution is above 1.0, then the zirconium and hafnium complexes will be hydrolysed and therefore be anionic. It could also happen that acid anions coordinate to the metal atoms, in which case the complexes remain anionic. Therefore, if the extraction occurs by a mechanism where the complexes are extracted as anionic complexes, then the complexes would have to bind to extractants that are protonated to be positive.

According to the predictions made in this study, in the absence of strongly coordinating acid anions there is very little difference between the speciation of ZrF_4 and HfF_4 . Therefore, separation can only be achieved by either exploiting possible differences in the tendency of acid anions to coordinate more preferentially to either zirconium or hafnium, or by exploiting differences in the reactivity of extractants towards ZrF_4 and HfF_4 .

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CHAPTER 4 SOLVENT EXTRACTION

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4.1 Introduction

In this chapter the work that was done in pursuit of the second objective of this study, namely to use a combined molecular modelling and experimental approach to investigate the bonding and reactivity between the aqueous ZrF_4 and HfF_4 complexes and phosphorus based extractants, is presented. To be able to understand the mechanisms and rationalise the trends that underpinning the solvent extraction of ZrF_4 and HfF_4 by phosphorus based extractants, it is necessary to understand the overall ability of a given extractant to transfer zirconium and hafnium into the organic phase, referred to as the extractant's extractability towards zirconium and hafnium, as well as the ability of a given extractant to transfer either zirconium or hafnium more preferentially into the organic phase, referred to as the extractant's selectivity towards these specific metals.

Investigating the reactivity between the ZrF_4 and HfF_4 complexes and phosphorus based extractants provides insights about the extractability and selectivity of these extractants. If a given extractant reacts with the aqueous ZrF_4 and HfF_4 complexes to yield stable organometallic complexes, then zirconium and hafnium will be transferred into the organic phase. If there is a difference in the stability between these organometallic complexes, then the metal which is associated with the more stable organometallic complex will be extracted selectively.

Investigating the bonding between the ZrF_4 and HfF_4 complexes and phosphorus based extractants during solvent extraction reactions, allows the trends in extractability and selectivity to be related to the trends in the structures of the aqueous ZrF_4 and HfF_4 complexes, and the extractants. For instance, if a given extractant forms stable bonds to both the ZrF_4 and HfF_4 complexes, the both zirconium and hafnium will be extracted. If there is a propensity for the extractant to form more stable bonds to one complexes than to the other, then the metal associated to that complex will be extracted selectively. Therefore, understanding which structural properties of the aqueous ZrF_4 and HfF_4 complexes, and extractants give rise to the formation of stable bonds and differences in bond stability can grant new insights into extractability and selectivity, respectively.

To attend to the abovementioned objective, a combined molecular modelling and experimental approach was used, since these two approaches are complementary in terms of the kinds of data which can be obtained. Experimental work can provide real-world data regarding extractability and selectivity; while molecular modelling can provide information regarding bonding at the atomistic level. Therefore, the combined use of molecular modelling and experimental work allows the trends in extractability and selectivity to be interpreted as consequences of the trends in bonding. Note however that since real-world solvent extraction reactions are complicated, the scope of the molecular modelling had to be limited for the purposes of this M.Sc. project. For instance, it has been

reported that the results of solvent extraction reactions depend on the type and concentration of acid in the aqueous phase and the concentration of extractants in the organic phase.¹⁻⁴ Modelling of such effects would have extended the study beyond the allotted time for a M.Sc. project. To be clear, these limitations were however only imposed on the molecular modelling, and not the study as a whole - the effects of varying acid type, acid concentration and the concentration of the extractants were investigated experimentally.

In this study phosphorus based extractants, specifically phosphorus oxide and phosphorus acid extractants, were investigated, since these two categories of extractants are prominent for their use in solvent extraction. For instance, tributylphosphate is used in the TBP and PUREX processes³⁻⁴, while di-(2-ethylhexyl)phosphoric acid is used for the extraction of base metals⁵. It has been shown that the results of solvent extraction reactions change as the number of oxygen atoms that are bound to the central phosphorus atoms change³. Therefore, the extractants which were investigated in this study were chosen such that their chemical structures represented opposite extremes with regard to the number of oxygen atoms bound to the central phosphorus atom. Derivatives of phosphate oxide and phosphoric acid were chosen as extractants for which a maximum number of oxygen atoms (i.e. four) were bound to the central phosphorus atoms, and derivatives of phosphine oxide and phosphinic acid were chosen as extractants for which a minimum number of oxygen atoms (i.e. one and two, respectively) were bound to the central phosphorus atom.

The molecular modelling presented in this chapter was divided into two sections: the study of the structures of the aqueous complexes and the study of the structures of the extractants. The structures were studied in such a way that the properties that give rise to their reactivity could be related to trends in extractability and selectivity. Therefore, the Hirshfeld atomic charges⁶, local hardnesses (see Chapter 2), bond lengths and Mayer bond orders⁷ were calculated on the key elements and bonds that underpin the reactivity of the species that were studied. Furthermore, the HOMO, LUMO and Fukui functions were calculated, of the aqueous complexes and extractants, which allows predictions to be made regarding the regioselectivity with which these species might react. The specific extractants which were investigated in the modelling portion of this study are shown in Figure 4-1.

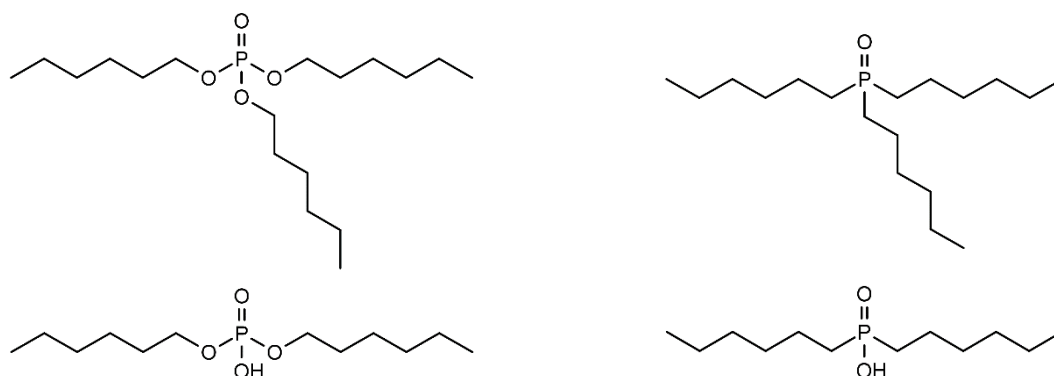


Figure 4-1. The four extractants that were modelled in this study. Top left: trihexylphosphate. Top right: trihexylphosphine oxide. Bottom left: dihexylphosphoric acid. Bottom right: dihexylphosphinic acid

Experimentally, solvent extraction was done by using a batch-wise approach, during which aqueous phases, consisting of mixtures of ZrF_4 and HfF_4 dissolved in either HClO_4 , HCl , HNO_3 or H_2SO_4 , were contacted with organic phases, consisting of a single extractant dissolved in cyclohexane. The specific extractants investigated in the experimental portion of this study are shown in Figure 4-2. Note that Cyanex 923 was used as a phosphine oxide extractant, since it is a mixture of four derivatives of phosphine oxide. Although the extractants that were used experimentally differs from those that were modelled with regards to the alkyl chains, the extractants that were used experimentally had the same functional groups than the corresponding extractants that were modelled. Therefore, the extractants that were used experimentally had similar reactive properties compared to the corresponding extractants that were modelled.

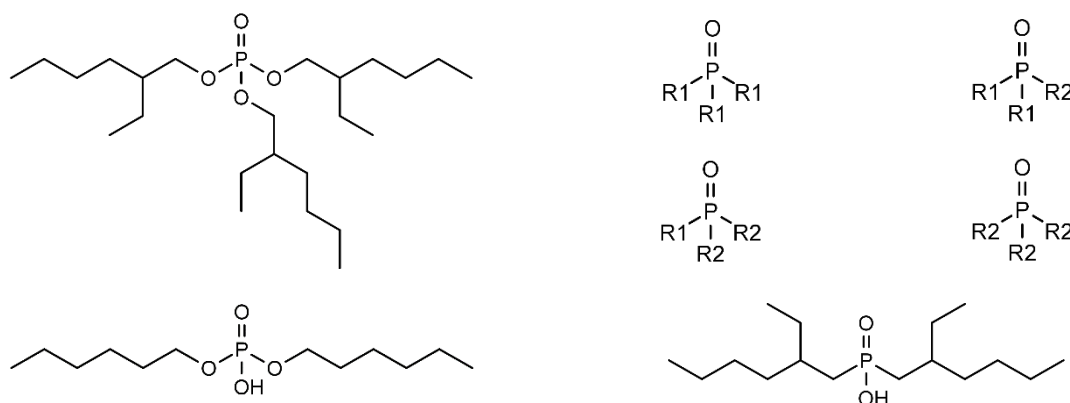


Figure 4-2. The four extractants that were used for the experimental work. Top left: tri-(2-ethylhexyl)phosphate. Top right: the four active components of Cyanex 923, where R1 is n-hexyl and R2 is n-octyl. Bottom left: dioctylphosphoric acid. Bottom right: di-(2-ethylhexyl)phosphinic acid.

Although industrial solvent extraction processes are typically done using large mixer-settler chambers or columns, batch-wise solvent extraction was used in this study, which is a standard method used to investigate solvent extraction due to the relative ease with which reactivity trends,

which would still be applicable to industrial scale processes, can be obtained regarding extractability and selectivity. Given these reactivity trends, inferences can be made about the effects of acid type, acid concentration and extractant concentration on extractability and selectivity.

The rest of this chapter is presented as follows. In Section 4.2 the method used for the molecular modelling of the aqueous complexes and extractants, and experimental solvent extraction, is presented. In Section 4.3 the molecular modelling and experimental results and the discussion thereof are presented, while the conclusions which were made regarding the molecular modelling and experimental work are presented in Section 4.4.

4.2 Methods

4.2.1 Molecular Modelling

The DMol³ code⁸⁻⁹, as implemented in Accelrys' Materials Studio (v 6) molecular modelling software package, and Gaussian09 code¹⁰ were used for the molecular modelling presented in this chapter. The calculations were done within the framework of density functional theory, where the PBE¹¹, B3LYP¹² and PW91¹³ functionals were used, at different times, to calculate the electron correlation and exchange terms of the Kohn-Sham¹⁴ energy expression.

Geometrical optimization calculations were done on all structures by using the Gaussian09 code. Initially, these calculations were done at the PBE level of theory, then at the B3LYP level of theory, with the convergence criteria set at 10⁻⁵ Ha for the total energy and 0.005 Å for the displacement of the nuclei. During these geometrical optimization calculations, the cc-pVTZ-PP basis set¹⁵ was used to represent the electron densities on Zr and Hf, and the 6-311+G* basis set¹⁰ was used for all other elements. These basis sets were chosen based on other studies where accurate results have been obtained using these basis sets to study the solvent extraction of actinide by di-(2-ethylhexyl)phosphoric acid.¹⁶ Hessian calculations were done to certify that these structures represented minima on their respective potential energy surfaces. The effects of the solvent environment were accounted for by the SMD method¹⁷, since this method has been shown¹⁸ to produce more accurate results compared to other similar methods.

Subsequently, various energy and property calculations were done on these structures using the DMol³ code, including calculating the HOMOs, LUMOs, Fukui functions¹⁹, Hirshfeld atomic charges⁶ and Mayer bond orders⁷ (see Chapter 2). Specific details about these energy and property calculations are given below. For all the energy and property calculations the electron densities for all elements were represented by the relativistic, unrestricted, numerical double zeta basis sets

(DNP+) with added polarization and diffusive functions on all elements.⁸⁻⁹ Solvent effects were accounted for by the COSMO method²⁰⁻²¹, which is the only implicit solvation model available in DMol³.

4.2.1.1 Aqueous complexes

Since it was concluded in Chapter 3 that $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ dominate aqueous solutions for the pH ranges of interest in solvent extraction, calculations were done on these structures only. The energies of various cis and one trans conformations of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ were calculated and compared to determine which conformations are more stable, and therefore which conformations should be used for further calculations.

Subsequently, the HOMOs, LUMOs, f_+ and f_- Fukui functions were calculated and compared for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$, which allowed predications to be made regarding the regioselectivity with which these complexes would react. Furthermore, Hirshfeld atomic charges were calculated for all the elements in $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ so that the local hardnesses on these elements could be calculated and compared. Finally, bond distances and Mayer bond orders were calculated for all the bonds in $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ so that predictions could be made about possible substitution reactions that could occur on these complexes. These properties calculations were done for all the cis conformations, and the average values were reported. The reason for doing so was to avoid biasing the results by only doing calculations for a specific structure.

4.2.1.2 Extractants

The calculations which were done on the extractants were similar to those that were done on the aqueous complexes. The HOMOs, LUMOs, f_+ Fukui functions and f_- Fukui functions were calculated and compared for the extractants, which allowed predictions to be made regarding the regioselectivity with which these extractants could bind to the aqueous complexes. Hirshfeld atomic charges were calculated for all the phosphorus and oxygen atoms, as well as some of the hydrogen atoms on the hydroxy groups of the phosphoric acid and phosphinic acid extractants, and local hardnesses on these atoms were calculated and compared.

4.2.2 Experimental Solvent Extraction

Batch-wise solvent extraction was done in which aqueous phases were contacted to organic phases that contained one of the extractants presented in Figure 4-2. The aqueous phases consisted of mixtures of ZrF_4 and HfF_4 , dissolved in either HClO_4 , HCl , HNO_3 or H_2SO_4 (all acids obtained from Sigma Aldrich as reagent grade). Every acid was standardised by titration with potassium hydrogen phthalate, which had been dried at 50 °C for 48 hours. For each acid type, stock solutions

with concentrations of 0.5, 1.0, 2.0, 4.0 and 8.0 M were prepared, by dissolving the appropriate amount of acid in Milli-Q water to prepare the 8.0 M solutions, then diluting this solution to obtain the other solutions. A mixed powder of ZrF_4 and HfF_4 which had been prepared by treating naturally occurring zircon ore using the Plasma Dissociated Zircon process (see Chapter 1), was obtained from NECSA SOC limited. Between 0.0442 and 0.0449 g of the provided powder was dissolved in 200 ml of each acid stock solution. Upon dissolving the powder mixture, it became clear that ZrF_4 and HfF_4 is kinetically slow to dissolve in aqueous phases. Therefore in order to ensure that the mixture was fully dissolved, solutions were placed in an oven at 50 °C for four hours, then in a sonication bath at room temperature for a further four hours, then magnetically stirred at room temperature for a week, prior to being used in solvent extraction experiments. The stock solutions were inspected to confirm that the mixtures were fully dissolved.

The organic phases consisted of either tri(2-ethylhexyl)phosphate (Sigma Aldrich, reagent grade), Cyanex 923 (Cytec Canada Inc.), dioctylphosphoric acid (Sigma Aldrich, reagent grade) or di(2-ethylhexyl)phosphinic acid (Sigma Aldrich, reagent grade) dissolved in a mixture of 3 % (v/v) n-octanol (Sigma Aldrich, reagent grade) and 97 % (v/v) cyclohexane (Sigma Aldrich, reagent grade). The n-octanol was added to avoid the formation of third phases once the aqueous and organic phases were mixed. Organic stock solutions were prepared by dissolving about 4.7040 g of each extractant in 1 L of the organic solvent, which were diluted to obtain solutions which were half the concentration of the initial solutions and a tenth of the concentration of the initial solutions. Therefore, sets of organic phases were prepared, for each extractant, in a way such that the ratio of total metal concentration to extractant concentration was 1 to 1, 1 to 5 and, 1 to 10. All of these solutions were aged for at least a day prior to use in solvent extraction experiments, to ensure that these solutions were thoroughly mixed.

The aqueous and organic phase were placed into contact by adding 15 ml of a single aqueous stock solution and 15 ml of a single organic stock solution into a polypropylene bottle, and mechanically shaking (240 rpm) these polypropylene bottles in a rotary shaker for an hour at 25 °C. It was assumed that after shaking for 60 minutes, the reaction would have reached equilibrium. This was done for all 240 combinations that were tested. The mixtures of aqueous and organic phases were separated immediately after being shaken. The zirconium and hafnium concentrations in the aqueous phases, before and after being brought into contact with the organic phases, were analysed by ICP-OES (Thermo Scientific, iCap 6000). The R^2 value for the analysis was always greater than 0.9999; and the detection limit was always within 10% of the measured value. The percentage zirconium and hafnium that were extracted was calculated by a mass-balance (i.e. by assuming that the total mass of each metal had to remain constant).

4.3 Results and Discussion

Recall from Section 4.1 that if an extractant binds to the aqueous ZrF_4 and HfF_4 complexes, then these metals will be transferred into the organic phase, since the resulting organometallic complexes would favour dissolution in the organic phase. Furthermore, if a given extractant binds more preferentially to either of the zirconium or hafnium complexes, then the metal that corresponds to that complex would be extracted selectively. In principle, the extractants can bind to the aqueous ZrF_4 and HfF_4 complexes either by addition or substitution reactions. In the event of an addition reaction, the extractant would either bind to the metal atoms directly, by the formation of covalent bonds, or bind to the aqueous complexes' ligands, by the formation of covalent or ionic bonds. In the event of a substitution reaction, the extractant would have to substitute a ligand on the aqueous complexes. The results that are presented in Section 4.3 are therefore discussed within the context of these possibilities.

In Chapter 3, it was predicted that, in the absence of acid anions, aqueous solutions of ZrF_4 and HfF_4 are dominated by $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ for the pH ranges of interest in solvent extraction. However, when acid anions are present, it is possible that these anions also coordinate to the aqueous complexes, either by addition to the metal atoms or by the substitution of other ligands. These possibilities are also taken into account during the discussion.

4.3.1 Molecular Modelling

4.3.1.1 Aqueous Complexes

Since the chemical properties of a molecule is determined by its geometrical structure, various conformations of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ were compared to determine which structures are more stable. These trans and cis conformations of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ are shown in Figure 4-3. Since the average of the energies of the cis conformations were predicted to be lower than the trans conformations (5.9 kcal/mol for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and 6.5 kcal/mol for $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$), the cis conformations were predicted to be more stable. Therefore, both $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ were predicted to exist in the cis conformations.

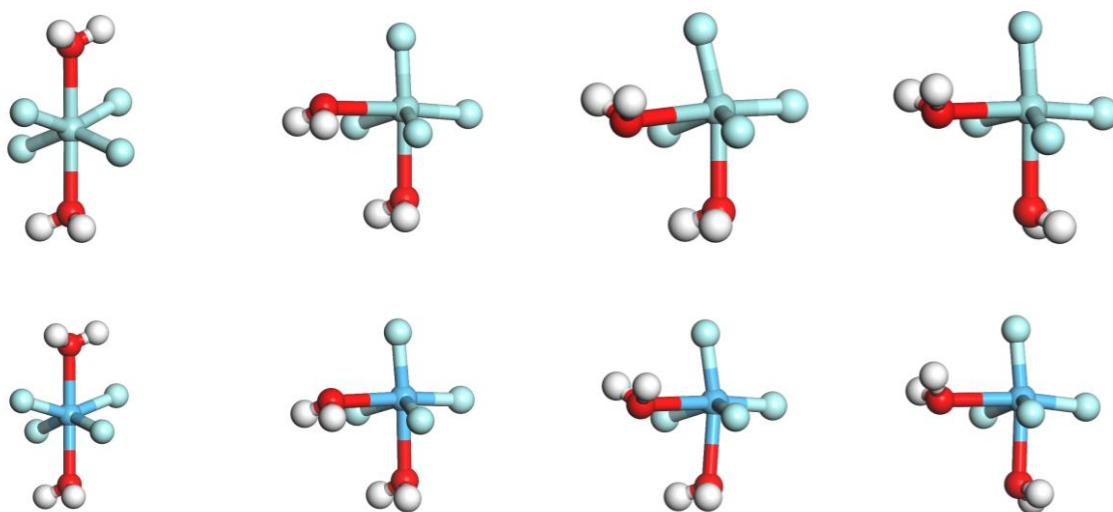


Figure 4-3. Various geometries for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ that were produced by geometrical optimisation calculations. The structures of the zirconium complexes are presented in the top row, while the structures of the hafnium complexes are presented in the bottom row.

This prediction can be interpreted as being a consequence of hydrogen bonding between the fluoride ligands and the aqua ligands' protons. The formation of hydrogen bonds would have caused the fluoride ligands to distort, as can be seen for the trans conformations in Figure 4-3, where the fluoride ligands are distorted from what would otherwise have been four fluoride ligands lying in an equatorial plane. The formation of such hydrogen bonding would have lowered the energy of the system, at the expense of weakening the metal-fluoride bonds. Both the trans and cis conformations had four hydrogen bonds. However, for the trans conformations all four fluoride ligands were predicted to be distorted; while for the various cis conformation less than four of the fluoride ligands were predicted to be distorted.

For covalent bonds to be formed, there must be a favourable overlap between the HOMOs and LUMOs of the participating molecules. In the specific case of coordination complexes, the formation of a coordination bond between a ligand and the metal atom involves an electron pair being donated from the ligand to the metal, and therefore requires the favourable overlap of a HOMO on the ligand and a LUMO on the metal atom. Therefore, if there are LUMOs localised on the zirconium or hafnium atoms, then the coordination of ligands (i.e. extractants or acid anions) to these metal atoms are possible if not, then such coordination is impossible.

The HOMOs and LUMOs for various conformations of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ are shown in Figure 4-4. As can be seen from Figure 4-4, it was predicted that there are LUMOs available on the metal atom for the zirconium complexes; while for the hafnium complexes, there were no LUMOs available on the metal atoms, except for the last hafnium complex in the fourth row of Figure 4-4. However,

when comparing the LUMO on this hafnium complex, to those on the zirconium complexes, it is clear that the LUMO on the hafnium complex was predicted to be less localised on the metal atom compared to the zirconium complexes. Therefore, the overlap of the LUMO on this hafnium complex with HOMOs on potential ligands would be very little in such a way that the formation of a coordination bond is unlikely.

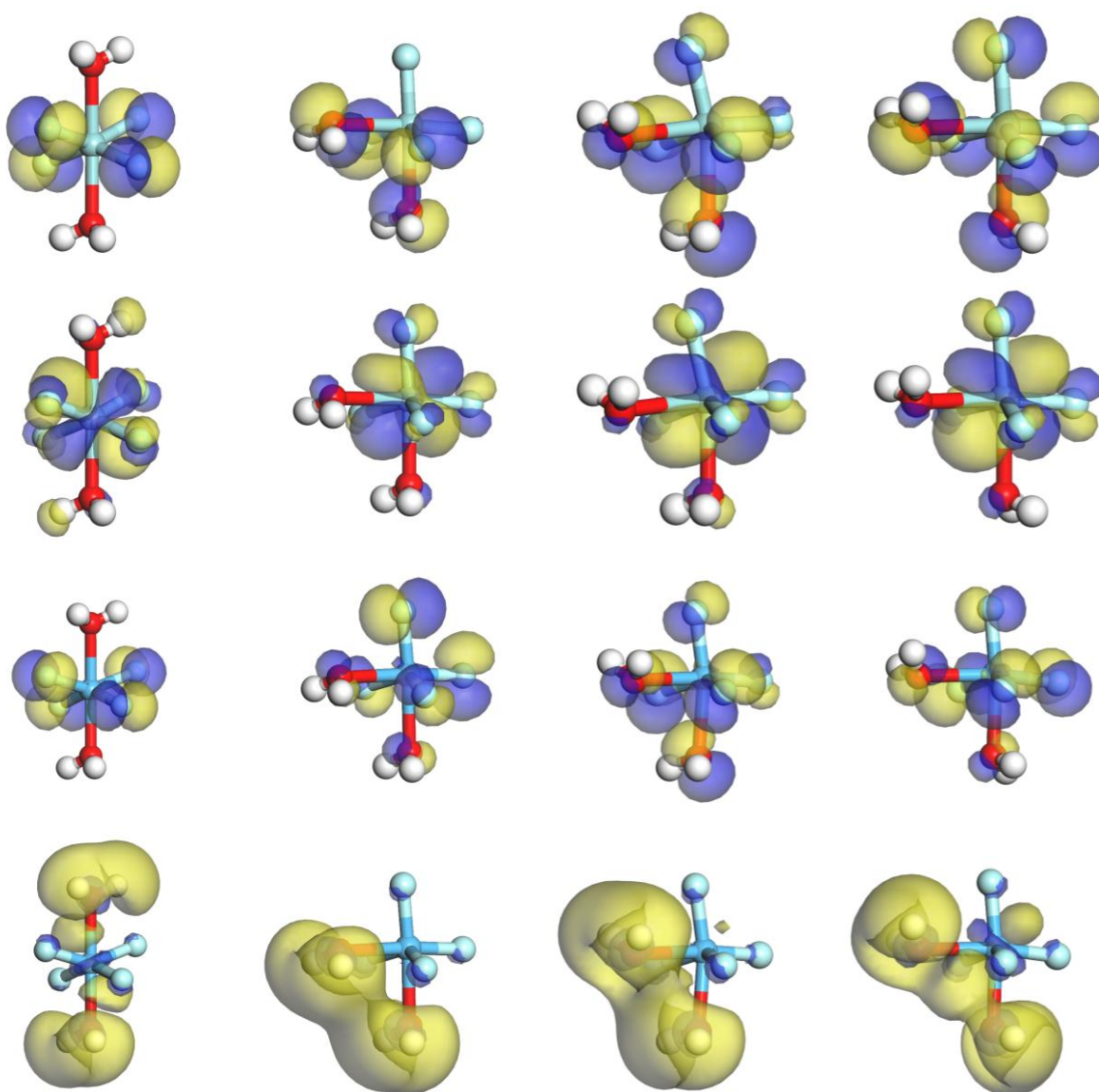


Figure 4-4. HOMOs and LUMOs on various conformations of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. The HOMOs and LUMOs of the zirconium complexes are presented in the first and second rows, respectively. The HOMOs and LUMOs of the hafnium complexes are presented in the third and fourth rows, respectively. The cis conformations differ with regards to the orientations of the aqua ligands' protons.

Since it was predicted that only the zirconium complexes have LUMOs localised on their metal atoms in such a way that overlap with the HOMOs of potential ligands are possible, the coordination of extractants or acid anions to the aqueous complexes' metal atoms are only possible for zirconium. To be clear, the prediction that such coordination is possible for zirconium does not mean that it will

necessarily occur. For example, it could turn out that the steric hindrance which would be associated with the potential coordination of an extractant or acid anion to the $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ complex is too large so that the formation of a bond is energetically not allowed. For instance, the prediction in Chapter 3 that two aqua ligands, and not three aqua ligands, coordinate to ZrF_4 suggests that the coordination of ligands to the zirconium atom in $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ do not occur. However, it is possible that for other ligands the resulting bond would be strong enough to overcome the steric hindrance and therefore result in the coordination of those ligands to the zirconium atom.

Another way by which extractants can bind to the $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ complexes is through the formation of bonds between the extractants and complexes' ligands, where the complexes' ligand could in principle be aqua, fluoride or acid anion ligands. As mentioned in Section 4.1, the scope of the molecular modelling was limited in a way such that the effects of the acid anions were not modelled. Nonetheless, the effects of the acid anions were investigated experimentally, as will be discussed in Section 4.3.2. The extractants are likely to bind either by the donation of electron pairs to form covalent bonds or by hydrogen bonding.

When considering the f_- and f_+ Fukui functions for the $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ cis complexes, for which a single set representative Fukui functions are shown in Figure 4-5, it became clear that for both complexes the fluoride ligands are the most likely sites for electrophilic attack, while the aqua ligands protons are the most likely sites for nucleophilic attack. Although the f_- Fukui functions for both complex were predicted to be localised on the oxygen atoms, the f_- Fukui functions were larger on the fluoride atoms, which indicates the higher likelihood that the fluoride atoms could act as electron donators. For the zirconium complexes, there was some localisation of the f_+ Fukui functions on the zirconium atoms, which again suggested that there is a likelihood that electron-donating ligands can coordinate to the zirconium atoms; however, the f_+ Fukui functions appears to be mostly localised on the aqua ligands' protons. For the hafnium complexes, the f_+ Fukui functions was mostly localised on the aqua ligands' protons.

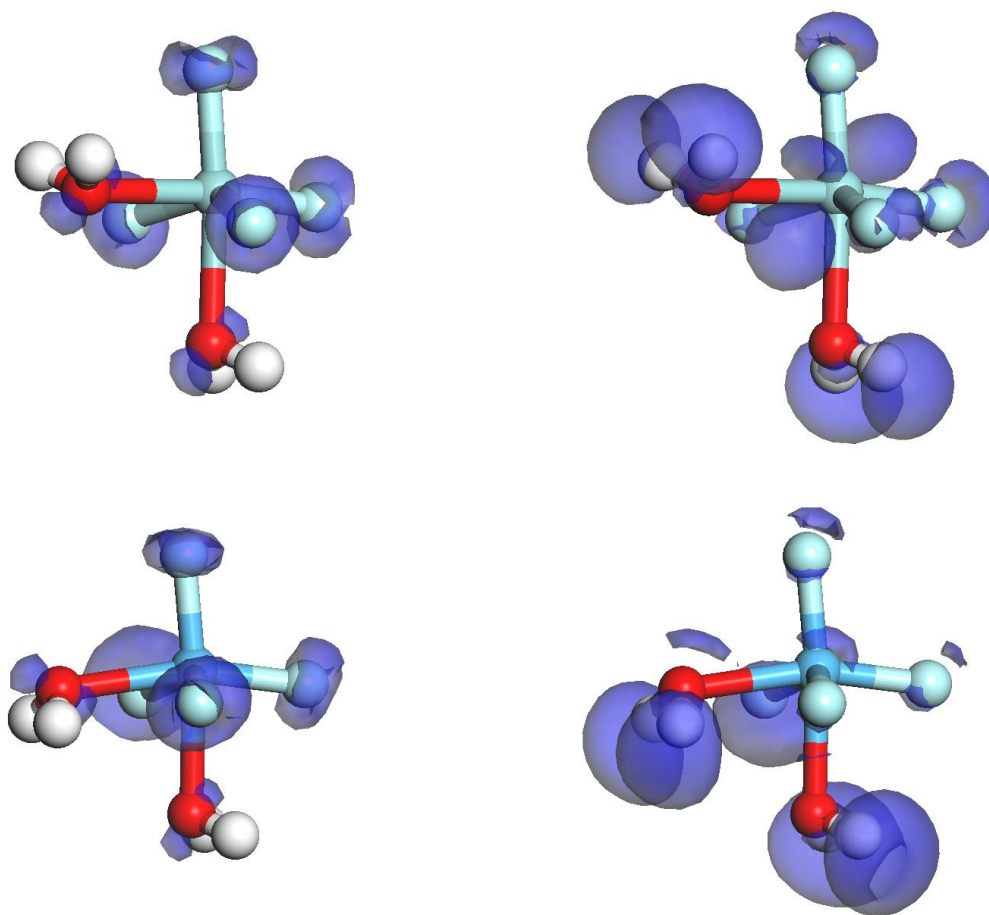


Figure 4-5. Representative Fukui functions of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ in the cis conformation. The f_- (left) and f_+ (right) Fukui functions for zirconium and hafnium are represented in the top and bottom rows, respectively.

Thus far, the discussion has focused on the possible bonds which could form between the $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ complexes, and the extractants, which is related to the possible overall extraction of these metals. In order to discuss selectivity, differences in the tendency of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ to form bonds to extractants or acid anions has to be considered. Considering the differences in bond distances and Mayer bond orders, as shown in Table 4-1, for various bonds of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ allowed predictions to be made about selectivity.

Table 4-1. Average bond distances and Mayer bond orders of various bonds for the $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ cis complexes

	Zirconium		Hafnium	
	Average bond distance (Å)	Average Mayer bond order	Average bond distance (Å)	Average bond order
M – F (trans to O)	1.944	0.774	1.953	0.746
M – F (cis to O)	1.979	0.707	1.988	0.682
M – O	2.460	0.158	2.460	0.196
O – H	0.974	0.933	0.974	0.925

When comparing the averages of the bond distances and Mayer bond orders for the metal fluoride bond it became clear that it was predicted that zirconium forms stronger bonds to fluoride compared to hafnium. This prediction is consistent with the prediction that was made in Chapter 3 that the Gibbs reaction energies for the fluoride dissociation are larger for hafnium than for zirconium.

Comparison of the averages of the Mayer bond orders for the metal-oxygen bond suggests that zirconium was predicted to form weaker bonds to aqua ligands compared to hafnium. This prediction implies that aqua ligands on the zirconium complexes are more easily substituted than aqua ligands on the hafnium complexes. Furthermore, since the average of the Mayer bond orders are larger for the metal-fluoride bonds than for the metal-oxygen bonds, it was predicted that in the event that an extractant or acid anion substituted a ligand on the complexes, an aqua ligand would be substituted rather than a fluoride ligand.

Other predictions which also bare on the discussion of selectivity are those presented in Table 4-2, namely the predictions of the average charge and local hardnesses of various key atoms in $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. The fact that compounds of zirconium and hafnium have similar chemical properties and that these two metals are therefore difficult to separate is well illustrated by the prediction that the local hardnesses of zirconium and hafnium are very similar.

Table 4-2. The average Hirshfeld charges and average local hardnesses of various atom types for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. For the calculation of the local hardnesses, it was assumed that the metal and hydrogen atoms act as acids, and the fluoride and oxygen atoms act as bases.

	Average charge		Average local hardness (Ha)	
	Zirconium	Hafnium	Zirconium	Hafnium
M	0.756	0.767	0.052	0.054
F (trans to O)	-0.269	-0.272	0.031	0.028
F (cis to O)	-0.292	-0.296	0.023	0.021
O	-0.192	-0.190	0.026	0.030
H	0.188	0.187	0.017	0.017

It was predicted that the hafnium atoms are slightly harder acids than the zirconium atoms. Since fluoride is a hard base, the prediction that hafnium is a harder acid than zirconium is consistent with the predictions that the hafnium-fluoride bond is slightly stronger than the zirconium-fluoride bond and that the Gibbs reaction energies for the fluoride dissociation for $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ is slightly greater than those for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$.

Furthermore, given that it was predicted that the local hardnesses on the fluoride ligands and the aqua ligands' protons are similar. Therefore, reactions in which extractants bind to these ligands are not expected to result in significant selectivity, since the resulting bonds would likely be equally stable for both the zirconium and hafnium complexes.

To summarise, it was predicted that extractants are likely to bind to $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ or $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ only by substitution of the fluoride ligands, nucleophilic addition to the aqua ligands' protons or electrophilic addition to the fluoride ligands; except for $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ where addition of a ligand to the metal atom may be possible. Should extractants bind to $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ or $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ by the substitution of an aqua ligand, softer ligands were predicted to bind more preferentially to zirconium. Should extractants bind by addition reactions, very little selectivity can be expected.

With regards to the solvent extraction of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ from acid mediums, it is also possible that the acid anions substitute aqua ligands, or coordinate to the metal atom in the case of zirconium. In this case, the aqueous complexes would be anionic, and therefore positively charged extractants (i.e. extractants which have been protonated) would be needed to extract zirconium or hafnium. Furthermore, the protonated extractants could bind to the acid anion ligands, in which case selectivity could be observed, since the tendency for acid anions to bind to either of the metal complexes might differ.

4.3.1.2 Extractants

The modelling of the phosphorus oxide and phosphorus acid extractants are discussed within the context of the possible ways in which these extractants can bind to $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. The predictions regarding the HOMOs, LUMOs and Fukui functions of the extractants are discussed first, followed by a discussion on the local hardnesses of the key atoms within the extractants.

As can be seen in Figure 4-6, the HOMOs of the phosphate oxide and phosphine oxide extractants were predicted to be localised on the terminal oxygen atom. Therefore, it was predicted that the formation of a covalent bond between these extractants and a metal would involve the donation of a lone electron pair from the terminal oxygen atoms. Since it was predicted in Section 4.3.1.1 that only $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ has LUMO orbitals that are localised on the metal atom, these phosphate oxide and phosphine oxide extractants can potentially form covalent bonds to the zirconium atom in an addition reaction. It was predicted that this kind of addition could not occur for hafnium.

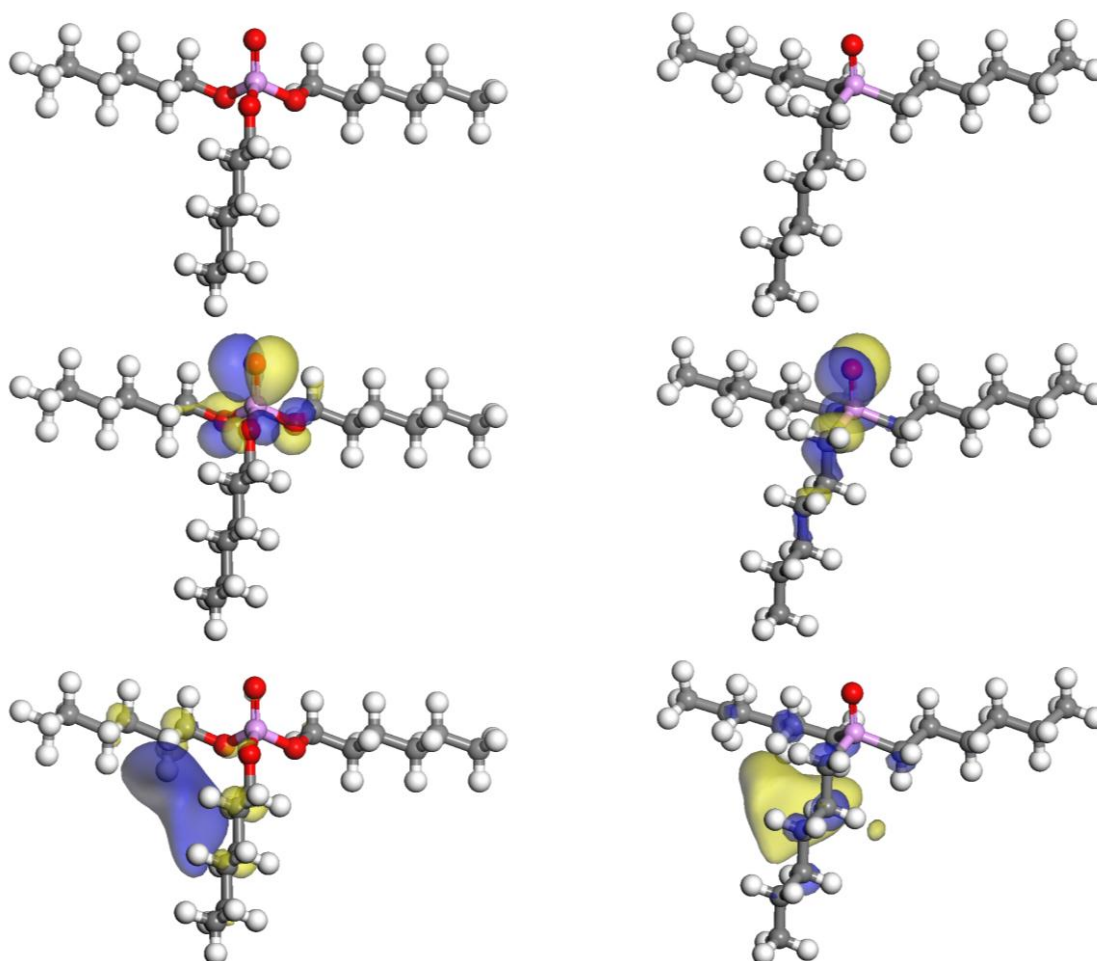


Figure 4-6. The structures of trihexylphosphate oxide (left column) and trihexylphosphine oxide (right column) that were produced by geometrical optimisation calculations, together with HOMOs (second row) and LUMOs (third row).

Since the f_+ Fukui functions for the phosphate oxide and phosphine oxide extractants, which are shown in Figure 4-7, were predicted to be localised mostly on the terminal oxygen atoms. Therefore, in the event that the extractants were to bind to the aqueous complexes, it was predicted that it is possible that these oxygen atoms could attack the aqueous complexes' aqua ligands' proton. Although the f_+ Fukui function on the phosphate oxide extractant is also localised on the oxygen atoms that are bound to the alkyl chains, the f_+ Fukui function is larger and the terminal oxygen atom, and therefore it was predicted that this terminal oxygen atom is more likely to donate electrons compared to the other oxygen atoms.

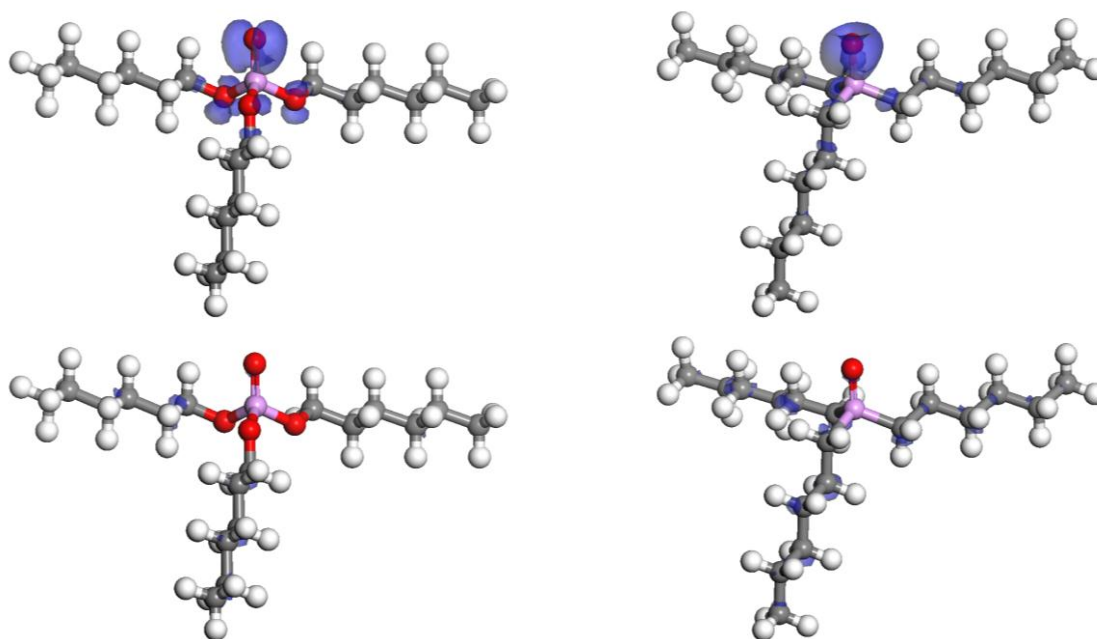


Figure 4-7. The f_+ (top row) and f_- (bottom row) Fukui functions for trihexylphosphate oxide (left column) and trihexylphosphine oxide (right column)

Since there are no visible f_- Fukui functions on the phosphate oxide and phosphine oxide extractants, it was predicted that these molecules are not likely to participate in electrophilic attack on the aqueous complexes. In other words, it was predicted that the phosphate oxide and phosphine oxide extractants will not bond to fluoride or acid anion ligands.

Since the HOMOs on the phosphoric acid and phosphinic acid are localised on the terminal oxygen atom, as can be seen in Figure 4-8, these extractants were also predicted to form use the terminal oxygen atom in the formation of covalent bonds.

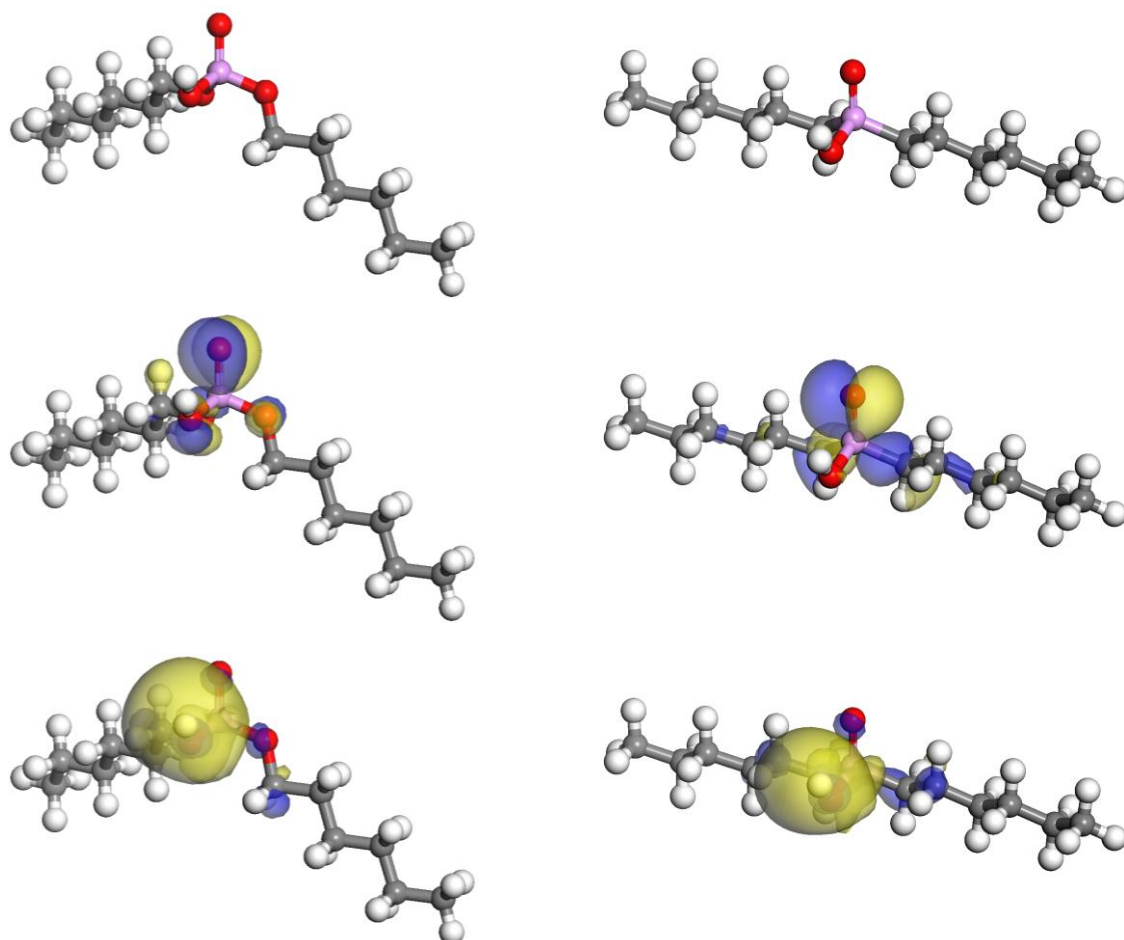


Figure 4-8. The structures of dihexylphosphoric acid (left column) and dihexylphosphinic acid (right column) that were produced by geometrical optimisation calculations, together with HOMOs (second row) and LUMOs (third row).

When considering the f_- Fukui functions for the phosphoric acid and phosphinic acid extractants were localised on the terminal oxygen atom, as shown in Figure 4-9, it was predicted that these terminal oxygen atoms act as electron donators. Since the f_+ Fukui functions are localised on the hydroxide groups' hydrogen atoms, these atoms are likely to participate in hydrogen bonding.

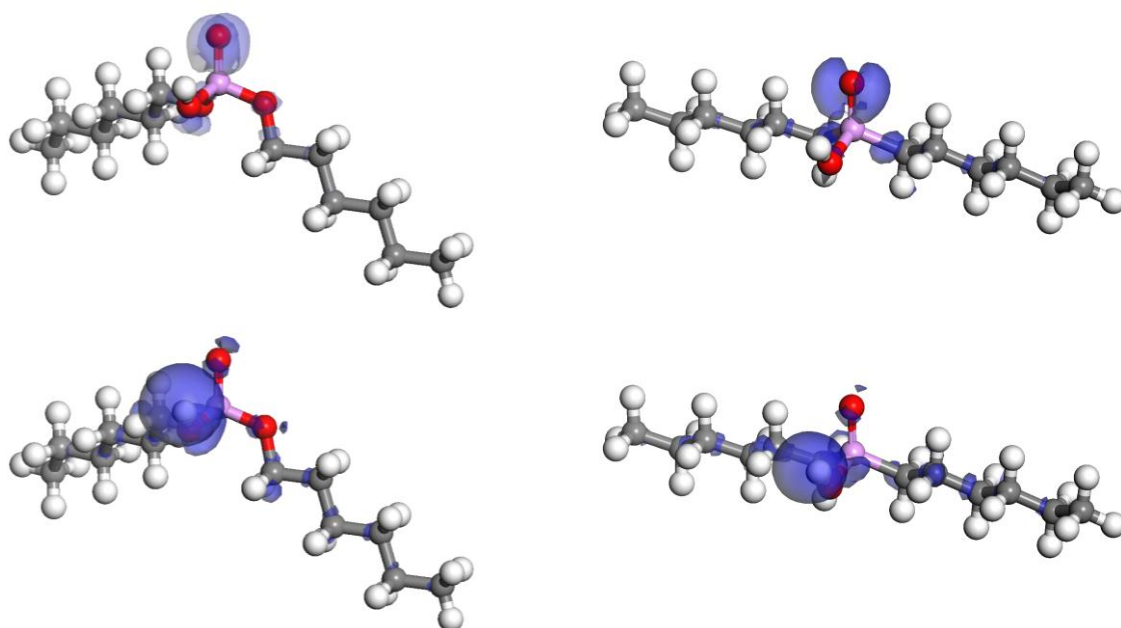


Figure 4-9. The f_- (top row) and f_+ (bottom row) Fukui functions for dihexylphosphoric acid (left column) and dihexylphosphinic acid (right column)

Since the local hardnesses on the terminal oxygen for all of the extractants, shown in Table 4-3 Table 4-4, are much lower than the hardness of the zirconium atom, shown in Table 4-2, it was predicted that none of the extractants would coordinate to the metal atoms. Therefore, the only remaining possibility is that the extractants would bind to the aqueous complexes' ligands.

Table 4-3. The average Hirshfeld charges and Local Hardnesses of various atom types for trihexylphosphate oxide and trihexylphosphine oxide

	Average charge		Average local hardness	
	Phosphate oxide	Phosphine oxide	Phosphate oxide	Phosphine oxide
P	0.478	0.394	0.002	0.002
O (P = O)	-0.370	-0.397	0.006	0.006

Table 4-4. The average Hirshfeld charges and Local Hardnesses of various atom types for dihexylphosphoric acid and dihexylphosphinic acid

	Average charge		Average local hardness	
	Phosphoric acid	Phosphinic acid	Phosphoric acid	Phosphinic acid
P	0.478	0.433	0.008	0.006
O (P = O)	-0.376	-0.387	0.010	0.009
O (O – H)	-0.229	-0.236	0.012	0.010
H (O – H)	0.175	0.169	0.041	0.032

4.3.2 Experimental Solvent Extraction

In this section, the results of the experimental batch-wise solvent extraction are presented. Although experiments were done for which H_2SO_4 was present in the aqueous phase, these results are not shown here. The reason for this omission is that many of the extraction values fall below 0 %, which does not make physical sense. A possible explanation for this is that ZrF_4 and HfF_4 has very poor solubility in aqueous H_2SO_4 , which would have caused these complexes to precipitate. The results for the experiments involving H_2SO_4 are given in Appendix A.

In Section 4.3.1, the molecular modelling predictions regarding the bonding and reactivity of the aqueous complexes and extractants were presented and discussed. In this section the results of the experimental solvent extraction are presented, and discussed within the context of the discussion in Section 4.3.1. The results pertaining to the experiments where HClO_4 was present in the aqueous phase are discussed first, followed by the results pertaining to HCl , then the results pertaining to HNO_3 .

When considering the results for the extractions from aqueous phases where HClO_4 was present, as presented in Figure 4-10, Figure 4-11, Figure 4-12 and Figure 4-13, it is clear that the extractions were such that either no selectivity was achieved or that hafnium was extracted selectively. It is also clear that the extraction was generally higher for extractants where the phosphoric acid (Figure 4-12) and phosphinic acid (Figure 4-13) extractants were used, compared to when the phosphate oxide (Figure 4-10) and phosphine oxide extractants (Figure 4-11) were used.

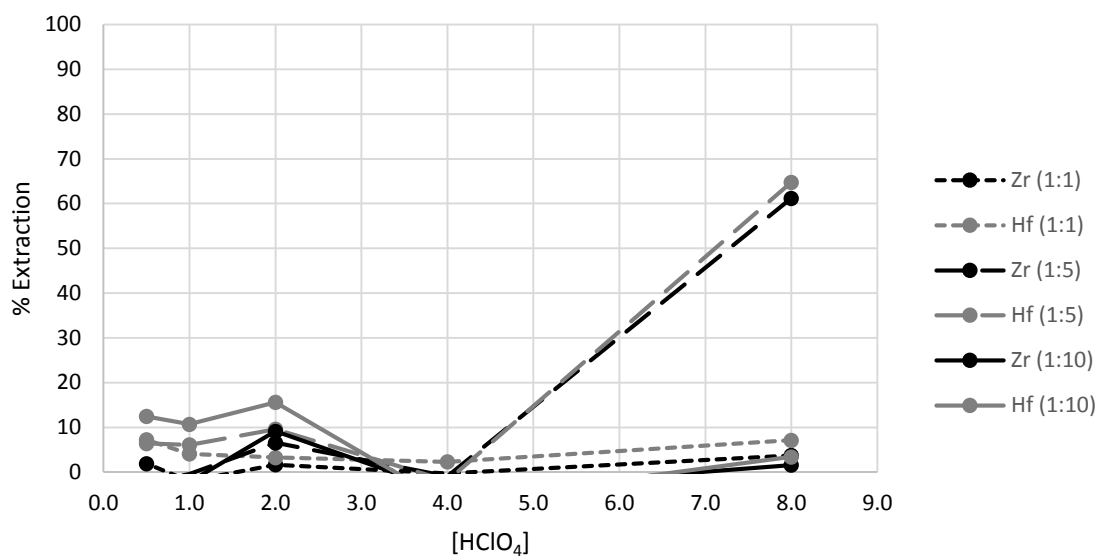


Figure 4-10. Percentage extraction, using tri(2-ethylhexyl)phosphate, as a function of HClO_4 concentration

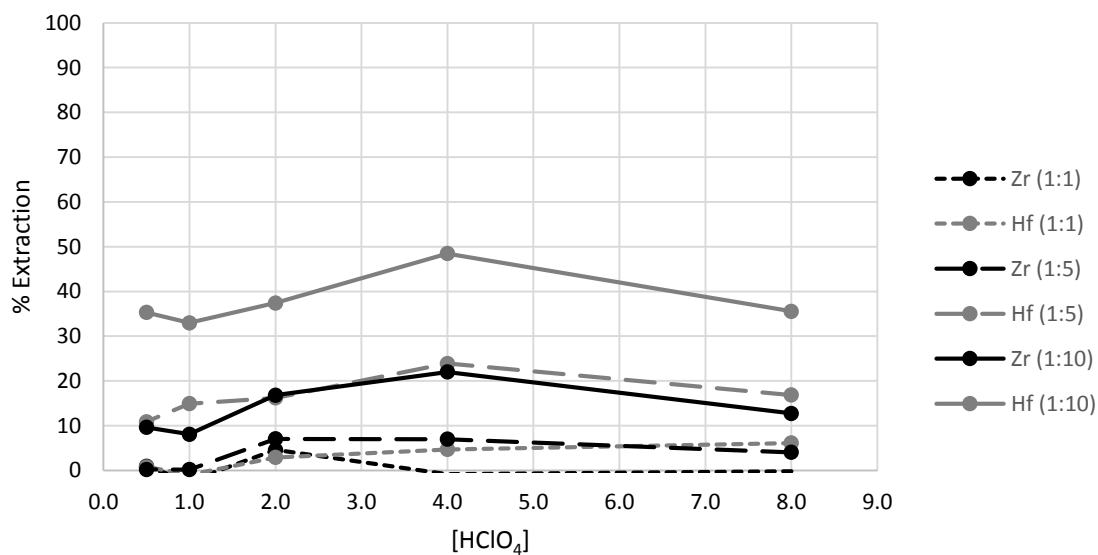


Figure 4-11. Percentage extraction, using Cyanex 923, as a function of HClO_4 concentration

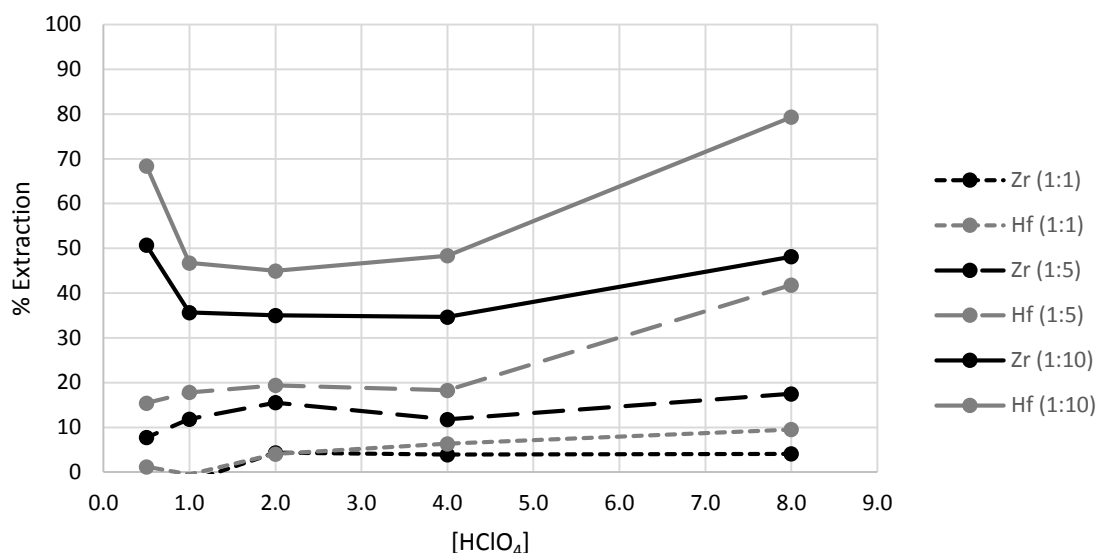


Figure 4-12. Percentage extraction, using di(2-ethylhexyl)phosphoric acid, as a function of HClO₄ concentration

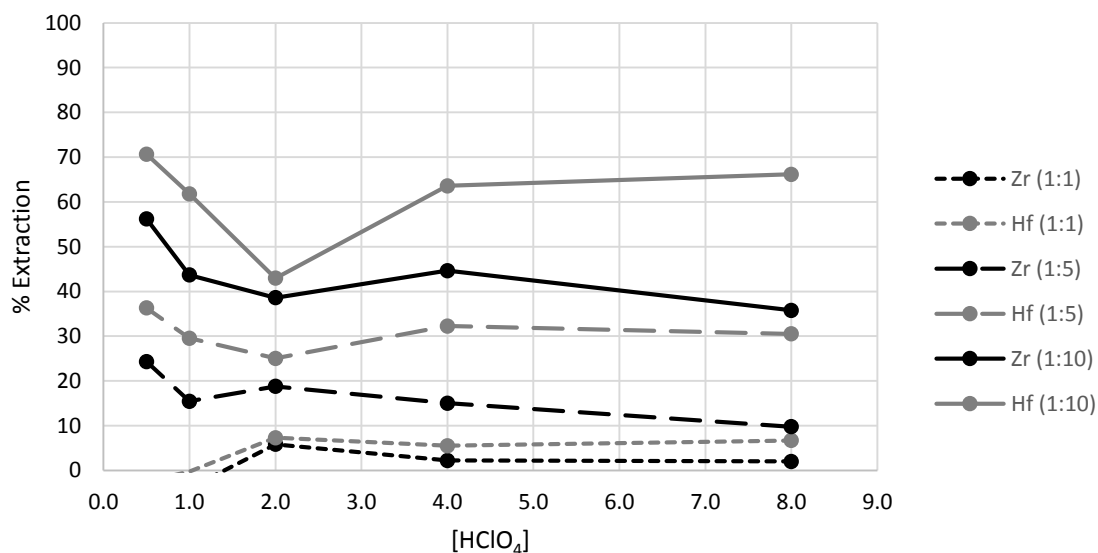


Figure 4-13. Percentage extraction, using dioctylphosphinic acid, as a function of HClO₄ extraction

The observation that the phosphoric acid (Figure 4-12) and phosphinic acid (Figure 4-13) extractants resulted in higher overall extraction, compared to the other extractants, suggests that protonated extractants were required to bind to the aqueous complexes. The observation that for the phosphate oxide extractant, extraction increased with an increase in HClO₄ concentration is also consistent with this conclusion, since a low pH environment would have resulted in the protonation of these extractants. However, the observation that for the phosphine oxide extractant, extraction was independent of HClO₄ concentration is inconsistent with this conclusion.

The observation that selectivity generally increased with an increase in HClO_4 concentration, suggests that ClO_4^- anion substitute the aqua ligands on the aqueous complexes, that this substitution occurred more preferentially for hafnium and that the extractants bonded to the resulting ClO_4^- ligands. If the extractants bonded to the fluoride ligands, then selectivity would not have increased with HClO_4 concentration. If the ClO_4^- bonded to the zirconium by addition to the metal atom, then the selectivity would have been in favour of zirconium. The only remaining possible explanation is that the ClO_4^- anion substituted the aqua ligands and that the extractants bonded to ClO_4^- . Furthermore, since the extractants would have formed equitably strong bonds to the ClO_4^- ligands, independent of whether these ligands are bound to zirconium or hafnium, it must have been the case that ClO_4^- bonded more preferentially to the hafnium complex.

Considering the results for the extractions where HCl was present in the aqueous phase, the extractions occurred with either no selectivity or very little selectivity in favour of hafnium, as can be seen in Figure 4-14, Figure 4-15, Figure 4-16 and Figure 4-17. The observation that there was extraction for the phosphoric acid (Figure 4-16) and phosphinic acid (Figure 4-17) extractions, and for the phosphate oxide (Figure 4-14) and phosphine oxide (Figure 4-15) extractants at HCl concentration, again suggests that protonated extractants are needed to extract these metals.

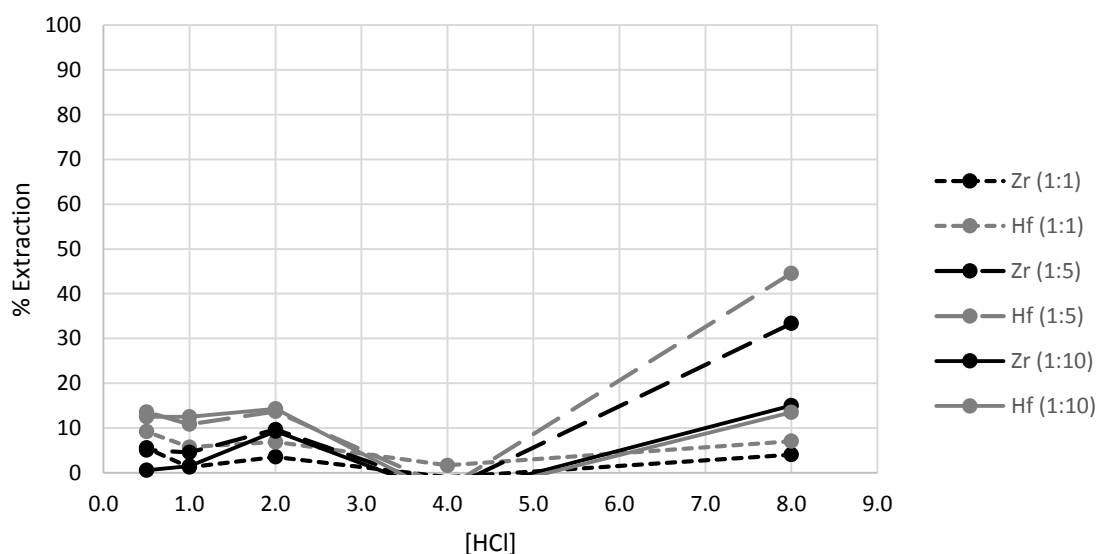


Figure 4-14. Percentage extraction, using tri(2-ethylhexyl)phosphate, as a function of HCl concentration

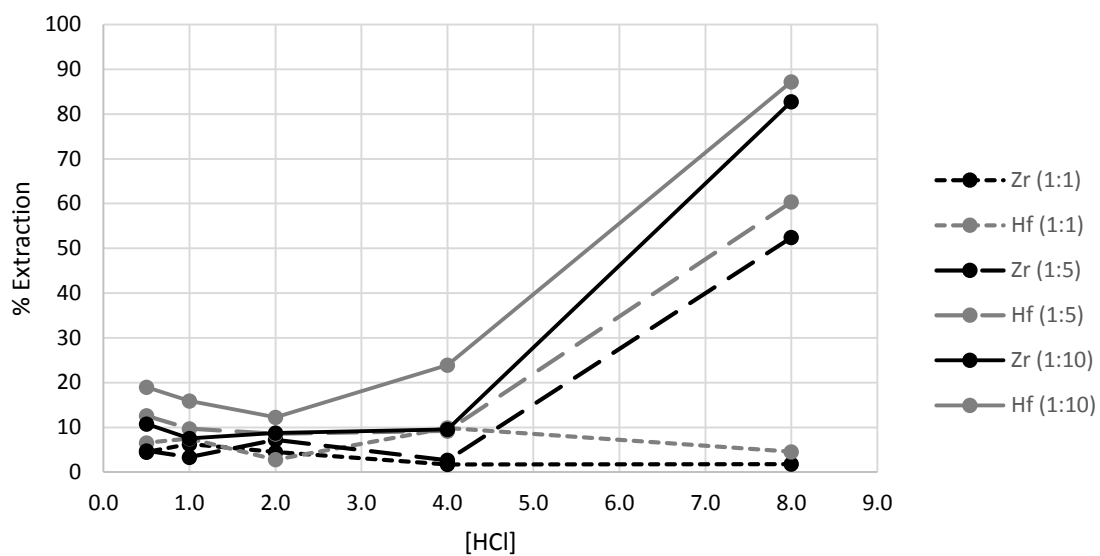


Figure 4-15. Percentage extraction, using Cyanex 923, as a function of HCl concentration

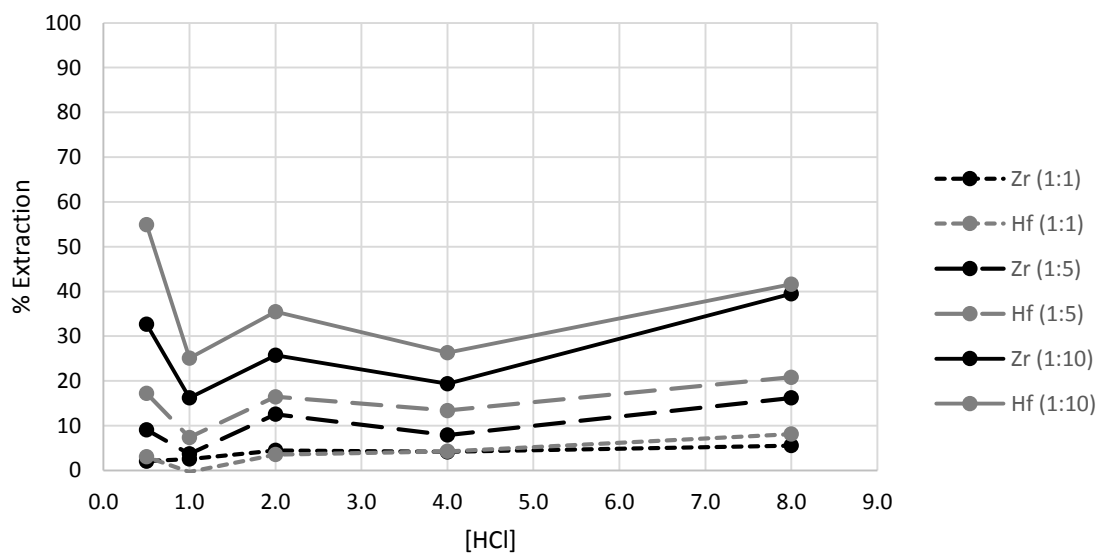


Figure 4-16. Percentage extraction, using di(2-ethylhexyl)phosphoric acid, as a function of HCl concentration

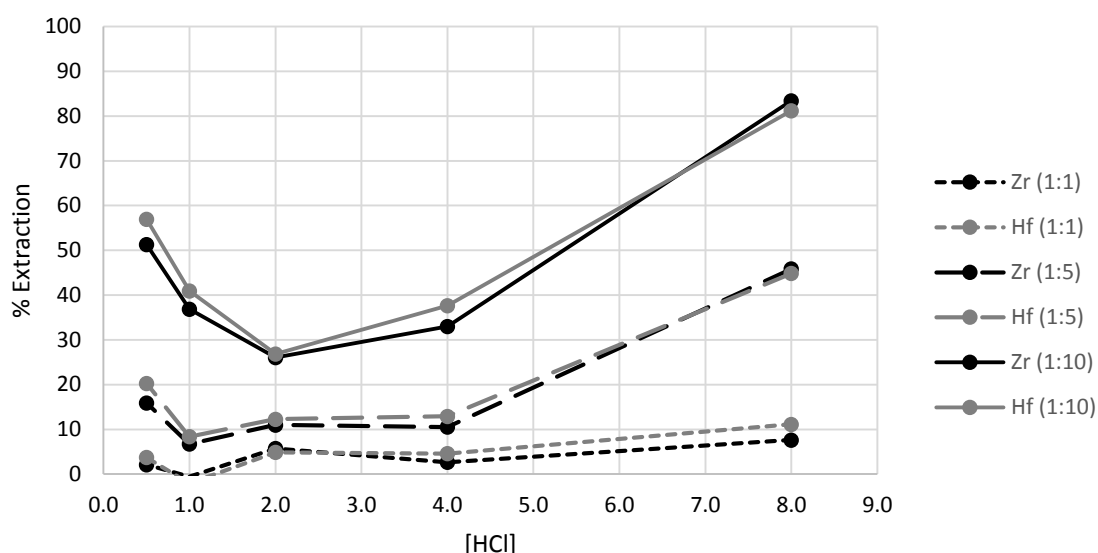


Figure 4-17. Percentage extraction, using dioctylphosphinic acid, as a function of HCl extraction

The observation that selectivity did not increase as the HCl concentration increased, suggests that either the Cl^- anion did not bond to the complexes and the extractants bonded to the fluoride ligands, or that the Cl^- did bond to the complexes and the extractants nonetheless bonded to the fluoride ligands.

When comparing the phosphate oxide (Figure 4-14) and phosphoric acid (Figure 4-16) extractants to the phosphine oxide (Figure 4-15) and phosphinic acid (Figure 4-17) extractants, it appears that extractants with less oxygen atoms resulted in greater extraction at high HCl concentrations. Furthermore, at low HCl concentrations, the extraction were the same for the phosphoric acid and phosphinic acid extractants (30 % extraction). This also suggests that protonated extractants are needed to extract these metals, since extractants which contain less oxygen atoms would be more easily protonated.

For the phosphoric acid and phosphinic acid extractants the extraction was high at 0.5 M HCl, then the extraction decreased as the HCl concentration increased to 2.0 M, before increasing again as the HCl concentration was increased to 8.0 M. This observation can be explained as follows. At low HCl concentration the complexes existed mostly as neutral $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$ complexes and the extractants existed as neutral molecules. In this case, the extractants could form hydrogen bonds to the fluoride ligands to extractant these complexes. When the HCl concentration increased, the Cl^- ions substituted the aqua ligands on the aqueous complexes, and therefore the neutral extractants could not extract the anionic complexes. Only when the HCl concentration was high enough that the extractants became protonated could the extractants again extract the aqueous complexes.

Considering the results for the extractions from aqueous phases where HNO_3 was present, as presented in Figure 4-18, Figure 4-19, Figure 4-20 and Figure 4-21, it again appears as if a protonated extractant is needed to extract the metals. There were overall increases in extraction as the HNO_3 concentration increased. As before, the phosphate oxide extractant resulted in the greatest extraction for metal to extraction concentration ratio of 1:5.

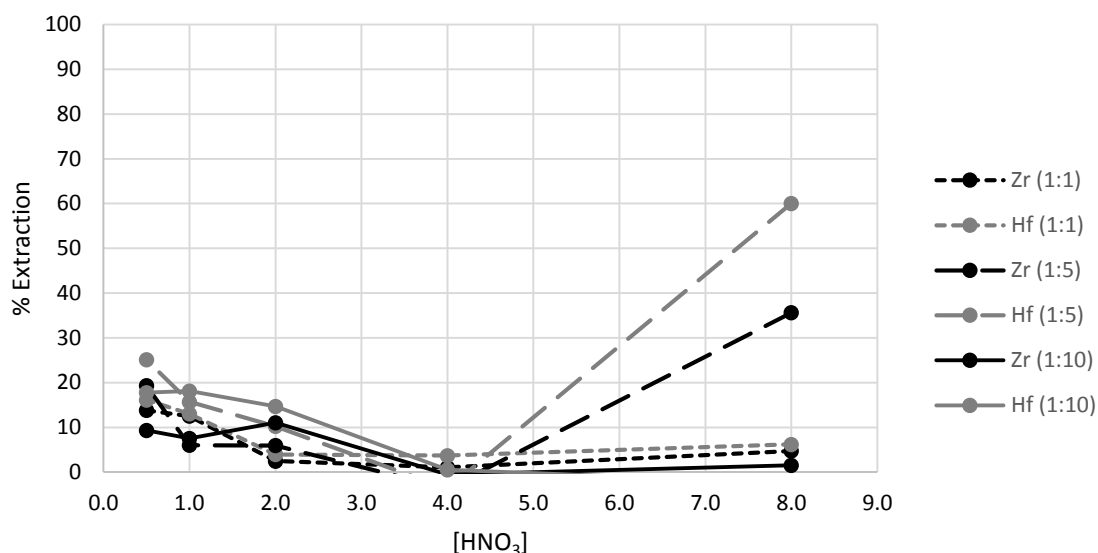


Figure 4-18. Percentage extraction, using tri(2-ethylhexyl)phosphate, as a function of HNO_3 concentration

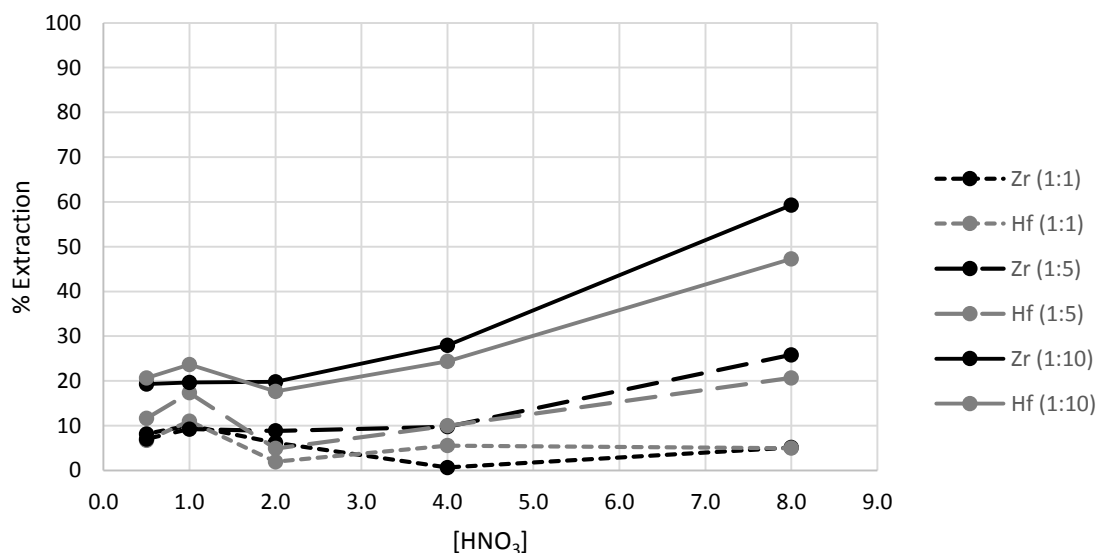


Figure 4-19. Percentage extraction, using Cyanex 923, as a function of HNO_3 concentration

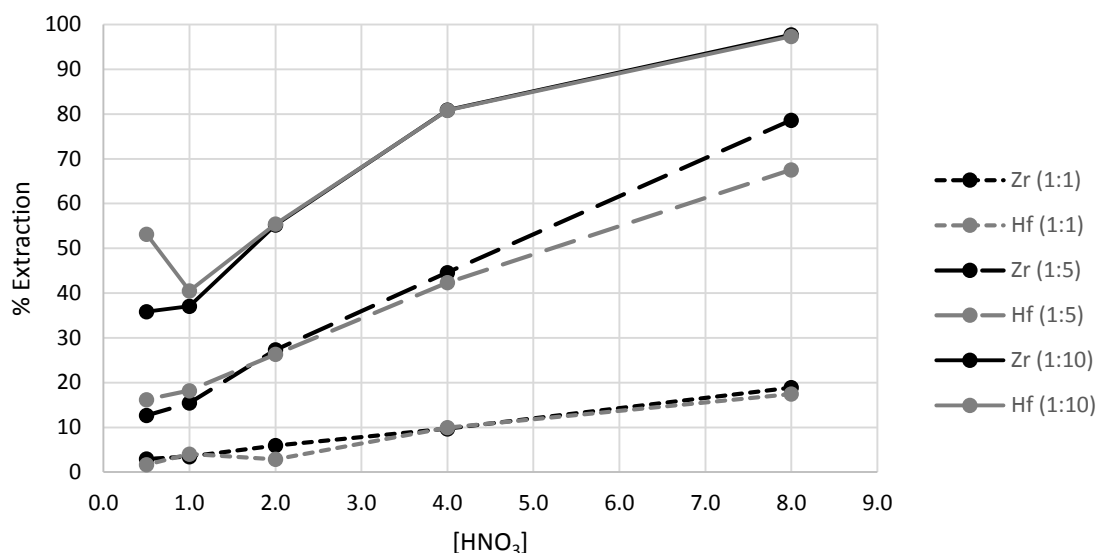


Figure 4-20. Percentage extraction, using di(2-ethylhexyl)phosphoric acid, as a function of HNO₃ concentration

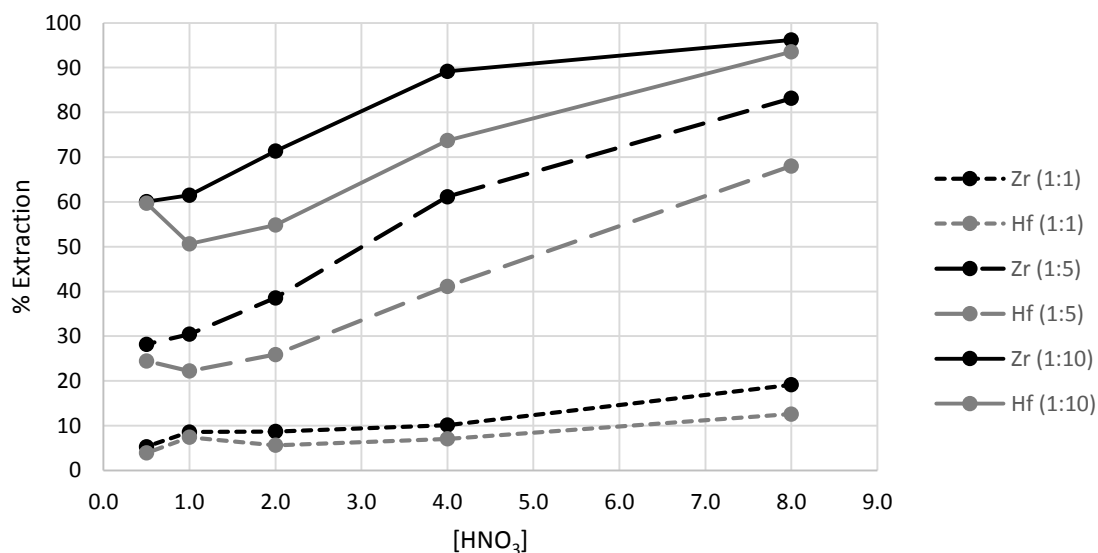


Figure 4-21. Percentage extraction, using dioctylphosphinic acid, as a function of HNO₃ concentration

For the HNO₃ aqueous feed solutions, the selectivity trends that were obtained are quite complicated. Furthermore, these extractions are the only extraction for which selectivity in favour of zirconium was observed. For the phosphate oxide extractant (Figure 4-18) the selectivity was in favour of hafnium, while for the phosphine oxide (Figure 4-19) and phosphinic acid (Figure 4-21) extractants the selectivity was in favour of zirconium. The phosphoric acid extractant (Figure 4-20) exhibited no selectivity.

A possible explanation of the selectivity trends are as follows. The NO₃⁻ ligand binds to each complex in a different way. For instance, for one of the complexes it could bind by a single oxygen atom, while

for another complex it could bind by two oxygen atoms to form a chelate. The propensity of a given extractant to bind to either kind of NO_3^- ligand is determined by the number of oxygen atoms on the extractant. Extractants with a small number of oxygen atoms would then bind to the zirconium complex, while extractants with a large number of oxygen atoms would bind to the hafnium complex. The apparent lack of selectivity for the phosphoric acid could then be explained as the result of multiple different extraction reactions which happen to have resulted in non-selective extraction.

4.4 Conclusions

Recall that the second objective of this study was to use a combined molecular modelling approach to investigate the reactivity and bonding of the reaction between ZrF_4 and HfF_4 complexes and phosphorus based extractants. In Chapter 3, it was predicted that ZrF_4 and HfF_4 exist in the aqueous phase as $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$. Therefore, in Chapter 4 the molecular properties of $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ and $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$, together with the molecular properties of phosphate oxide, phosphine oxide, phosphoric acid and phosphinic acid extractants were investigated by means of molecular modelling. It was predicted that selective separation could only occur if the extractants substituted an aqua ligand on $\text{Zr}(\text{H}_2\text{O})_2\text{F}_4$ or $\text{Hf}(\text{H}_2\text{O})_2\text{F}_4$, or if an acid counter anion substituted an aqua ligand and the extractants bound more preferentially to the acid counter anion. It was also predicted that extraction could occur by the formation of hydrogen bonds between the extractants and the aqueous complexes' ligands, but that this kind of extraction would not be selective.

Concerning the batch-wise solvent extraction, the overall extractability improved as the number of oxygen atoms on the extractant decreased and when the extractant had a hydroxyl group. It is clear that higher acid concentration resulted in greater extraction, which indicates that a protonated extractant is necessary for extractability. Furthermore, for the cases where the extractions were selective they were always selective, except for the case where HNO_3 was used together with extractants which contained less oxygen atoms. This suggests that the NO_3^- ion binds more selectively to zirconium than to hafnium, and that the extractants had a propensity to bind to the NO_3^- group. A maximum separation of 30 % in favour of hafnium was observed at 8.0 M HClO_4 using dioctylphosphinic acid.

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CHAPTER 5 EVALUATION

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5.1 Conclusions

The aim of the research presented in this dissertation was to investigate the mechanisms that underpin the solvent extraction of ZrF_4 and HfF_4 with phosphorus based extractants. In this regard, the aqueous speciations of ZrF_4 and HfF_4 were modelled, and the bonding and reactivity of the reactions between the aqueous ZrF_4 and HfF_4 complexes and phosphorus based extractants were investigated by a combined molecular modelling and experimental approach.

It is clear that the investigation of the aqueous speciation of ZrF_4 and HfF_4 contributed a great deal towards the elucidation of the extraction mechanism. In Chapter 3, it was predicted that in the absence of acid anions, the speciation of these complexes would result in species which are either anionic or neutral, depending on the pH of the aqueous phase. Furthermore, it was predicted that F^- ligands would not dissociate, and therefore cationic species would not exist in the aqueous phase. As was explained in Chapter 2, the statement that these zirconium and hafnium complexes exists as either anionic or neutral species, and not cationic species, has certain logical implications which are useful with regards to understanding the extraction mechanisms.

For instance, given that the aqueous zirconium and hafnium complexes were not cationic species, the mechanism would not involve the substitution of acidic protons on the extractants by the zirconium or hafnium complexes. Therefore, the extraction and separation of these metals were not expected to be enhanced by low acid concentrations. In fact, it was observed, as presented in Chapter 4, that the extractions and separations were enhanced by having a higher acid concentration.

On the other hand, given that the zirconium and hafnium complexes could have been extracted as either anionic or neutral complexes, the extraction mechanism would have had to involve positive or neutral extractants to bind to the aqueous complexes in order to extractant these complexes. Moreover, in order to extract anionic complexes, extractants would have had to be protonated in such a way that the extractants become positive. This is precisely the mechanism that was inferred in Chapter 4, where it was observed that extraction was greater when using phosphorus acid based extractants and high acid concentrations.

Given the predictions made in Chapters 3 and 4, together with the experimental observations made in Chapter 4, it was argued that the extraction mechanisms by which zirconium and hafnium were extracted involve the formation of a hydrogen bond between anionic aqueous complexes and cationic extractants. Furthermore, these hydrogen bonds were formed between hydrogen atoms on the extractants and either fluoride atoms on the F^- or acid anion ligands on the aqueous complexes.

It was argued that for selective extraction of either of the metals, the extractants would have to have formed a bond to the acid anion. This argument was supported by the observation that the selectivity increased as the acid concentration increased. Specifically, in HClO_4 mediums, the extractions were hafnium selective. No selectivity was observed in HCl mediums. For HNO_3 mediums, the extractions were either hafnium selective, zirconium selective or not selective, depending on how many oxygen atoms were present on the extractant.

Concerning the bonding and reactivity of ZrF_4 and HfF_4 with phosphorus based extractants, it is clear that investigation of the extractant mechanisms within the context of bonding and reactivity contributed towards the elucidation of the extraction mechanism, and especially understanding how selectivity was achieved. Furthermore, it is clear that the molecular modelling and experimental approaches used in this study complemented each other well, and that the combined use of these techniques allowed insights to be gained which would not have been possible using either method alone. For instance, it was predicted that the extractants were not hard enough to bond directly to the metal atoms, and therefore that the extractants would have to bind to the ligands. The experimental observations that phosphorus acid based extractants resulted in greater extraction complemented these predictions. Therefore, the combined use of molecular modelling and experimental approaches allowed the proposal that selective extraction is achieved due to the different propensities which with zirconium and hafnium bond to the acid anions. This key insight would likely not have been obtained by the use of either molecular modelling or experimental work alone.

Another prediction made in Chapter 3 was that the distribution of hydrolysis species for ZrF_4 and HfF_4 , in the absence of acid anions, is almost exactly the same. This prediction reinforces the notion that the preferential coordination of acid anions is necessary to achieving separation. If acid anions did not coordinate to the metals, then the observed selectivity would have to have been due to preferentially with which the extractants coordinate to the metal atoms. Since both of the phosphate and phosphine oxide extractants bind not extract any metal at low acid concentrations, this possibility can be disregarded.

5.2 Recommendations for Future Research

The work done in this study showed that acid anions play a role in achieving selective extraction of either zirconium or hafnium. Therefore, it is recommended that future research be directed at understanding more clearly how the acid anions interact with aqueous ZrF_4 and HfF_4 .

More direct experimental evidence is needed to conform the hypothesis set forth in this work that the ClO_4^- coordinated more preferentially to hafnium than to zirconium. Furthermore, more direct experimental evidence is needed to determine whether NO_3^- coordinates to zirconium and hafnium in different ways. For instance, does NO_3^- form a chelating ligand to one of the metals but not the other.

Answering these questions would require the use of an in situ analysis technique, such as UV-vis or NMR, with which to probe the aqueous speciation. Alternatively, the molecular modelling which was done in Chapter 3 can be expanded in such a way that the step-wise association of these acid anions to ZrF_4 and HfF_4 are modelled.

It is also recommended that the structures of the extracted organometallic complexes be analysed. Such analysis could reveal how the extractants bind to the aqueous complexes. Single crystal X-ray diffraction is a technique which could potentially be used in this regard, given that the extracted organometallic complexes form periodic crystals.

Lastly, a more in depth study of differences in the electronic structures of ZrF_4 and HfF_4 should be attempted. The modelling in Chapter 4 predicted LUMO localised on the metal atom within the zirconium complexes, while the hafnium complexes were predicted to not have significant LUMO localisation on the metal atoms. This difference presents a potential basis for the design of extractants which could result in highly selective extraction of zirconium. It is recommended that the electronic structures of these complexes be modelled by using so-called post Hartree-Fock methods, which are very accurate ab initio electronic structure methods.

APPENDIX A

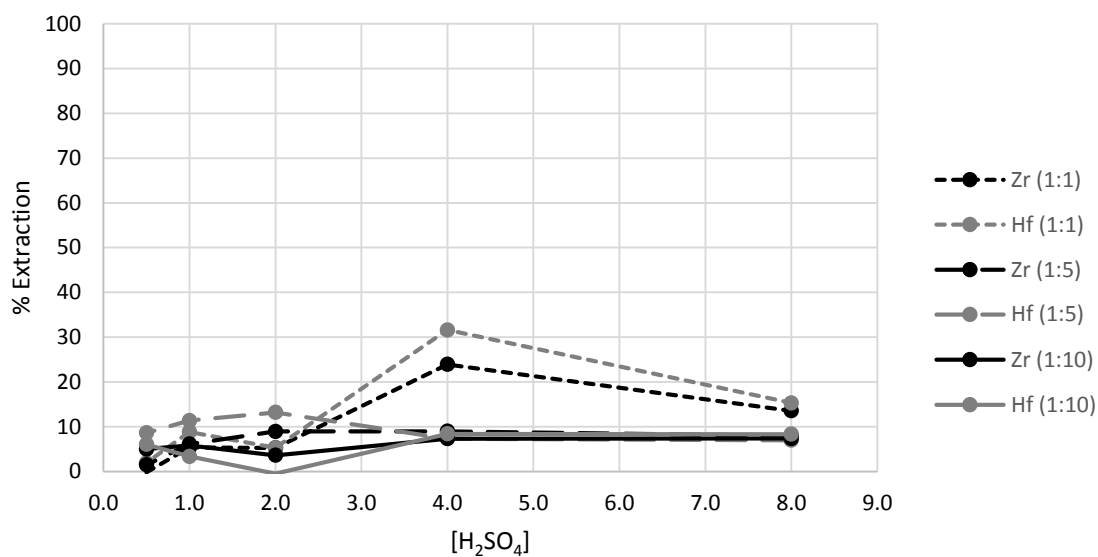


Figure B-1. Percentage extraction, using tri(2-ethylhexyl)phosphate, as a function of H_2SO_4 concentration

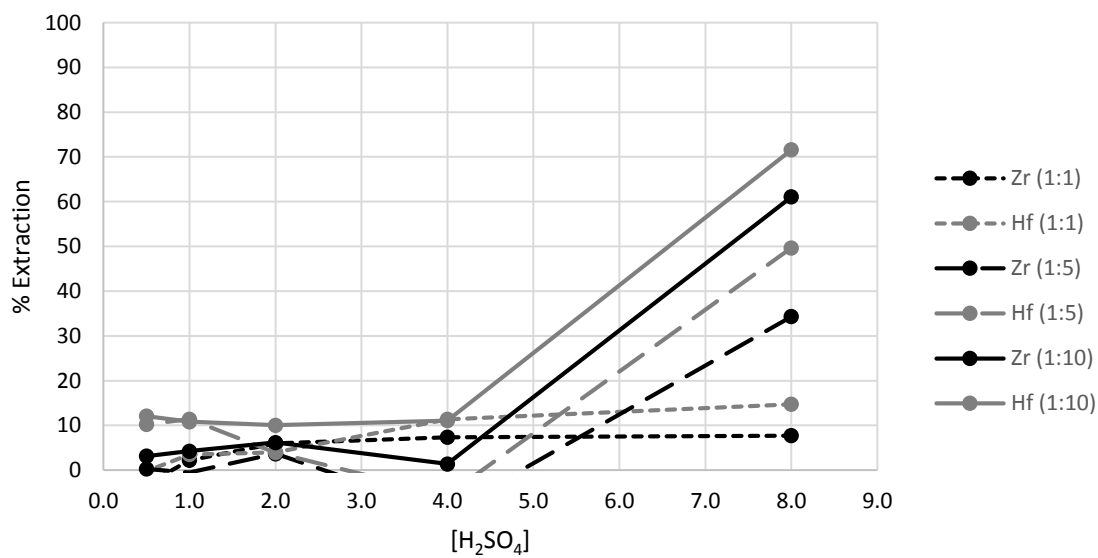


Figure B-2. Percentage extraction, using Cyanex 923, as a function of H_2SO_4 concentration

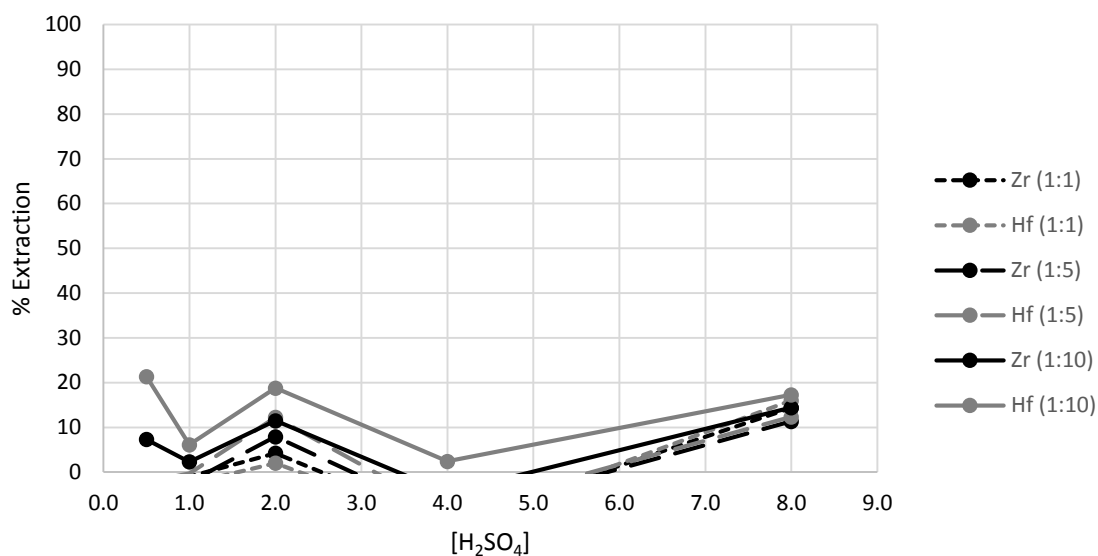


Figure B-3. Percentage extraction, using di(2-ethylhexyl)phosphoric acid, as a function of H_2SO_4 concentration

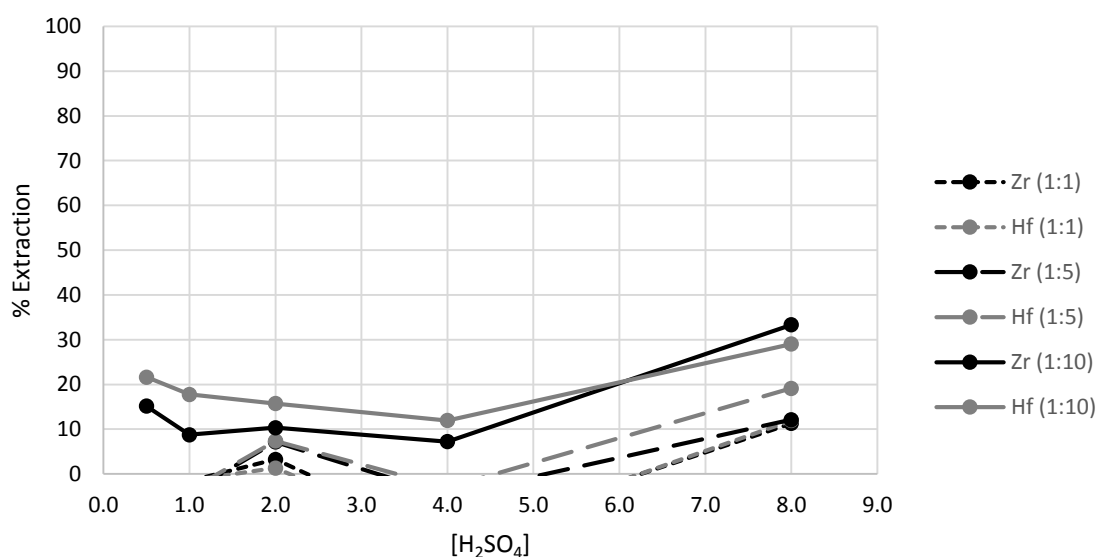


Figure B-4. Percentage extraction, using dioctylphosphinic acid, as a function of H_2SO_4 concentration