Nuclear Fuel Waste Extraction - Third Phase Revisited

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

Sept 2014

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Abstract

The problem of third phase formation plays a key role in the plutonium and uranium extraction process (PUREX). This process is responsible for the recycling of used nuclear fuel in order to save fuel usage and more importantly to reduce the amount of waste created (and afterwards disposed or stored) after the end of a nuclear fuel cycle. Understanding the role and behaviour of its components in the aqueous and organic phase, and more in depth on the process’ extractant tributyl phosphate (TBP), will help give a better understanding of what causes the phase separation of the organic phase and the interactions occurring at that interface. The focus of this project is on the mean activity coefficients of aqueous uranyl nitrate (and other salts) under varying concentrations using the Statistical Associating Fluid Theory (SAFT). Also, apart from the thermodynamic aspect of the above, molecular dynamic simulations were performed on tributyl phosphate and its interactions with other third phase components to study the effects on the structure and behaviour of TBP. By studying TBP in dodecane mixtures it was found that TBP forms aggregates and filament structuring throughout the organic diluent at most TBP concentrations. Also nitric acid hinders this formation by contacting the polar group (P=O) of TBP via intermolecular forces; its action is physical (based on intermolecular interactions) as opposed to chemical. It is expected that this structuring of TBP in the organic phase has an important effect in the transport of metal nitrates from the aqueous to the organic phase in the PUREX process.
Declaration

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I would like to thank Prof. Andrew J. Masters for giving me the opportunity and providing the essentials to carry on and complete this work.

I would be negligent not to acknowledge team CEAS - MMS’ contribution to my work; Anna-Laura, Adam, Rob, and Selina thank you for your help and training. Without you this work would be much more difficult.

For the loads of coffee over lunch break, beer, the endless conversations which helped to relieve the mind from work and the continual support they provided, I would like to thank my friends here in Manchester. Pantelis, Leonidas, Neophytos, Fanos, and Adam you were there when I needed help or just a friend to chat to.

Last, but certainly not least, I would like to thank my family for always supporting me. To my parents, Yerasimos and Athena, and to my brother Nikolas; thank you for always believing in me.

Finally, I thank the numerous people that don’t appear here but have contributed to the completion of this work and encouraged me to go on.
Chapter 1

Introduction

Nuclear power has, for quite some time now been, established as an important form of electricity, already accounting for around 20-30% of the world’s supply and growing. In Europe as a whole it is the dominant source[9], with France having around 75% of its electricity supply provided from nuclear power. Belgium, Czech Republic, Hungary, Slovakia, Slovenia, Sweden, Switzerland and Ukraine get a third or more of their power from nuclear energy and it is becoming increasingly important in Japan, South Korea and India. In the United Kingdom, over 20% of our electricity is supplied from nuclear stations.

But nuclear power and the nuclear fuel cycle in particular have been controversial issues in recent years. A major concern about nuclear energy is the ultimate fate of spent fuel. Almost every industry produces waste. In the nuclear industry some of this waste is highly dangerous. Even though radioactive materials are not indefinitely harmful and radioactive, since they decay through time, some of these elements’ half-lives are so long that they need to be considered as an indefinite threat to the human environment. On the other hand, other compounds present in nuclear waste have a very short half-life (their radiotoxicity is short-lived) and/or are in such small quantities that they present much less of a hazard. The International Atomic Energy Agency (IAEA) describes nuclear waste in six categories [1]:

1. **Exempt waste (EW)** - this is waste with such low radioactivity content that it requires no regulatory control.
2. **Very short-lived waste (VSLW)** - waste that can be stored for decay over a limited period of time (up to a few years). This class includes primarily radioisotopes with very short half-lives often used for research and medical purposes.

3. **Very low level waste (VLLW)** - has a higher level of radioactivity than EW but may not need a higher level of containment. It includes soil and rubble with low levels of radioactivity originating from contamination and can be disposed in near-surface landfills.

4. **Low level waste (LLW)** - waste that is above clearance levels but with limited amount of long-lived radionuclides. It requires robust isolation and containment in engineered near-surface facilities of up to a few hundred years. UK regulations specify that LLW must contain less than 4 GBq of alpha radiation or 12 GBq of beta/gamma emitters per tonne [10].

5. **Intermediate level waste (ILW)** - waste that requires a greater degree of containment and isolation than that provided by a near-surface disposal due to its content of particularly long-lived radionuclides. Therefore waste of this class requires disposal at greater depths (in the order of tens to a few hundred meters). However ILW needs limited provision for heat dissipation during its storage.

6. **High level waste (HLW)** - waste that encompasses high enough activity concentration to generate significant quantities of heat due to radioactive decay. Contains large amounts of long-lived radionuclides that require the design of deep and geologically stable disposal facilities at several hundred meters.

The schematic that follows, shown in Fig.1, shows the concept behind the way of categorizing different levels of waste depending on their actinide content and subsequent radioactivity.
Figure 1.1: A simple illustration of the waste classification scheme[1].

Through recommendations by the International Commission on Radiological Protection (ICPP), and governed in Britain by the Department of Environment (DoE), Her Majesty’s Inspectorate of Pollution (HMIP) and the Ministry of Agriculture (where waste dispersal is concerned), the dispersion and disposal of nuclear waste is undertaken. Apart from dispersal, where is it allowed for scarcely radioactive waste, the current practical options are: supervised above-ground storage, shallow burial (trench or vault disposal) and deep repository disposal. The choice for which of these options is more suitable is taken according to the level of radioactive waste, as discussed above in their characterisation. After the use of nuclear fuel within a reactor to produce electricity, the back end of the nuclear fuel cycle begins. This can be classified as an “open fuel cycle” (without spent fuel reprocessing) or as a “closed fuel cycle” (with spent fuel reprocessing). Of course the “closed fuel cycle” also produces waste
but the amount is less than that without spent fuel reprocessing where all fuel used within the reactor is sent for storage and disposal. Figure 1.2 shows the steps that are followed in an open and closed nuclear cycle. When classified as waste, spent fuel is immobilised in ceramic hosts or dry cask storage (steel cylinders internally containing inert gas to surround the waste and are externally surrounded usually by concrete), after it is cooled (usually for a few years) in spent fuel pools within the facility where the fuel rods are surrounded by water which absorbs the heat generated and shields from radiation. Another way to encase spent fuel is through vitrification[11], where after a certain treatment the fluid solidifies (vitrifies) into the glass and is then put into stainless steel containers.

![Figure 1.2: A schematic of the nuclear fuel cycle[2].](image)

After encapsulation of nuclear waste, their storage and disposal needs to take place. This can be done in a geological disposal facility (GDF) which involves isolating radioactive waste deep inside a suitable rock volume to ensure that no harmful quantities of radioactivity ever reach the surface environment. It is not a matter of simply disposing waste underground; the GDF will have engineered barriers that protect the packed waste in case of a leak and will also encompass engineered features (tunnels and vaults) where the waste packages will be placed in. Furthermore the facility should be sited in a geologically stable setting. The form of radioactive waste is also of importance (especially ILW and HLW in liquid form), which are treated in ways
discussed in the above paragraph (e.g. vitrification), before storage and disposal. An alternative to GDF is deep borehole disposal (DBD). This option arose from concerns of highly radioactive waste of higher heat output which put constraints on the size and content of waste packages in a GDF (size, siting, cost and suitability of certain host rocks). Higher burn up of fuel is achieved by creating more fissile material in the reactor during its operation. For example, fast breeder reactors have higher burn ups because they have a higher conversion ratio (rate at which fissile material is produced and consumed inside a nuclear reactor)[2]. It also addresses the need for protracted cooling of used fuel prior to disposal, in cooling spent fuel water pools within the facility. The basic principle of DBD can be summarised as follows: drilling cased boreholes of 4-6 km long, of a diameter of about 0.5 m, into a suitable host rock; usually the granitic basement of the continental crust. At such depth it is believed that encased wastes will be safe from climate change, sea-level rises and even earthquakes[12][13].

It is not yet quite clear if the UK will be disposing its nuclear waste in a deep geological disposal facility or if it will consider changing its current plans and moving onto a deep borehole disposal project. The certain thing is that at present there are no finalised designs for ILW and HLW disposal but it is expected that a disposal facility will be developed by around 2040[14].

The need for reprocessing the spent fuel is acute, both for the reduction of volume waste and for a reduction of the high level radioactivity/ radiotoxicity of the waste. It can also reduce the risk of nuclear proliferation since plutonium is always separated together with other materials such as uranium and minor actinides and will spent most of its lifetime within a reactor, as well as reducing the usage (and mining) of natural uranium. Of course the extent of these benefits is determined by the efficiency of the separation process. There are a few separation techniques available for reprocessing such as pyroprocessing, precipitation, ion exchange and solvent extraction[15][16]. The process should be reversible, should have rapid chemical reaction and phase-transfer kinetics, be adaptable to remote operation and have the ability to operate continuously[17]. Of these methods, solvent extraction has more advantages for use in large scale reprocessing plants and includes the basic criteria mentioned above such as continuous operation, high throughput and remote handling. The uranium and plutonium isolated from reprocessing of spent fuel can be used for the production of
novel new fuel, like mixed oxide fuel (MOX). For the creation of MOX, used nuclear fuel is to be processed. The first step is to separate the plutonium and the remaining uranium from the rest of the fission products and waste that comprise the used fuel; then plutonium is further separated from the uranium. After this separation process, and now as plutonium oxide, it is mixed with depleted uranium (a by-product of the uranium enrichment process) or with natural uranium, essentially creating what is called MOX (PuO$_2$+UO$_2$). MOX can be burned in light water reactors (LWR) with some modifications and in fast breeder (neutron) reactors; further development of fast reactors could support the reuse of spent MOX fuel[2]. Unfortunately though, up to this date, spent MOX is not to be further reprocessed (and ultimately used as a fuel) and is considered waste where it is temporarily being stored for future disposal.

Reprocessing is employed commercially in the United Kingdom, France, Russia and Japan but it is still not used in the United States[18]. Most of the uranium used in nuclear reactors is not fissile, therefore typically not used in weapons. Operating reactors, however, breed fissile plutonium that could be used in bombs, and therefore the commercialization of nuclear power has raised concerns about the spread on weapons [19]. It is worth noting that there is a ban of reprocessing in the U.S.. The technology was banned by President Carter, President Reagan lifted the ban and later on President Clinton reinstated it, mainly because of proliferation concerns (unlawful diversion of fissile material for military purposes). But nuclear energy is pretty much here to stay and no one can deny its superiority in comparison to fossil fuel energy production in matters such as efficiency and affordability (as a source of electricity), with almost no harmful greenhouse emissions. The low cost electricity production with no harmful emissions (for example one uranium pellet, approximately the size of a little finger, can produce the same amount of electricity as 805 kilograms of coal or 149 gallons of oil) gives nuclear energy the boost to take over as the world’s main electricity supplier.

The PUREX process is a liquid-liquid extraction process where spent nuclear fuel from the reactor are dissolved in nitric acid, and after a certain cycle (further and more detailed discussion in Chapter 2) are separated and purified so that they can be used again as nuclear fuel. The third phase problem arising during this process is that after a certain metal concentration, the organic phase is separated into two phases. This of course hinders the extraction process reducing its efficiency and also
may pose some criticality issues.

1.1 Overview

The aim of the project was to investigate the interactions of the components present in third phase formation. During this process we established a number of gaps in the literature regarding the structure and behaviour of the extractant of the PUREX process, tributyl phosphate, which were investigated using molecular dynamics simulations. This thesis aims to provide thermodynamic properties (such as activity coefficients) on some important third phase components (uranyl nitrate and nitric acid) in order to further enhance the existing data available in literature. It also aims to show that the Statistical Associating Fluid Theory (SAFT) is able to predict thermodynamic properties of aqueous solutions of third phase components. Another aim is to try and extend SAFT into ternary mixture properties’ calculation. Molecular Dynamics simulations will provide a further insight into the third phase structure and will allow for further discussion on the matter on third phase formation, aggregation, filament formation and will offer a concept on how the metal nitrates transfer from the aqueous phase into the organic phase.

The outline of this thesis is as follows:

**Chapter 2** summarises the current knowledge around the PUREX process and the cause of third phase formation.

**Chapter 3** states the methodology and background theory of the simulations techniques and methods used throughout this thesis.

**Chapter 4** Here the SAFT method is used to evaluate the excess chemical potentials of uranyl nitrate and other single strong electrolyte solutions.

**Chapter 5** Here with the help of molecular dynamics simulations, the molecular and microstructure of tributyl phosphate along with other third phase components, such as dodecane, will be addressed.

**Chapter 6** After a modification on the SAFT in-house code, nitric acid was added to the aqueous uranyl nitrate solution and the calculation of thermodynamic data of
this ternary mixture is now possible. A series of molecular dynamics simulations was also performed on the tributyl phosphate - nitric acid - water ternary mixture and also with the addition of n-dodecane.

**Chapter 7** is the concluding chapter where the outcomes and findings of this study will be discussed along with recommendations for future work.
Chapter 2

Background

2.1 Nuclear energy

2.1.1 Fundamental forces

In science, the reason we are able to study materials and how they behave is because they exist, holding together by some kind of forces. These fundamental forces are the interactions in physical systems that do not appear to be reducible to more basic interactions. The four fundamental forces (or fundamental interactions of nature) are, in order of increasing strength:

1. Gravitational
2. Weak (or weak nuclear force)
3. Electromagnetic
4. Strong (or strong nuclear force)

Although the gravitational force is by far the weakest of the physical forces, it is very important for macroscopic objects and over macroscopic distances. It is the only force interacting on all particles that have mass, energy and/or momentum. It has an infinite range like electromagnetism but unlike weak and strong force; it always attracts and never repels. Even though the electromagnetic force is far stronger than
the gravitational, it is not relevant for any bodies that have a net electric charge of zero. The weak and strong force have a much shorter range of interaction, which lies in the subatomic range, but they are the ones that are of interest in this study simply because of their involvement in radioactivity.

The weak force is responsible for the radioactive decay of subatomic particles and plays an important role in nuclear fission. For example, it is responsible for nuclear beta decay and other similar decay processes involving fundamental particles. The beta decay is possible due to the weak interaction which enables the transformation of a neutron (or a proton) into a proton (or a neutron), an electron and an electron antineutrino (nuclear fission and beta decay are discussed further in the following paragraphs).

The strong force is the strongest of the four types of physical forces and is responsible for the binding of the nucleus. It ensures the stability of ordinary matter since it confines the protons together within a nucleus, which would otherwise be repelled due to their like charges (as a result of the electromagnetic force). It can be observed in two areas: on a larger scale it is the force that binds protons and neutron together to form a nucleus, and on a smaller scale it holds quarks together to form protons and neutrons.

### 2.1.2 Radiation and radioactive decay

Different forms of radiation may be emitted from an unstable radioactive nucleus. Energy is released and a new and more stable nucleus is formed. The three types of radiation to be considered are alpha, beta and gamma radiation; a brief description of each type follows [20].

**Alpha radiation**

Alpha decay occurs when an atomic nucleus emits an alpha particle consisting of 2 protons and 2 neutrons (essentially the nucleus of a helium-4 atom). Since it consists of 2 protons and no electrons, the alpha particle is positively charged and the originating atom that underwent the radioactive decay is now transformed into an
atom with a mass number that is reduced by 4 and an atomic number that is reduced by 2, an example of which can be seen in Equation 2.1. Due to their charge and mass, alpha particles interact strongly with matter and only travel a few centimetres in air.

\[
\frac{238}{92}U \rightarrow \frac{234}{90}Th + \alpha (or \frac{4}{2}He) \tag{2.1}
\]

**Beta radiation**

Beta decay is a type of radioactive decay where a proton is transformed into a neutron or vice versa inside an atomic nucleus. This allows the emitting atom to move closer to the optimal ratio of protons and neutrons, and results in the emission of a beta particle which is either an electron (\(0^-1e\) or \(\beta^-\)) or a positron (\(0^+1e\) or \(\beta^+\), a particle with the size and mass of an electron but with a positive charge). In \(\beta^-\)-decay a neutron is transformed into a proton and the process produces an electron and an electron antineutrino, whilst in \(\beta^+\)-decay a proton is transformed into a neutron alongside the emission of a positron and an electron neutrino. Due to its smaller mass the beta particle can travel up to a few meters in air, in contrast to the alpha particle, and can be stopped by several millimetres of light metals (e.g. aluminium).

**Gamma radiation**

Gamma radiation is an electromagnetic radiation of a very high frequency and consists of high-energy photons, emitted from an unstable nucleus. It is the most penetrating form of radiation considered in this section. Having no mass or charge, it can travel much farther through air than alpha or beta particles. To be shielded from \(\gamma\)-radiation thick or dense enough materials with high atomic numbers are required, such as lead, concrete or even depleted uranium.

Should two atoms of the same chemical element contain different numbers of neutrons in their nuclei, they are called isotopes. Most of the naturally occurring elements are found in nature in more than one isotopic form. In this context "most" means with the exception of a few elements, such as fluorine or phosphorus, which are monoisotopic. The vast majority of these isotopes are stable isotopes (they do not decay).
Radioisotopes by contrast are unstable and undergo radioactive decay during which the parent element is transformed into a daughter element with a different atomic number. Most radioisotopes are a product of nuclear fission or cosmic rays-induced reactions in the upper atmosphere.

Actinide decay series are any of four independent sets of unstable heavy atomic nuclei that decay through a series of $\alpha$ and $\beta$ decays until a stable nucleus is achieved. The members of each set are genetically related by $\alpha$ or $\beta$ decay. The four sets of series are the uranium, thorium, actinium and neptunium series. Three of these (uranium, actinium and thorium) are called natural series because they are headed by naturally occurring species of unstable nuclei. In a uranium deposit, if a self-sustained nuclear chain reaction occurs under certain conditions, the actinide decay series are put to effect and this can be proven by examination of isotope ratios. The location is characterised as a natural nuclear fission reactor; the only known in the world so far is located at Oklo in Gabon, Africa and was active about 2 billion years ago [21]. The neptunium series’ members are produced artificially by nuclear reactors and do not occur naturally.

Because the two decay processes ($\alpha$ and $\beta$) result in either a change of 4 or no change in the mass number (see previous paragraphs for more on $\alpha$ and $\beta$ - decay), the mass number of all the series’ members are divisible by four with a constant remainder. The uranium series begins with U-238 and ends with Pb-206, the actinium series begins with U-235 and ends with Pb-207, the thorium series begins with Th-232 and ends with Pb-208 and the neptunium series (named after its longest-lived member, Np-237) ends with Bi-209.

The source of nuclear energy lies in the equivalence of mass and energy according to Einstein’s equation

$$E = mc^2$$  \hspace{1cm} (2.2)

This predicts that, the total annihilation of a single gram of mass produces an enormous ($9 \times 10^{13}$ Joules) amount of energy. Of course there is no process on Earth that can totally annihilate matter, but there are some where in the atomic scale can con-
vert a small amount of mass (about one part in a thousand) which is enough to be of use [10]. For instance, when combined together to form nuclei, protons and neutrons lose a small fraction of their mass in the form of energy. Along the same lines when light nuclei are combined with heavier ones, a process known as fusion, the slightest conversion of mass releases great amounts of energy; in fact fusion and more specifically the conversion of four hydrogen nuclei into a helium nucleus is the main reaction powering stars, a perfect example of which would be our sun.

A different process, called fission, occurs when heavier nuclei are split into two parts and part of this energy can be collected. Both processes have been used to generate energy and in principal fusion could yield an almost unlimited source of power. Unfortunately under controlled conditions, fusion cannot be sustained for more than a couple of seconds. Sustaining fusion currently requires more input energy than the energy amount received from the process and although recent advances have brought fusion closer to reality, a reactor that is able to contain fusion and produce more energy than it requires has yet to be developed.

Until then, nuclear energy means fission. It can happen naturally and spontaneously but to ensure it does at a desired time and amount, a disturbance in the atomic structure is required i.e. the absorption of a neutron. Being uncharged, the neutron is not repelled by the positively charged core nor by the negatively charged surrounding electrons and can penetrate the atomic structure given the right amount of speed. After the initial impact, more neutrons are dislodged, free to scatter, and anyone of them can cause the next fission event and so on, ending up with what is called a chain reaction. Figure 2.1 illustrates the fission process.

Of course for fission to occur, nuclear fuel is needed to provide materials to “burn” and produce power. Uranium is firstly extracted as on ore which is then concentrated (or milled) to produce a mixture of uranium oxides. It is then converted into uranium hexafluoride, UF$_6$, where now in solid form is further chemically processed to form uranium dioxide (UO$_2$) powder. Then, depending on which type of nuclear reactor the fuel is destined, it is appropriately constructed into fuel assemblies[10]. For example, for use in light water reactors (LWRs), the powdery form of UO$_2$ is pressed into pellets, sintered into ceramic form, loaded into zircalloy tubes and constructed
into fuel assemblies; one such fuel assembly might contain more than 200 fuel rods and be more than 3 metres long. The fuel rods mostly consist of U-238 with 3-4% of U-235 which is the workhorse. It is the most fissile, releasing large amounts of energy absorbing neutrons (thermal, low-energy neutrons). Only a small portion of U-238 is fissile and adds to the amount of the released energy (power output). However it readily absorbs the fast neutrons (high-energy neutrons which are more scarce than low-energy ones and cause transmutations, e.g. U-238 into Pu-239) and eventually converts into Pu-239, which is very fissile. Close to the end of the cycle, almost half of the reactor power output comes from Pu-239.

When the cycle ends, spent nuclear fuel needs to be removed from the reactor because it is no longer able to sustain the fission process and hence produce power. The composition of spent fuel consists of very high atomic weight (actinides) elements, such as uranium and plutonium, and also other lighter atoms such as strontium and caesium, which are products of fission. It also contains a very small amount of transuranic elements such as neptunium, americium and curium. A crude diagram of the components of nuclear fuel and spent nuclear fuel is shown in Figure 2.2. An important note is that plutonium (Pu-239) is virtually non-existent in nature. It is formed in these uranium-containing nuclear reactors as a result of neutron capture by uranium (U-238)[22].
Figure 2.2: The average composition of nuclear fuel and spent nuclear fuel in a typical LWR. Note the high percentage of spent nuclear fuel that can be recycled, the process of which is detailed in section 2.3.

In order to move on to the description of how a nuclear plant works, and more importantly on the process of recycling spent nuclear fuel, a small section has to be dedicated to the theory behind used fuel extraction.
### 2.2 Solvent Extraction

Solvent extraction is a common separation technique which has been widely used for actinide separations[17][23][24]. The process consists of the transport of a solute from one phase to another; in this case from aqueous to organic (of course the phases must be immiscible). Considering the case of nuclear fuel separation, this method involves the transfer of selected actinides between two phases with the variation of parameters such as concentration, temperature, solvent composition, pH and oxidation states. This is a major advantage for this technique since, depending on the chemistry of the system, parameters can be changed in order to optimise the performance of the process.

One of the phases will contain the extractant while the other will have the desirable product to be extracted. The extractants used in such systems can be classified into three major categories: acidic extractants, solvating extractants and ion pairing extractants [25][26]. Acidic extractants operate by the cation exchange of hydrogen ions for the selected cations. pH is an important parameter to consider in these systems because it can drive the reaction equilibrium. The second type of extractant for solvent extraction systems is the ion pairing extractant. These extractants are made of bulky ionic molecules, usually alkylamine salts. The associated anion in the organic phase exchanges with negatively charged metal coordination complexes formed in the aqueous phase. Unfortunately though, due to their polar properties, ion pairing extractants tend to form reverse micelles in most organic solutions [17] (micelle is an aggregate of surfactant molecules dispersed in a liquid colloid - a reverse micelle occurs in non-polar solvets and has the opposite formation of the micelle i.e. polar headgroups sequestered in the micelle core and hydrophobic tails extending away from the micelle center). The remaining class of extractants, solvating extractants, are the most prevalent in solvent extraction systems for actinide separation. Such a system is PUREX which uses tributyl phosphate (TBP) as its solvating extractant. This kind of extractant works by carrying a neutral salt into the organic phase.

\[
M^{m+} + mX^- + nS \rightleftharpoons M_{Xm}S_n
\]  

(2.3)

where \(M^{m+}\) is the metal ion, \(X^-\) the complexing anion and \(S\) is the solvating ex-
tractant molecule. The underlining represents the organic phase species. The correct (stoichiometric) amount of anions must be present to form the neutral complex with the metal ion, which will be then coordinated with the solvate molecules at the interface and be transported to the organic phase. But for this transfer to happen, as noted above, the extractants have to be neutralised. The metal cation comes into contact with two solvate molecules (TBP) and forms a neutral complex which then can be transferred from the polar to the non polar phase.
2.3 The PUREX process

The PUREX process is an acronym for Plutonium - URanium EXtraction (or Plutonium Uranium Recovery by Extraction, or Plutonium Uranium Reduction Extraction) and is based on liquid-liquid extraction ion-exchange. One also notes that PUREX is not the only extraction process used in the nuclear industry; there are also others such as TRUEX [27], DIAMEX [28], TALSPEAK [29], CYANEX [30], SANEX [31] and GANEX [32] which use different ligands instead of TBP. However all of these processes apart from PUREX, have not been used in large scale separations; most of them being in various development stages.

PUREX is well known to the scientific community since it has its origin more than sixty years ago when the ‘Manhattan Project’ was running in the U.S. That being said, more than 50 years of cumulative industrial scale experience exists on the PUREX process. It was invented by Herbert H. Anderson and Larned B. Asprey at the University of Chicago as part of the United States’ nuclear program. Their patent “Solvent Extraction Process for Plutonium” [33] has tributyl phosphate (TBP) as the major reactant to accomplish the bulk of the chemical extraction. This process involves many steps that can be separated into five main categories[34]:

1. feed separation
2. decontamination cycle
3. partition cycle
4. second uranium and plutonium fuel cycle
5. final purification of plutonium

The first step is the dissolution of the spent nuclear fuel in nitric acid. During this stage, radioactive gases are released that have to be collected and treated. After the fuel has dissolved, fine solids are removed. The removal of these fine solids is vital so as not to cause adverse changes to the liquid-liquid interface. It is known that fine particles can stabilise an emulsion - in this case the emulsion stabilisation is synonymous with third phase formation. Then usually $\text{H}_2\text{O}_2$ or $\text{HNO}_2$ is added in
order to bring plutonium to its most extractable form of + 4. The next step consists of the addition of TBP to the mixture and the co-extraction of uranium and plutonium in the TBP (oil) phase. The concentration of TBP is normally about 30% by volume typically in a paraffinic hydrocarbon diluent. It is important to note that when studying TBP extraction of other spent nuclear fuel components, such as technetium or other actinides and lanthanides, it was found that uranium was far more extractable than the other metal nitrates[35]. This can be seen in Table 2.1. for a mixture of spent nuclear fuel in 1M nitric acid and 50% per volume of TBP. Note that $K_d$ is the ratio of concentration of solute in the organic phase divided by the concentration of solute in the aqueous phase. One can see the different extraction ratios based on the desired extraction products using the same solvent.

**Table 2.1:** Distribution ratios for spent nuclear fuel components (50%TBP/1M HNO$_3$)

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>20</td>
</tr>
<tr>
<td>Plutonium, Neptunium</td>
<td>1</td>
</tr>
<tr>
<td>Remaining actinides</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Lanthanides</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Technetium</td>
<td>4</td>
</tr>
<tr>
<td>Remaining fission products</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Only the tetravalent and hexavalent actinides are known to be extracted by TBP, but it is the trend that is most interesting. For the tetravalent actinides, extraction into TBP increases with increasing atomic number just like the trend of lanthanides. The hexavalent actinides however follow the opposite trend where their extraction into TBP decreases with increasing atomic number. The extraction of Pu(III) was measured as well [36], mostly to understand how this oxidation state can be used to selectively backextract plutonium in to the aqueous phase in order to separate plutonium from uranium in PUREX. One of the things Best’s study provided was confirmation of the selective extraction of TBP (for Pu(III) it yielded a very low organic to aqueous concentration ratio, which is considered inextractable).

When TBP is introduced in the solution, it forms organic phase complexes with
uranium and plutonium with $\text{UO}_2(\text{NO}_3)_2\cdot 2\text{TBP}$ and $\text{Pu(NO}_3)_4\cdot 2\text{TBP}$ being the most extractable species. In this way, these two metals are co-extracted to the oil phase leaving behind over 99% of the (mostly undesirable) fission products, trivalent actinides and neptunium in the aqueous phase. A very important fact is that only tetravalent and hexavalent metals are extracted alongside TBP. This means that Pu(IV), Pu(VI), U(IV) and U(VI) are extracted to the oil phase, leaving behind Pu(III) and Np(V). Neptunium is in its pentavalent state so as to not be extracted with uranium and plutonium, although there is no specific control of its oxidation state; it stays as Np(V) for most of its time in PUREX. Step three involves the separation of plutonium from uranium by reduction. Plutonium is reduced to its trivalent state, Pu(III), which is organically insoluble; a strong reductant is necessary but not as strong as to reduce uranium as well (most commonly used are ferrous sulfamate or U(IV)). The consequence of this is for Pu(III) to be stripped in the aqueous phase while uranium remains in the organic phase and is later stripped with dilute nitric acid solution. Step four is the repetition of step three for both aqueous phases. The initial one with Pu, which was added in the third step coexisting with other actinides and fission products, and the latter with uranium which was stripped with very dilute nitric acid solution, in order to increase the recovered material amount. The final step of purification consists of purifying the plutonium and uranium by using additional TBP solvent extraction steps. It is worth noting that additional TBP is needed due to degradation of the initial TBP quantities because of radiation and other issues, but still most of the initial solvent is also recycled in PUREX. The last stage in order to get the desirable products is the conversion of plutonium and uranium nitrates, either by evaporation or precipitation, commonly into $\text{PuO}_2$ and $\text{UO}_3$. A schematic of a PUREX flowsheet is shown in Figure 2.3 for the main stages of the process.

Past PUREX flowsheet modelling has been based on equilibrium conditions, but the optimum separation does not necessarily occur at equilibrium[37]. The extraction of actinides is more rapid than that of the waste products. Therefore, upon reaching equilibrium conditions for the actinide, additional contact time only decreases the fission product (waste) decontamination. This has the effect of decreasing product purity and increasing the amount of degraded solvent; hence adding to the amount of waste. Flowsheets now incorporate the fundamental diffusion and chemical kinetic processes required to study time-dependent behaviour, but it is still up to the specific requirements of each plant and its production for an optimum PUREX flowsheet. This is said because, increasing the number of extraction stages will improve product
recovery but decrease decontamination (product purity). Increasing the number of scrub stages will improve decontamination but will reduce product recovery. So a compromise must be made with regards to each plant’s requirements.

Overall, the PUREX process has several advantages over previously used processes such as the decreased volume of radioactive waste being generated, due to the fact that no salting agent is used and that TBP is recycled for the elimination of undesirable byproducts such as monobutyl or dibutyl phosphate. Another benefit of PUREX is the fact that TBP is less volatile, less flammable and more stable against attack by nitric acid, than for other diluents used in nuclear extraction process.
2.4 ‘Third Phase’

The formation of third phase is observed when the organic phase is separated into two layers, which occurs after the actinide concentration surpasses a certain value; note that third phase can also be formed without the presence of actinides, it can be formed even without the presence of any metals in certain acid/extractant mixtures but this is out of the scope of this project. These two layers consist of a light one, which is mostly diluent and little extractant with some desirable metal complexes, and a heavy one (which is called third phase) encompassing a high concentration of extractants and metals and little diluent. The most simple way to demonstrate this is to keep increasing the concentration of the metal in the organic phase. At some point, as noted above, the maximum attainable actinide concentration that the oil phase can withstand will be reached, and when this occurs the third phase starts forming (in other words, the organic phase begins to phase separate into a light and heavy phase as explained above). This effect can be reversed by simply adding more of the organic phase i.e. more extractant in diluent. An example of this is shown in Figure 2.4, where pictures of a third phase-appearance and disappearance experiment are presented.

![Third phase occurring in the left picture (light green layer) and then by adding more dodecane it disappears. These are solutions of Zr/HNO$_3$/TBP/n-dodecane, courtesy of Dr. Peter Ivanov](image)

**Figure 2.4:** Third phase occurring in the left picture (light green layer) and then by adding more dodecane it disappears. These are solutions of Zr/HNO$_3$/TBP/n-dodecane, courtesy of Dr. Peter Ivanov

A phase is homogeneous region of matter in which there is no spatial variation in average density, energy, composition or other macroscopic properties. Phases can also
be distinct in their molecular structure. It can be considered a distinct system with boundaries that are interfaces with container walls or (in this case) other phases. The notion of phase equilibrium means that there are two or more phase systems present. These systems exist spontaneously on their own, and since they are in mutual equilibrium they can exchange energy, volume and particles.

This maximum actinide concentration is also called LOC, which stands for Limiting Organic Concentration and is most often presented as a function of the concentration of nitric acid. This can also be used to illustrate temperature effects and diluent and extractant concentration effects, by measuring the LOC vs. HNO$_{3}$ concentration for different temperatures and/or different initial compositions of the above variables.

It is important to note the effect of one actinide on the LOC of the other, since they are co-extracted. Z. Kolarik in 1979 carried out a study that showed the effect of U(VI) on the LOC of Pu(IV). He also collaborated with Nakashima, and in their paper published in 1983 [38], reported the effect of U(VI) in U(IV), Pu(IV) and Th(IV) solutions. To clarify, it was observed that actinide (IV) nitrates can form a third phase at any concentration of nitric acid in the aqueous phase, but uranyl nitrate only does it at acid concentrations above 9 M. It was also noticed that a third phase formed by an actinide (IV) nitrate at a moderate acidity of the aqueous phase also contained U(VI), if uranyl nitrate was present in the system. After this it was thought that uranyl nitrate could influence the maximum concentration of an actinide (IV) nitrate in the organic phase, at which third phase was not yet formed. Therefore it was decided to check experimentally the influence that U(VI) has on the third phase formation by U(IV), Th(IV) and Pu(IV) nitrates. Hexavalent uranium was found to decrease the LOC of U(IV) and Th(IV), for 1-6 M HNO$_{3}$ in the aqueous phase, but the finding that stood out more was the effect it had on Pu(IV). The LOC in this case was shown to increase with increasing concentrations of U(VI) but in moderate aqueous acidic concentrations of 1-3 M. On the other hand when the acid concentration is high (>5 M), the LOC is decreased. Srinivasan et al. [39] also studied the Pu(IV)-U(VI)-TBP system, and they showed clearly that the LOC of Pu(IV) is decreased in acidities smaller than those reported by Nakashima and Kolarik, from 2.2 M, with more pronounced effect at higher molarities (4-5 M). They actually concluded that the LOC values are seen to decrease with increasing uranium loading (uranium nitrate in the oil phase) at all the acidities studied (with the decrease, as
mentioned before, being more pronounced at higher acidities). Their data seem to be more robust than those reported by Nakashima and Kolarik, since they have a much greater number of experimental points and studied the effects on LOC under a wide range of acidities and uranium loadings. Considering that any factor that would reduce the free TBP concentration should therefore reduce the LOC, and also that the more HNO$_3$ is added, the more it will be extracted by TBP, their conclusions find great support.

It should be noted though, that pure TBP in a reprocessing plant is undesirable due to its physical properties; TBP in high concentrations in dodecane can self associate [40]. When diluted (with dodecane i.e. lower TBP to dodecane ratio), the mixture’s density and viscosity become lower, shifting towards the properties of the diluent. From a careful study of how the PUREX process operates coupled with a detailed review of the relevant literature, one can see that the optimum TBP concentration in hydrocarbon diluent, for a large scale reprocessing plant, is around 30%(v).

Another interesting result on the effects of actinide co-extraction is the effect of Pu(VI) on Pu(IV) studied by Plaue et al.[41]. The LOC is much lower now than when Pu(IV) is only present in the solution and it is postulated that Pu(VI) promotes third phase formation probably due to its tri-nitro complex, PuO$_2$(NO$_3$)$_3$ (it was not experimentally examined but the authors suggest a complete investigation on the Pu(VI)-TBP-alkane diluent system).

A number of studies have been performed to understand this phenomenon. In their paper Zemb et al.[42] demonstrate that organic solutions of extractant molecules can be treated as reverse micelles. The system they have worked with though, was not an MOx - HNO$_3$ - TBP/dodecane one (MOx is the metal ligand e.g. UO$_2$(NO$_3$)$_2$). Instead, they used a different extractant, dimethyldibutyltetradecylmalonamide (DM-DBTDMA) which is used in the TRUEX and DIAMEX processes [27, 28]. On the same note, Osseo-Asare [43] has found that concentrated solutions of the extractant TBP form nanometer-size water-in-oil microemulsions; structures known as reverse micelles. Zemb continued his research and in his 2003 publication, it is shown that organic phases of TBP in equilibrium with acid solutions are organised in reverse interacting aggregates and that, in the analysis of his findings, these are the interactions that govern third phase formation [44]. They also state that these aggregates
disappear at high temperatures even in the presence of HNO$_3$ (the attractive potential between aggregates increases with the addition of acid), to form regular molecular solutions. Their SAXS and SANS data indicate that reverse aggregates of aqueous polar core surrounded by 2 to 5 TBP molecules are formed up to initial concentrations of 10 M of HNO$_3$. Small-angle X-ray scattering (SAXS)[45] is a small-angle scattering technique where the elastic scattering of X-rays, by a sample which has inhomogeneities in the nanometer scale, is recorded at low angles (typically between 0.1-10$^\circ$). This angular range provides information about the shape and size of macromolecules, characteristic distances of partially ordered materials, pore sizes and other data. Small-angle neutron scattering (SANS)[46] is very similar in many respects to the SAXS; it uses elastic neutron scattering to investigate the structure of substances in the nanometer range. Both SAXS and SANS are small-angle scattering techniques which are widely used, with SANS having the advantage over SAXS when it comes to the investigation of light elements, isotope labelling and the strong scattering by magnetic moments.

An increase in TBP concentration would result in larger aggregates but their spherical shape would remain the same. On the other hand variation in acid concentration would only change the interparticle interactions, resulting in increasing the attraction between polar cores. Charizia et al. [47] have indicated with chemical analyses and spectroscopic data that U(VI) is extracted as the UO$_2$(NO$_3$)$_2$ • 2TBP complex whilst third phase has the average composition of UO$_2$(NO$_3$)$_2$ • 2TBP • HNO$_3$. With neutron scattering measurements in the presence of U(VI), they observed the presence of ellipsoidal aggregates, very likely of the reverse micellar type before phase splitting - Figure 2.5 shows the structure of a reverse micelle.

Although a significant number of authors agree that uranium is extracted as the UO$_2$(NO$_3$)$_2$ • 2TBP adduct and the composition of third phase for uranium is UO$_2$(NO$_3$)$_2$ • 2TBP • HNO$_3$, there is still disagreement about whether the third phase should be characterised as being composed of reverse micelles. Mark Jensen et al.[48] have stated that the formation of third phase in a U(VI)-HNO$_3$-TBP-alkane system is probably not caused by extensive solute aggregation. More likely, a dramatic change in solution, which leads to third phase formation, takes place when one molecule of HNO$_3$ becomes part of the U(VI) complex. At this point the solute becomes too polar to exist in an alkane diluent and collects in a separate phase. This point of view is embraced by many, that the partially dissociated metal complexes which are
poorly soluble in a 30% TBP-alkane solution are separated in a second phase [49] [50] [48], containing more than 50% TBP. A reaction has been proposed[18] which occurs at the time of third phase formation

\[
M(NO_3)_x \cdot yTBP + HNO_3 \cdot TBP \rightleftharpoons M(NO_3)_x \cdot yTBP \cdot HNO_3 + TBP \quad (2.4)
\]

It is postulated that, at third phase formation, the normal solvate $UO_2(NO_3)_2 \cdot 2TBP$ reacts with limiting $HNO_3 \cdot TBP$ to form $UO_2(NO_3)_2 \cdot 2TBP \cdot HNO_3$ and the free TBP is transported back to the water-oil interface to take part in $TBP \cdot H_2O$ formation. It is further postulated that in the third phase, the amount of uncomplexed TBP is very little; basically all TBP can be accounted for in the following forms: $UO_2(NO_3)_2 \cdot 2TBP \cdot HNO_3$, $UO_2(NO_3)_2 \cdot 2TBP$, $TBP \cdot H_2O$ and $HNO_3 \cdot TBP$ solvates.

In order to achieve higher decontamination from fission products, higher loading of metal ion in the organic phase might be deemed necessary[51]. As mentioned before though, during higher metal ion loading, there is a possibility of formation of the third phase which of course may lead to criticality or operational problems. For example, third phase can lead to increased losses of plutonium in a nuclear reprocessing plant. Questions on the exact structure of the third phase, the accurate prediction and
detection of third phase formation and also on various thermodynamics properties’ values still remain partially answered. Many studies, some of them cited throughout Chapter 2, have investigated this system but still there are many questions and scientific challenges remaining that surround third phase. This is the main reason why this study will try to provide further evidence and simulation methods and results to better understand the third phase conundrum. Thermodynamic properties of uranyl nitrate and nitric acid (activity coefficients, vapour pressures and solution densities) are calculated; such applications are important given the need to understand and predict the aqueous thermodynamics of actinide species in nuclear waste disposal areas. Also molecular dynamics simulations are performed on the various components that constitute third phase, to shed some light on their interactions, general behaviour and structure of this system.
Chapter 3

Methodology

In this chapter, the methods used and theories behind these methods will be discussed and analysed in an effort to provide the reader with the theoretical tools to better comprehend how the study results were acquired. The first part of this chapter will concentrate on the Statistical Associating Fluid Theory which was used in the initial stages of this research in order to study uranyl nitrate in the aqueous phase. The latter section will be on the molecular modelling methods that followed to study various third phase components in the organic phase.

3.1 Statistical Associating Fluid Theory (SAFT)

More than twenty years have passed since the publication of the first papers describing the statistical theory for associating fluids [52] [6]. SAFT was conceived as a method to combine Wertheim’s thermodynamic perturbation theory (TPT) for associating fluids with modern ideas on physically based equations of state [53]. Of course there are other models, developed before SAFT which are able to predict activity coefficients in liquid mixtures. Some of the most adopted ones are given below.

Debye-Hückel model

Models used to describe deviations from ideality (such as activity coefficients) in
electrolyte systems all have the simple Debye-Hückel model[54] as a starting point. The model/equation has a firm theoretical basis and does not contain any empirical parameters. For more on this, the reader is directed to Chapter 4, section 4.2.1 where this model is discussed further.

**Davies model**

The Davies equation[55] has been used to calculate activity coefficients of electrolytes at fairly low ionic strengths. At 298 K, for an ion $i$ of charge $z_i$, the activity coefficient is equal to

$$\log_{10} \gamma_i = -A z_i^2 \left( \frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3 I_m \right)$$

(3.1)

where the quantity $A$ has the same value for all ions and $I_m$ refers to the ionic strength of the solution. The equation is empirical but was found to work well for single electrolytes at low ionic strengths (less than 0.1 mol/kg). It is, however, not able to take electrolyte-specific effects into account.

**Ion association approaches**

This set of approaches considers ion-pair information in order to account for differences in mean activity coefficients for electrolytes at the same ionic strength. The activity coefficients are interpreted using association constants and an expression for the dependence of activity coefficients of all species only on an effective ionic strength.

To formulate an ion association model, it is necessary to specify the solution components, the activity data for all model species as functions of effective ionic strength and stability constants for ion-pairs under infinite dilution conditions.

**Specific ion-interaction methods**

These methods take both short-range and long-range specific ion-ion interactions into account and are based on the following assumptions:

- Interactions between ions A and B are specific for those particular ions and remain the same even in the presence of other ion species
• Magnitude of deviation from ideality depends on the concentration of solutes and solvent

• Deviation from ideality can be described with virial equations (first term based on Debye-Hückel theory)

• The estimation of deviation from ideality (such as activity coefficients) must approach the Debye-Hückel limit with increasing dilution

Roughly, all of the formulations of the specific ion approach can be described as giving the logarithm of activity coefficient as a sum of a calculated extended Debye-Hückel term plus a virial expression in the molalities of ions with coefficients depending on the nature of the ions. One such formulation is Pitzer’s model[56, 57]. By using a virial expansion, Pitzer has described the measured activity coefficients of several electrolytes over a large concentration range. From a modelling perspective, the use of Pitzer’s model is ponderous because of its limited availability range for very dilute aqueous electrolyte systems and its requirements for ternary interaction parameters[58].

Some other widely referenced activity coefficient models include the OLI MSE model of Wang et al.[59], the extended UNIQUAC model of Thomsen et al.[60] and the electrolyte nonrandom two-liquid (eNRTL) model[61]. The OLI MSE model suffers from the inconsistent treatment of ion-ion and ion-molecule interactions with the virial expansion-type equation and molecule-molecule interaction with the UNIQUAC equation. Also questionable is its use of pure ions as reference state. The extended UNIQUAC model is faulted for its incisistent treatments in both the reference state and the concentration scale. Pure ion reference state and mole fraction concentration scale are used with the short-range UNIQUAC term while the aqueous phase infinite dilution reference state and the molality concentration scale are used with the long-range Debye-Hückel expression[58].

Some of the aforementioned methods may have similar results with the method used in this thesis (SAFT), for single electrolytes. But SAFT remains a preferred way to calculate activity coefficients because of its advantages over the other models. A theory based in statistical mechanics offers several advantages. One such advantage is that each of the approximations made in the development of SAFT has been tested
versus molecular simulation results. Another, is that one can systematically refine
the equation of state. Also, the SAFT parameters have physical meaning; for an
associating or hydrogen-bonding molecule the association energy is needed (related
to change in enthalpy of association) as well as the bond volume (related to change
in entropy on association). Parameters for new systems can be estimated from those
of previously modelled systems[62].

There is still a bit of confusion surrounding SAFT, partly because SAFT is not a
specific equation of state but rather a method that allows for the incorporation of
associating effects into a given theory. More details on SAFT are given in Chapter
4, section 4.1.

Raoult’s law is a law of thermodynamics which states that the partial vapour pressure
of each component of an ideal mixture of liquids is equal to the vapour pressure of
the pure component multiplied by its mole fraction in the mixture. Of course this
is well-grounded for ideal solutions and not for real solutions (although it can be
adapted to non-ideal solutions by incorporating two factors, the fugacity coefficient
and the activity coefficient), which deviate from Raoult’s law because there is no uni-
formity of attractive forces between the two liquids. Until very recent years (1990s
and onwards), the engineering community’s dealings with associating mixtures was
largely based on the “chemical theory” approach, in which the associating complexes
are treated as new chemical species. Hence their different (anomalous) physical be-
avour is ascribed to the change in chemical composition (higher molecular mass,
fewer molecules etc). It is however an approach of limited predictive value because
one must know in advance all the reactions involved and be able to measure or pre-
dict the equilibrium constants as a function of temperature [53]. A more fundamental
statistical mechanical approach results from Wertheim’s papers, although he was not
the first to conceive this way of approach (see following paragraphs). What results
from these papers, are new theoretical equations that can relate the thermodynamical
properties to intermolecular forces, which allows for associating liquids to be treated
as simple liquids of more weakly interacting molecules. It is therefore not necessary
to know all the chemical reactions that are going to take place in advance, or to
measure and use in equations the equilibrium constants.
One of the first published methods for describing the nonidealities of associating mixtures come from Dolezalek [63] and is based on the assumption that the association can be treated as a chemical reaction. Thus, if a substance $A$ has the ability to self-associate and form dimers then

$$A + A \rightleftharpoons AA$$  \hspace{1cm} (3.2)

Dolezalek’s theory assumes that the non-ideality of any fluid can be explained solely by the formation of associated species, but, the n-mers (dimers, trimers and so on) are treated as ideal gases or solutions. In any case, as the number of association complexes increases, so does the number of fitted parameters needed hence making this method difficult to handle.

The original quasi-chemical theory proposed by Guggenheim[64] postulated that non-idealities in fluids could be assigned to the existence of non-random mixing at the molecular level. In opposition to the chemical approach, the formation of distinct association compounds is not considered and association is not explicitly distinguished from all other van der Waals-type interactions. Although quite successful in predicting properties of associating mixtures, this method is not of practical use over the whole fluid range or for very large molecules. Although not inherently incorrect, the fact that the equilibrium constant in chemical theories must be empirically obtained, limits their use as predictive tools.

A more promising route for understanding the associating fluids properties, is provided by recent theories that are based on statistical mechanics. The scientific community started to use statistical mechanical treatments for associating fluids and the first papers emerged in the early 1970s [53]. The nature of the interactions was described as a short-ranged attraction site embedded in a repulsive core. Among the first statistical mechanical treatments of associating fluids were those of Andersen[65, 66], in which the geometry of interaction was introduced at an early stage by considering a short-range attraction site embedded in a repulsive core. Andersen’s ideas inspired later theories of associating fluids that used similar expansions but with respect to fugacity. One of this later approaches was used by Hoye and Olaussen [67], who took this a step further and introduced the multidensity formalism. All these ideas were
Chapter 3. Methodology

extended in a series of papers by Wertheim, where a coherent statistical mechanical theory of associating fluids was presented. In this, molecules are treated as different species according to the number of bonded associating sites and separate densities are defined for each possible bonding state of a molecule. In principle, statistical mechanics provides ‘recipes’ for calculating the thermodynamics (and structure) of a fluid given its intermolecular potential function. However, for most systems this solution requires the use of approximations, for example the hard-sphere assumption discussed later, which in the end determine the accuracy of the given theory. The next obstacle to overcome was the equations of state that were going to be used. Most of them are variations on the van der Waals equation, which means that they are based on the assumption of a hard-sphere term to represent the repulsive forces and a mean-field term to account for the dispersion of long-range forces. The problem here is that the assumption of a hard-sphere term is inappropriate for most fluids which contain non-spherical associating molecules. Hence a more appropriate reference in this case, is the one that also accounts for chain length and molecular association, as well as other interactions such as dispersion and long-range dipolar forces which can be treated via a perturbation or approximate mean field term [53]. Wertheim’s theory provided such methods and such an approach was incorporated by Chapman et al. [6, 52], called the statistical associating fluid theory (SAFT).

More importantly (for this study at least), a version of SAFT to model chain molecules of hard-core segments with attractive potentials of variable range has been developed by Gil-Villegas et al. [68] in order to improve the description of liquid phase behaviour (for more on this version of SAFT see section 4.1). This was for non-conformal fluids which gives a very good approximation of the phase behaviour of water with non-electrolytes. More importantly, an extension to this approach with SAFT, was developed in order to extend this method to deal with strong electrolyte solutions, named SAFT-VRE [4]. A detailed explanation of this particular method, along with the equations and terms used in this study, are written in section 4.2. This is the approach that is used in this study to describe the aqueous phase of uranyl nitrate and several other 1:1 aqueous electrolyte solutions, in order to get a good description of the model and to provide the foundations before moving on to the more ‘treacherous’ oil phase. More on this will be written in Chapter 4, where all the work done with SAFT will be presented.
3.2 Molecular modelling

It was only in 1953 that the meaning of molecular modelling started to change with the publication of the first computer-based study of a liquid in two dimensions [69]. Presently, computer-based techniques and methods are considered to be the connection point between theory and experiment, used for validating a new theoretical or existing model and to predict experimental results.

Molecular mechanics, for example, offer a simpler representation of larger systems (polymers and biological molecules) rather than quantum mechanics that can describe molecules at the subatomic level with more detailed description of matter but for relatively small systems. Molecular mechanics, also known as force field theory, offers a good compromise between the system’s attainable information and an acceptable and achievable time scale [70].

Building the initial configuration stage of the system in question is the first step of a computational study. Consider a system of \( N \) particles where a macroscopic property \( A \) will be measured. The measurement will depend on the momenta and particle positions and an instantaneous value for \( A \) will be produced for the \( N \) momenta and particle positions at time \( t \). This instantaneous value of \( A \) will of course fluctuate over time as a result of the particles’ interactions, so this macroscopic property has to be obtained as an average over time. At this point it is worth stating that the time averaged values of phase functions values will only converge once the system has reached a steady state (equilibrium state). Theoretically, this is possible to calculate since the property is converging with time; the gradient of energy given by the particles’ interactions gives the force acting between them, which in turn by using Newton’s second law can yield the acceleration and the integration of the motion equations can give the particles’ positions and velocities over time.
3.2.1 Molecular Dynamics

The first molecular dynamics (MD) simulation was performed by Alder and Wainwright in 1957 [71] for the purpose of investigating the phase transition of a system of hard spheres. MD is a deterministic method; it calculates the “real” dynamics of the system, from which time averages of properties can be calculated, and the state of the system can be predicted at any time from its current state [70]. In MD, the average value of a property, say $A$, is calculated from:

$$\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_{0}^{t} A(t) \, dt = \frac{1}{M} \sum_{i=1}^{M} A(i \Delta t)$$ \hspace{1cm} (3.3)

where $M$ is the number of snapshots of the ensembles and $\Delta t$ is the timestep. The successive configurations of the system can be obtained from Newton’s laws of motion, giving a trajectory of variable positions and velocities with time. To clarify, it is by integration of the laws of mechanics (Newton’s equations) that these trajectories are obtained - not by the equations themselves which tell us only about the rates of change. For example, to simulate the motion of a particle $j$ in a system, the second law of motion has to be solved:

$$\frac{d^2}{dt^2} \mathbf{r}_j(t) = \frac{d}{dt} \mathbf{v}_j(t) = \mathbf{a}_j(t) = \frac{\mathbf{F}_j(t)}{m_j}$$ \hspace{1cm} (3.4)

where $\mathbf{r}_j(t)$ is the position of particle $j$ at time $t$, $\mathbf{v}_j(t)$ is its velocity, $m_j$ its mass and $\mathbf{F}_j(t)$ is the force acting on the particle at time $t$. This force, as noted before, is generated on the particle due to interactions with other particles in the system. When many particles are involved and their motions are coupled together, as is often the case, it is unfeasible to calculate the total force analytically. The equations of motion are then solved using numerical integration of finite differences. If we assume to know the positions and velocities of each particle at time $t$, we can find the position and velocity of each particle at time $t + \delta t$ by integrating the equation above. Using the new results, with the same way we can find their new positions and velocities at time $t + 2\delta t$ and so on. $\delta t$ is constant and an appropriate choice for its value has to be made; a too small timestep will be very precise but very computationally expensive and a too large timestep will be responsible for inaccurate results.
Different algorithms have been developed to calculate the finite difference techniques of numerical integration; the most common is the Verlet algorithm [72], (although Euler’s scheme is more famous despite its poor accuracy), with one of the valid alternatives being the Leap-Frog algorithm [73]. In this work, the Leap-Frog algorithm is used, which happens to be the default integrator in Gromacs [74], as the velocities are calculated explicitly and the positions depend on quantities of the same order of magnitude. Also it is less expensive computationally than the velocity Verlet where positions and velocities are calculated explicitly at every time during the simulation. There is a flaw though, because positions and velocities are not calculated at the same time, and an average between two timesteps is used to find a mid point value for positions after the velocity is calculated.

3.2.1.1 Molecular dynamics ensemble

Molecular dynamics simulations, as noted above, are based on the classical equations of motion. The total energy is conserved and the simulations are traditionally carried out in a NVE (microcanonical) ensemble. This, for example, means that under a constant number of molecules, volume and energy ensemble, the temperature of the system can be calculated (strictly speaking, basic molecular dynamics probes a subset of the microcanonical ensemble since Newtons’ equations conserve linear momentum). However, most quantities that are wished to be calculated are actually from a constant temperature ensemble. In order to enable MD to simulate different ensembles, such as the NVT (canonical) and the NPT (isothermal-isobaric), a thermostat or a barostat needs to be implemented.

Thermostats and Barostats

For several reasons such as drift during equilibrium or force truncation and heating due to frictional forces, it might be considered necessary to control the temperature of the system. The velocity of the molecules is altered in order to obtain an average kinetic energy equal to that expected for that system under the desired conditions. The most famous thermostats used in MD simulations are the Berendsen [75] and the Nosé-Hoover [76, 77].
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The Berendsen coupling algorithm is very efficient for relaxing a system to a target temperature but when the system has reached equilibrium, it might be more important to probe a correct canonical ensemble (although the difference is usually negligible) [74]. The former can be reduced to ad hoc rescaling of the relaxation time is equal to the timestep. The Nosé-Hoover ensemble comes into play, where a system is extended by introducing a thermal reservoir and a friction term. Hence the particles’ equation of motion is replaced by

\[
\frac{d^2 \mathbf{r}_i}{dt^2} = \frac{\mathbf{F}_i}{m_i} - \xi \frac{d\mathbf{r}_i}{dt} \tag{3.5}
\]

where the friction force is proportional to the product of each particle’s velocity and a friction parameter \(\xi\). Note that this parameter can take either positive or negative values, i.e. it is not only for macroscopic friction which is irreversible and hence the coefficient will only be positive. This friction parameter has its own equation of motion where the derivative is calculated from the difference between the current kinetic energy and the reference temperature.

\[
\frac{d\xi}{dt} = \frac{1}{Q} (T - T_o) \tag{3.6}
\]

where \(T\) is the current instantaneous system temperature, \(T_o\) is the reference temperature and \(Q\) is a constant called ‘mass parameter’ which is calculated by the software when the user selects an appropriate period of oscillations \(\tau_T\) from

\[
Q = \frac{\tau_T^2 T_o}{4\pi^2} \tag{3.7}
\]

The relaxation time, \(\tau\) was selected judiciously, after a discussion with Prof. A.J. Masters. In the same spirit as with the temperature coupling, the system can also be coupled to a desired pressure. This has to happen if one is looking to obtain an \(NPT\) ensemble. In this case, barostats are used, the most commonly implemented of which are the Berendsen [75], the Nosé-Hoover [76, 77] and the Parrinello-Rahman [78]. In this study the Nosé-Hoover is used since the same thermostat is also in use. It is quite important to note that, whilst the Berendsen was considered for ease of implementation and because it can deal with large pressure oscillations in the system, its pressure control algorithm cannot yield the exact \(NPT\) ensemble. Instead it gives
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a simulation with the correct average pressure and it is not yet clear as to what errors this approximation might produce.

3.2.2 Periodic boundary conditions

Even though simulation methods are continuously improving and encompassing even more systems that were inaccessible before for computational study, there are still restrictions by the existing computing power to model relatively large systems. As noted above, the size of a macroscopic material to be simulated is beyond the reach of classical simulations but there is a solution for this limitation. This is why periodic boundary conditions are applied; so that only a portion of the whole system can be the real simulation and replicas of this ‘main box’ can be replicated and placed on each side of the box as image cells. Therefore for every particle that moves in the main box there will be a replica for each image cell moving in the same way. A schematic of this is shown in Figure 3.1 on the next page.

Periodic boundary conditions are paramount, not only because they solve the computational limitations of molecular dynamics simulations but also because they allow for the control of the boundary effects that a bulk material experiences, hence providing a more realistic behaviour of the bulk phase. However there is a risk of introducing artifacts within the results and therefore some limits have to be placed; it cannot explore any structure whose length scale is equal or larger than half the box length. Also it cannot explore times that are bigger than the time to move across the box’s length. Effectively, periodic boundary conditions allow for the description of a quite large system but still the size of the main box that is the real simulation has to be sufficiently big to accommodate the main features of the system such as the size of the particles involved.

Minimum image convention

As a result of applying periodic boundary conditions the number of interacting pairs increases enormously. This is due to the fact that each particle interacts with other particles in the box as well as with their images. This conundrum can be dealt with by choosing a finite range potential with minimum image convention. The minimum
image convention is a procedure where one takes the nearest neighbour to an actual particle, regardless of whether this neighbour is an actual particle or an image particle. This means that only interactions between each molecule and the closest periodic image of its neighbours are considered.

In the course of the simulation, if an atom leaves the basic simulation box, attention can be switched to the incoming image. To do so, a finite range potential is used so that the interaction between two distant particles on or beyond this user-defined range (length) can be neglected. An appropriate choice of this cut-off distance is fundamental: if it is too large, the particles might interact with their own image, while if it is too small then it will cause an unwanted neglection of interactions between particles. This cut-off distance, $r_{\text{cut-off}}$, is set up to be less than half the simulation box length[70]. This is shown in Figure 3.1, where it is represented as a red circle of radius $r_{\text{cut-off}}$.

**Ewald summation**

The insertion of a cut-off distance affects the calculation of the long-range electrostatic interactions. To overcome this, the Ewald summation[79] is used. Ewald summation is a method for computing long-range interactions (e.g. Coulombic interactions) in periodic systems. It is a summation method where the long-range interaction between particles is split in two parts: one part is the short-range contribution and the other is the long-range contribution, where this long-range contribution is calculated using a Fourier transform. The advantage of this method is a rapid conversion of energy which gives the opportunity for a high-accuracy and speed on the computation of long-range interactions.

In this work the long-range interactions are treated with the Ewald method and the particle-mesh Ewald (PME)[80], a variation of the Ewald method for periodic systems. PME calculates direct-space interactions within a finite distance and in reciprocal space using a Fourier transform, to build a ‘mesh’ of charges. From this charge interpolation long-range forces can be calculated and incorporated into the non-bonded interactions of a simulated system.
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Figure 3.1: An example of periodic boundary conditions. The highlighted blue cell is the user-inputed simulation cell and the dotted cells around it are the replicas (image cells). The cut-off spherical volume is represented by the red circle.

3.3 Summary

In this chapter a description of the main simulation methods used in this project are presented. These methods enabled the study of properties of the systems in question by using quite different approaches. While MD is a deterministic method where true dynamic information can be obtained and can also give insight to the structure and species associated with each other within the system, Monte Carlo (MC) is a stochastic approach based on exploring the energy surface by randomly probing the geometry of the molecular system i.e. its configuration state. SAFT on the other hand is a more approximate equations of state method where with little input information it can examine the phase behaviour and provide average thermodynamic properties.
Chapter 4

Statistical Associating Fluid Theory - electrolytes and uranyl nitrate in aqueous solutions

4.1 Introduction

In electrolyte solutions the nature of the electrostatic ion-ion and ion-solvent interaction is different from the nature of dispersive and repulsive interactions between neutral particles. To describe the thermodynamic properties of electrolyte solutions, two kinds of approaching this seem the more valid ones: the activity coefficient-based models, and the models consisting of equations of state (EoS) [81]. The first one, despite its simplicity in application, has some notable disadvantages such as the aspect of solution density which cannot be derived by the model itself and the fact that they are pressure independent[81]. The equation of state based models on the other hand, do not have these disadvantages but they need an additional Helmholtz free energy term to account for the electrostatic interactions between charge particles (ions). In our SAFT case, a simplified mean spherical approximation term (MSA) has been used for these long range interactions. Alongside Helmholtz’s free energy terms various thermodynamic quantities can be calculated, such as the activity coefficients, which are presented in the following sections. They are considered useful in order to be able to describe the thermodynamic properties of the solutions tested as well as being a reference point for future experiments on said systems. The mean
activity coefficient is also used frequently in electrolyte solution approaches to test the validity of the model in use.

A version of SAFT to model chain molecules of hard-core segments with attractive potentials of variable range has been developed by Gil-Villegas et al. [68] in order to improve the description of liquid phase behaviour. This was for non-conformal fluids which gives a very good approximation of the phase behaviour of water with non-electrolytes. More importantly, an extension to this approach with SAFT, was developed in order to extend this method to deal with strong electrolyte solutions, named SAFT-VRE [4]. This is the approach that is used in this study to describe the aqueous phase of uranyl nitrate and several other 1:1 aqueous electrolyte solutions.
4.2 The SAFT-VRE approach

4.2.1 Mean Spherical Approximation (MSA) and Restrictive Primitive Model (RPM)

In 1923 Debye and Hückel\cite{54} provided, in a simple theory, the correct equation for the behaviour of electrolyte solutions in the limit of very low concentration. At finite concentration the properties of an electrolyte solution depend in a complex way on short-range forces between solute ions, both direct and as modified by the solvent, in addition to the long-range electrostatic forces. The basic Debye-Hückel model is essentially a linearised Poisson-Boltzmann model which was eventually proven to provide a starting point for modern treatments of non-ideality of electrolyte solutions. The model’s main assumptions are that all ions can be considered as point charges, the only interactions between ions are electrostatic and that the effect of counterions on a particular ion of opposite charge can be described as due to a static ion-cloud. These assumptions lead to the limiting Debye-Hückel equation where the single ion-activity coefficient for an ion, $\gamma_i$, with charge $z_i$ is

$$\log_{10} \gamma_i = A z_i^2 \sqrt{I_m}$$

(4.1)

where the quantity $A$ has the same value for all ions and $I_m$ refers to the ionic strength of the solution. The ionic strength is calculated using

$$I_m = \frac{1}{2}(z_+^2 c_+ + z_-^2 c_-)$$

(4.2)

where $z_+$ and $z_-$ are the charge of the cation and anion respectively, and $c_+$ and $c_-$ are their concentrations.

In summary, the Debye-Hückel approach neglects the size of the ions and assumes that the structure of the fluid is fully governed by the electrostatic interactions. This approach is now recognised as representing the limiting behaviour of an electrolyte solution of infinite dilution, but it quickly breaks down for concentrations higher than
0.001 molal[5].

The MSA has proved to be a powerful tool for calculating thermodynamic properties of electrolytes. It is an integral equation theory. It is long and difficult to try and show the analytical solutions for the various MSA equations in this report, but Lee’s book provides them [82]. The MSA theory includes the excluded volume of the ions (which was not included in previous theories such as the Debye-Hückel model) and both the short and long-range interaction effects, making it suitable for use even at high electrolyte concentrations. These effects can be represented in the MSA model[83][84]. The MSA has been applied extensively and a lot of successful work was done for the calculations of thermodynamic properties of electrolyte solutions, after Blum[85] gave the analytical expressions of the MSA model for the thermodynamic and structural properties of electrolyte solutions. However, interactions between ions and molecules are taken into account through a dielectric constant set within the model, and this cannot reveal the microscopic aspects of these ion - solvent molecule interactions [86].

In this thesis, the MSA model was simplified and adopted to calculate the mean activity coefficients of aqueous $\text{UO}_2(\text{NO}_3)_2$ solution at different molalities, and was also implemented for 1:1 electrolyte solutions.

### 4.2.2 SAFT-VRE

Initially a fluid mixture of monomers is taken as a reference system at which corresponds to water, cation and anion molecules interacting through square-well potentials. It is then assumed that the remaining associating, chain and ionic contributions can be added as residual terms over the free energy of the monomer fluid, and hence the total free energy of the mixture can be given in terms of Helmholtz’s free energy for each contributing term

\[
\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO}}}{NkT} + \frac{A^{\text{CHAIN}}}{NkT} + \frac{A^{\text{ASSOC}}}{NkT} + \frac{A^{\text{ION}}}{NkT}
\]  

(4.3)

where $k$ is the Boltzmann constant, $N$ the number of molecules and $T$ the temperature. $A^{\text{IDEAL}}$ is the free energy of the ideal gas, $A^{\text{MONO}}$ represents the residual free energy due to overlap and dispersion forces between monomers, $A^{\text{ASSOC}}$ is the contribution...
from the intermolecular association and $A_{ION}$ is the residual free energy due to ion-ion interactions. $A_{CHAIN}$ is the energy contribution due to chain formation but in this case there are no chains formed since we are dealing with spherical molecules and therefore it is equal to zero.

4.2.2.1 Ideal contribution

The free energy of the ideal mixture is given as

$$A_{IDEAL} = \frac{n}{N} \sum_{i=1}^{n} x_i \ln \left( \frac{\rho_i \Lambda_i^3}{N} \right) - 1$$

(4.4)

where $\rho_i = \frac{N_i}{V}$ is the number density and $\Lambda_i$ is the thermal de Broglie wavelength (average de Broglie wavelength of particles of an ideal gas at a specified temperature) of species $i$. The de Broglie wavelength is defined as

$$\lambda = \frac{h}{p}$$

(4.5)

where one can see that the de Broglie wavelength associated with a particle, is related to its momentum $p$ through the Planck constant $h$.

4.2.2.2 Monomer contribution

If this is to be taken as a general case of a fluid with chain molecules, then the monomer free energy is given in terms of the number of spherical segments comprising the chain of component $i$ for example

$$A_{MONO} = \left( \sum_{i=1}^{n} x_i m_i \right) \frac{A^M}{N_s kT}$$

(4.6)

where $m_i$ is the number of spherical segments and $A^M$ refers to the molar Helmholtz energy of the fluid if no chain connectivity occurred, evaluated at the monomer molar density. $N_s$ is the number of spherical segments, but since in this work all species are considered spherical ($m_i=1$) then the number of molecules $N_i$ is the same as the
number of spherical segments, \( N_s = N \). Therefore we can write

\[
\frac{A^{\text{MONO}}}{NkT} = a^M
\]  \hspace{1cm} (4.7)

where \( a^M \) is written as a high-temperature expansion

\[
a^M = a^{HS} + \beta a_1 + \beta^2 a_2
\]  \hspace{1cm} (4.8)

In the above equation, \( a^{HS} \) represents the free energy for a mixture of hard spheres, \( \beta = \frac{1}{kT} \) and \( a_1 \) and \( a_2 \) are the first two terms of the perturbation expansion associated with an attractive energy \( \epsilon_{ij} \). \( a_1 \) represents the mean attractive energy and is given by

\[
a_1 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_1^{ij}
\]  \hspace{1cm} (4.9)

and \( a_2 \) is related to density fluctuations in the hard sphere fluid

\[
a_2 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_2^{ij}
\]  \hspace{1cm} (4.10)

The attractive energy is described for a square-well potential of energy \( \epsilon_{ij} \) and range \( \lambda_{ij} \) as

\[
a_1^{ij} = -\rho a_{ij}^{VDW} \frac{g_{ij}}{g_{ij}^{HS}} \left[ \sigma_{ij}; \zeta_{eff}^{ij} \right]
\]  \hspace{1cm} (4.11)

where \( \zeta_{eff}^{ij} \) is equivalent to the segment packing fraction and \( a_{ij}^{VDW} \) is the van der Waals attractive constant for \( i-j \) interactions

\[
a_{ij}^{VDW} = 2\pi \epsilon_{ij} \sigma_{ij}^3 \left( \frac{\lambda_{ij}^3 - 1}{3} \right)
\]  \hspace{1cm} (4.12)

The dispersion and repulsion interactions are calculated using the Lennard-Jones 12-6
potential function

\[ V = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left( 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) \]  

(4.13)

where \( \epsilon_{ij} \) is the well depth of the potential curve between atom \( i \) and atom \( j \), \( \sigma_{ij} \) is the distance at which the potential between two particles is zero (also known as the collision diameter) and \( r_{ij} \) is the distance between them (Figure 4.1)

Figure 4.1: A schematic of the Lennard-Jones 12-6 potential.

As noted before, in this model only water-water and ion-water interactions are taken into account through the attractive square well. The ion-ion square well interactions are assumed to be zero (\( \epsilon_{22}=0 \), \( \epsilon_{33}=0 \) and \( \epsilon_{23}=\epsilon_{32}=0 \)). Therefore, equation 4.8 will include only three terms when expanded for water-water, water-anion and water-cation interactions:

\[ a_1 = x_1a_1^{11} + 2x_1x_2a_1^{12} + 2x_1x_3a_1^{13} \]  

(4.14)

For more details on the attractive energy equations, including the effective packing function and the radial distribution function, see Galindo et al. [4], pages 10275-6.
4.2.2.3 Association contribution

The contribution due to association of say, $s_i$ sites on species $i$ is given from Wertheim’s theory\[87\] as

$$
\frac{A^{\text{ASSOC}}}{NkT} = \sum_{i=1}^{n} x_i \left[ \sum_{a=1}^{s_i} \left( \ln X_{a,i} - \frac{X_{a,i}}{2} \right) + \frac{s_i}{2} \right]
$$

(4.15)

where the first sum is over the total number of species $i$ and the second the sum of all $s_i$ sites of type $a$ onto species $i$. $X_{a,i}$ is the fraction of type $i$ molecules that are not bonded at site $a$ (which can be obtained by numerical solution of mass action equations\[6\][87]). In our model, only water is assumed to associate. As noted before, at this first approximation only strong aqueous electrolyte solutions (assuming full dissociation) are tested over room temperature (298.15 K), so a disregard of ion-ion association is reasonable\[4\]. Hence, since we described water as a fluid with four associating sites, then the above equation can be rewritten as

$$
\frac{A^{\text{ASSOC}}}{NkT} = x_1 \left[ 4 \left( \ln X_1 - \frac{X_1}{2} \right) + 2 \right]
$$

(4.16)

where $X_1$ is the fraction of water molecules not bonded and is given by

$$
X_1 = \frac{1}{1 + 2\rho x_1 X_1 \Delta_{11}}
$$

(4.17)

where $\Delta_{11}$ is a function written in terms of the bonding volume available for the water sites $K_{11}$, the function for water-water site-site interaction $F_{11} = \exp(\epsilon_{11}^{HB}/kT) - 1$, and the radial distribution function of the water-water square-well segments $g^M(\sigma_{11}; \zeta_3)$ evaluated at contact.

$$
\Delta_{11} = K_{11} F_{11} g^M(\sigma_{11}; \zeta_3)
$$

(4.18)
4.2.2.4 Ionic contribution

For the ionic contribution, the restricted primitive model (RPM) was used where the anions and cations are represented as charged hard spheres of the same diameter and were set to interact through a uniform medium of dielectric constant $D$. 

$$ u_{ij}(r) = \begin{cases} +\infty & \text{if } r < \tilde{\sigma} \\ (q_i q_j)/D \rho & \text{if } r > \tilde{\sigma} \end{cases} \quad (4.19) $$

This is the pair potential for the ion-ion interaction[82] where $i$ and $j$ represent anions and cations, for $q_i = z + e$ and $q_j = z - e$. The new symbol $\tilde{\sigma}$ is the common hard-sphere diameter, that is used in the PRM and is given by

$$ \tilde{\sigma} = \sum_{j=2}^{\tilde{n}} \tilde{x}_j \sigma_{jj} \quad (4.20) $$

and the fraction of ions $\tilde{x}_j$ can be found by

$$ \tilde{x}_j = \frac{x_j}{\sum_{j=2}^{n} x_j} \quad (4.21) $$

where the sum is over the ionic species, and does not include water. Then, the excess free energy from the ionic contribution, i.e. the mean spherical approximation (MSA) contribution, is given [82]

$$ \frac{A_{IONS}}{NkT} = -\frac{3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}}{12\pi \rho \tilde{\sigma}^3} \quad (4.22) $$

where $x = K \tilde{\sigma}$ and $K$ is equal to

$$ K = \sqrt{\frac{4\pi}{DkT} \sum_{j=2}^{\tilde{n}} \rho_j q_j^2} \quad (4.23) $$

which is the inverse Debye length. Debye length is the measure of a charge carrier’s
electrostatic effect in solution, and how far those electrostatic effects persist.

The ions are restricted to the liquid phase, so that the ionic contribution would only contribute to the free energy of the liquid. This is a reasonable approximation due to the fact that we are dealing with nonvolatile inorganic salts at room temperature, where it is known that under these circumstances the vapour phase over the solution is almost exclusively comprised of water.
4.3 Model parameters

The first step to obtain a good model of aqueous electrolyte solutions, is a good description for water. The water molecules are modelled as hard spheres of diameter $\sigma_{11}$ with four short-ranged off-center attractive square-well sites for association. The four sites of course represent the two hydrogens in the molecule and the two oxygen lone pairs of electrons. As shown in Figure 4.2, the sites are situated at a distance $r_{d1}$ from the center and when they come closer than a distance $r_{c1}$, that is closer than the size of the square-well site, a hydrogen-electron hydrogen-bond interaction occurs of attractive energy $\epsilon_{HB}^{11}$. The relative positions of these sites are not important at this level of approximation. The weak long-range attractive forces (dispersion forces) are modeled via a second-order high temperature expansion; a square-well potential is used for the water molecules with an attractive range $\lambda_{11}$ and depth $\epsilon_{11}$.

![Figure 4.2: Models for the water, ions and the electrolyte solution. The system is a three component mixture of water, anions and cations in a dielectric constant (shaded area). The two H sites on the water model represent the hydrogen atoms and the other two sites e represent the lone pairs of electrons of oxygen. Only H-e bonding is allowed [4][5].](image)

The salt molecules are modelled as two hard spheres which represent the cation and the anion, of diameters $\sigma_{22}$ and $\sigma_{33}$ respectively in what concerns the repulsive interactions. Water-ion long-range attractive interactions are taken into consideration, as with the long-range attractive interactions between water molecules; via a square well potential of ranges $\lambda_{12}$ and $\lambda_{13}$ and depths $\epsilon_{12}$ and $\epsilon_{13}$. One should note though, that ion-ion interactions are considered to occur exclusively through the Coulombic contribution, which is described in the MSA for the implementation of a uniform dielectric constant to take care of the effective ion-ion interactions due to the solvent presence. Hence, ion-ion interactions through the square well potential are not considered i.e.
\( \epsilon_{22} = 0, \epsilon_{33} = 0 \) and \( \epsilon_{23} = \epsilon_{32} = 0 \). Another important assumption that is made, is for the fluid which is considered to be a mixture of water and ions in solution with every salt molecule being dissociated; no undissociated molecules are present.

\[ \text{Figure 4.3: Model approximations on the left figure where the repulsive molecule cores prevent more than two molecules to bond at a single site; no site is allowed to bond simultaneously to two sites; double bonding is not allowed. The right figure represents the physical basis of the SAFT model[6][7].} \]

Ji et al. [88] have stated that for studying thermodynamic properties in electrolyte solution models, an activity coefficient regression is more effective for fitting model parameters, rather than applying osmotic coefficient data.

To study the mean activity coefficients of \( \text{UO}_2(\text{NO}_3)_2 \) and several electrolyte solutions, three basic parameters had to be obtained in order for the model to have adequate data to calculate them: the square-well water-ion attractive energy \( \epsilon_{ij} \), the range of the square-well \( \lambda_{ij} \) and the ionic diameters \( \sigma_{jj} \) (j refers to the ions). From these the most obvious and relatively easy to find are the ionic diameters [89]. Various techniques have been used for the calculation of ionic diameters, notably by Pauling, Goldschmidt and by Lande, leading to the scales of ionic radii associated with each of their names. The issue is that almost every value for an ion taken from different techniques is slightly different from another (for the same ion of course). Therefore, due to the fact that a very similar model to Gil-Villegas is being used, then it is better for the same ionic diameters to be implemented. Table 4.1 shows the experimental
Pauling ionic diameters used for each of the ions[4]

**Table 4.1:** Pauling ionic diameters and optimised water-ion interaction parameters

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\sigma_{jj}$/Å</th>
<th>$(\epsilon_{ij}/k)/K$</th>
<th>$\lambda_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>1.90</td>
<td>2126</td>
<td>1.2</td>
</tr>
<tr>
<td>K$^+$</td>
<td>2.66</td>
<td>94.60</td>
<td>1.2</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1.36</td>
<td>782.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>3.62</td>
<td>307.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>3.92</td>
<td>149.1</td>
<td>1.2</td>
</tr>
<tr>
<td>I$^-$</td>
<td>4.40</td>
<td>152.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

where $\sigma_{jj}$ are the Pauling ionic diameters, $(\epsilon_{ij}/k)$ is the attractive square-well water-ion energy and $\lambda_{ij}$ is the range. The range of the square-well $\lambda_{ij}$ is set at 1.2 in all solutions because a good description of the solution densities is obtained with this value of the unlike range parameter[4].

As for the modelling parameters of water, these were again taken from Gil-Villegas et al., which were found by ways of a best fit to experimental vapour pressures and saturated liquid densities from the triple point to the critical point using a simplex method. For the ion parameters in Table 3.1 to be ‘trustworthy’ when implemented in the model, the following water parameters were used

**Table 4.2:** Water model parameters

<table>
<thead>
<tr>
<th>$\sigma_{jj}$/Å</th>
<th>$(\epsilon_{ij}/k)/K$</th>
<th>$\lambda_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.036</td>
<td>253.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

There are also the association parameters that have to be taken under consideration of the association contribution for SAFT. The sites are placed halfway between the center and the surface of the sphere ($r_{di}/\sigma_{11}$=0.25) and a cut-off range of $r_{ci}/\sigma_{11}$=0.692. This corresponds to a binding volume $K_{11}$=1.028 Å³. The hydrogen bonding
energy which occurs when two sites overlap is equal to $\epsilon_{11}^{KB}/k=1366$ K [5][4].
4.4 Results and Discussion

The mean activity coefficients of aqueous uranyl nitrate and eight aqueous solutions of single strong electrolytes were investigated. All simulation runs were performed under a constant temperature of 298.15 K, 1 bar pressure (\(1 \times 10^5 \text{ Pa}\)) and an initial volume of \(1 \times 10^{-3} \text{ m}^3\). The SAFT program first starts by reading the pressure and temperature so that the density and relative permittivity can be calculated. Then the molecule parameters are read by the model right before the final user input of the initial volume of the aqueous solution (where 1 kg of water is placed as a solvent) and the desired molality (moles of solute per kg of solvent) for each run. After all inputs are inserted, the program can now calculate the excess chemical potentials of all species, the main equations used for this are given below

\[
\mu_a = \left( \frac{\partial A}{\partial N_a} \right)_{V,T,N_a} \quad (4.24)
\]

where \(\mu_a\) is the chemical potential of species a and is equal to

\[
\mu_a = \mu_a^0 + RT \ln(\gamma_a m_a) \quad (4.25)
\]

where \(\mu_a^0\) is the chemical potential at infinite dilution, \(\gamma_a\) the activity coefficient and \(m_a\) its molality

\[
\mu_a^{ex} = \mu^{ex,0}_a + RT \ln \gamma_a \quad (4.26)
\]

where \(\mu_a^{ex}\) is the excess chemical potential of species a.

Then these results can be implemented in the following equation for the final calculation of the mean activity coefficients of the salt tested at the specified molalities

\[
\ln(\gamma_{mean}) = \frac{[n_2 (\mu_2 - \mu_{2\text{atm}=0}) + n_3 (\mu_3 - \mu_{3\text{atm}=0})]}{X_{n-tot}} \quad (4.27)
\]

where \(\mu_2, \mu_3\) are the chemical potentials of the cation and the anion respectively, \(m\) is the molality and \(X_{n-tot} = n_2 + n_3\), which are coefficients i.e. say that NaCl is
represented as $A_{n_2}^p B_{n_3}^q$ and it should satisfy $pn_2 + qn_3 = 0$.

4.4.1 $\text{UO}_2(\text{NO}_3)_2$/water system

The first runs of the model were done with uranyl nitrate and water as a solvent. At first the system was reproduced accurately by the program but for low molalities. After the threshold of 1.5-2 m (m for molality), the calculated results start to deviate from the experimental ones and as the molalities increase, this difference gets bigger.

![Figure 4.4: $\text{UO}_2(\text{NO}_3)_2$/water figure at T=298.15 K and 1 bar pressure.](image)

There is a good agreement with the experimental data [90] as can be seen from the figure above, but unfortunately this only happens up to molalities of 1.4 to 1.6 mol/kg. At molalities $\geq 2$ mol/kg, the model starts to deviate from experimental values. This can be observed in the following figure 4.5.

The model’s behaviour with uranyl nitrate is quite odd above molalities of 2 mol/kg and it is still unclear why there is such a deviation from the experimental results. To deal with this problem it was thought to try to represent the uranyl cation as a dimer but unfortunately the results at high molalities were still not in accordance with
the experimental data. Therefore it was thought to change the anion’s diameter. By reducing the nitrate’s diameter the calculated results were finally brought into agreement with the experimental data.

As can be seen in Figure 4.6, there is good agreement between the calculated and experimental data[90]. There is a slight concern about the size of the nitrate ion chosen, if it is indeed too small, so it was tested with other cations as well to see if the characterisation is correct. Also several other univalent salts were tested to further validate the precision and accuracy of the model. Experimental information about electrolyte activity coefficients is available[91], and it would be easier to spot and optimise certain sections of the model by having these data to compare to. These experimental values were obtained from a series of experiments based on vapour-pressure lowering, isopiestic vapour-pressure measurements, solubility, diffusion, and electromotive forces of galvanic cells with or without transference [90][91][92]. Freezing-point depression and boiling-point elevation are also common methods used but not for this study as the data range here is restricted to a temperature of 298.15 K.

As in the electrolyte graphs shown in Figures 4.7-4.10, it is expected that the mean activity coefficient will decrease at low molalities and then after a certain concentration to increase due to such reasons as the increasing fraction of molecules surrounding ions which become significant and of course ion pairing increases by increasing the
molality hence increasing the activity effects.

### 4.4.2 Electrolytes

#### 4.4.2.1 NaCl and other sodium salts

The first salt to be tested under this model was NaCl. The blue-square dotted line in Figure 4.7 are shown plots of the mean activity coefficients of NaCl vs molality, at 298.15 K and 1 bar against the experimental data set and it can be seen that after the agreement at minimum, the calculated data start to deviate ‘upwards’. A way to lower the data points (i.e. to decrease the ionic activity) is to introduce dispersion forces between the ions. One of the initial assumptions was that ion-ion interactions are considered to occur exclusively through the uniform dielectric constant implemented and therefore no ion-ion interactions through the square-well potential were considered. Hence the green-square dotted line in figure 4.7 was fitted for an anion-cation square-well potential with $\epsilon = 1352$. This value was calculated by trial and error, after contacting Professor Galindo and following her suggestion that if needed, the ion interaction potentials ($\epsilon_{23} = \epsilon_{32}$) value should be from 100 to around 1000-
Chapter 4. Statistical Associating Fluid Theory - electrolytes and uranyl nitrate in aqueous solutions

The same trend is observed in NaI as in NaCl. Since this ad hoc approach of fitting ion dispersion potential has proven to give very good agreement with the experimental data, therefore the same approach is used with NaI where after ion-ion dispersion component of the order of 575 K, the resulting solid blue line concurs with experiment. NaBr had a bigger divergence from experimental values than NaI so its resulting dispersion-forces component was found at 865 K. Sodium nitrate on the other hand behaves quite differently from the other sodium salts as can be seen in Figure 4.8.

It was expected for the mean activity coefficients to decrease at low molalities and after a certain concentration to increase due to reasons such as the increasing fraction of molecules surrounding ions which become significant and also the increase in ion pairing by increasing the molality (concentration of salt) hence increasing the activity effects. Also the water activity is expected to decrease at high molalities giving way for the increase of the activity coefficients. However the shape of the sodium nitrate curve is quite different than these predictions and with a dispersion-forces component of 1700 a better fit with the experimental data was achieved.

Figure 4.7: NaCl/water figure.
Figure 4.8: Various sodium salts tested. Note that the dotted lines are the experimental data and the solid lines come from the model’s predictions. Model data on all salts presented have been adjusted to account for dispersion apart from NaNO$_3$. 
4.4.2.2 The nitrate cation $\text{NO}_3^-$ and other univalent electrolytes

It was thought best to try other nitrate salts just to see if the description of this anion is accurate enough (less than 15% deviation from the experimental data) and can be used in general for any nitrate salt. Model runs on lithium and potassium nitrate were performed with good results as can be seen in Figure 4.9 below. Also since the input data for lithium and potassium are now known, it seemed reasonable to test lithium chloride and potassium bromide which are shown in Figure 4.10.

**Figure 4.9:** a) is $\text{KNO}_3$ and b) is $\text{LiNO}_3$ figure with water. They were done to further test our nitrate model.
It is worth noting that for the lithium ion, the square-well range value had to change from 1.2 (as with all ions) to 1.75. The model works far more accurately with this value for Li, and as long as it is within the range of 1.2 and 1.8 and the same value is used for all lithium compounds it shouldn’t pose any problems whatsoever.

![Diagram of KBr and LiCl figures with water.](image)

**Figure 4.10:** KBr (a) and LiCl (b) figures with water.
4.4.2.3 Hydronium ion $\text{H}_3\text{O}^+$

The next step after trying various salts and nitrate compounds, was to find an accurate description of the hydronium ion, $\text{H}_3\text{O}^+$, to be able to model nitric acid. It was decided to take on the assumption that the ions present were $\text{H}_3\text{O}^+$ and $\text{NO}_3^-$. A small modification was performed on the code to be able to account for this ion and its involvement with water:

$$N_{\text{H}_2\text{O}} - N_{\text{molesHNO}_3} \times N_A$$

where $N_{\text{H}_2\text{O}}$ is the number of water molecules, $N_{\text{molesHNO}_3}$ is the number of moles of nitric acid and $N_A$ is the Avogadro constant. Then the three parameters had to be specified, $\epsilon$, $\lambda$ and $\sigma$, for the description to be complete. Hence experimental data for HCl were found and by using water’s diameter of 3.036 Å with a $\lambda$ of 1.2, the square-well depth was found to be 750 K.

![Figure 4.11: HCl/water figure](image)

The same parameters were then used to calculate nitric acid’s activity coefficients.
They were found to give a very good description of the experimental data as can be seen in the following figure.

![HNO₃/water figure](image)

**Figure 4.12:** \(\text{HNO}_3\)/water figure

There is a concern about the degree of dissociation of nitric acid in water. Due to common ion effects and the fact that maybe some water molecules will be tied up by the hydrated cations (\(\text{UO}_2^{2+}\)), there might be some acid left undissociated. For the time being it did not affect the results, but it is a concern that will have to be addressed in the future if there will be adding of uranyl nitrate and tri-butyl phosphate in the mixture.

### 4.4.2.4 Vapour pressures and solution densities

With a small addition in the code, vapour pressures and solution densities were calculated for the third phase components which are more important in this study, uranyl nitrate and nitric acid. Unfortunately, finding experimental data to compare was not possible in the course of this study. This however was one of the reasons why they are presented here, because of the scarcity of experimental data on them so that
they can be used when experiments will occur, for comparison. A future use of these data could also be in flowsheet modelling. A software program which implements flowsheet modelling, called gProms[93], has recently been combined with a version of SAFT (gSAFT) where the data from the following plots from Figures 4.13 and 4.14 can be implemented for examining solution densities. Note that for ease of calculations the units for vapour pressure are in kilogram force per square meter and those for density in kilograms per cubic meter.

Figure 4.13: Water vapour pressures figure - vapour pressure units in kilogram force per sq. meter
Chapter 4. Statistical Associating Fluid Theory - electrolytes and uranyl nitrate in aqueous solutions

4.5 Summary

A version of the SAFT approach for molecules formed from spherical segments with attractive potentials of variable range has been presented. Using this, a study on the mean activity coefficients of uranyl nitrate and eight aqueous solutions of single strong electrolytes has been performed. The vapour pressures and densities of aqueous solutions of uranyl nitrate and nitric acid were also investigated.

There is agreement between the calculated data and the experimental ones which shows the adequacy of the SAFT-VRE approach in describing the phase equilibria of these compounds. One of the advantages of this approach is that it can be extended to solutions of mixed salts without further parameter optimisation. The parameters presented in table 4.1 for six ions allow the study of a wide range of single and multiple-salt solutions. Getting thermodynamic data for uranyl nitrate and nitric acid at any concentrations may help improve the understanding of these compounds.

What is achieved in this thesis is benchmarking the behaviour of these molecules in an established solvent extraction process - the SAFT approach could be used to predict the behaviour of these molecules in alternative, advanced solvent extraction procedures.
Still, this present treatment leaves room for improvement. More accurate approximations, for example, than the Restricted Primitive Model (RPM) can be used for the evaluation of the free energy due to the ion-ion interaction.
Chapter 5

Tributyl Phosphate (TBP) in organic diluent

An important family of extractants are the neutral organophosphorous ligands which can bind the cations via their phosphoryl group [94]. Among them the most widely used compound is tributyl phosphate (TBP) [95, 96]. As noted before, the PUREX process is widely used in the nuclear power industry for the extraction of desirable products (namely uranium and plutonium) from spent nuclear fuels [17, 10, 26, 97]. This spent fuel is dissolved in concentrated nitric acid where metal ions can bind with the nitrate ion. This solution is brought to contact with an organic system consisting of tributyl phosphate (TBP) dissolved in odourless kerosene, where the volume fraction of TBP is 30% [95, 98]. Liquid TBP is miscible in organic solvents such as long branched alkanes or chloroform while barely so in water with its solubility being 0.42 grams per litre at room temperature [95] (about 0.003 mol% of TBP). The uranium and plutonium nitrates bind with TBP at the system’s interface (where the oil and water phase meet) to create a non-polar complex which is now allowed to pass through to the organic phase. This helps separating the desired uranium and plutonium complexes from other metals and undesirable fission products which remain in the aqueous nitric acid solution.

In this chapter molecular dynamics simulation results will be presented, of a number of TBP/n-dodecane systems in order to investigate the structure, arrangement and behaviour of TBP in the organic diluent. For the scope of work that this thesis
was set to look into, Molecular Dynamics and Monte Carlo would have had similar results. Over the range of what was planned to be investigated with molecular simulations, one method did not have a significant advantage over the other. It was hence thought more prudent to go with Molecular Dynamics, since there was more knowledge and expertise on this within our work group. It was more accessible for the author of this study to begin with Molecular Dynamics and also less complicated, since trivial questions that arose could be answered by other colleagues in the group with no time lost. The simulations performed were done over a range of temperatures and compositions of TBP in n-dodecane. Odourless kerosene, which is the prevalent diluent used in industry as mentioned in Chapter 2, is a mixture of alkanes but the predominant component is thought to be dodecane. For this reason and for ease of computational calculations, this study will therefore concentrate on the use of linear dodecane (n-dodecane) as a diluent for TBP.

Radial distribution functions between atoms of importance within the tributyl phosphate molecule are also investigated to study the possibility and subsequently the distance within which TBP molecules come together and align. Structure factors (static, not dynamic) are calculated and presented in order to give an insight on how the molecule in question is set in the mixture, i.e. to give some information about the dimensions of aggregates, if any. These quantities can also be measured in neutron and X-ray scattering experiments.
Chapter 5. Tributyl Phosphate (TBP) in organic diluent

5.1 Introduction

Tributyl phosphate consists of a phosphate head group attached through ester bonds to three butyl chains. There are two types of oxygen atom bonded with the phosphorus - the \( sp^2 \) oxygen atom which is attached to the phosphorus through a double bond and the three \( sp^3 \) oxygens single bonded between the alkyl chains and the phosphorus, as shown in Figure 5.1 below.

![Figure 5.1: (a)The structure of the TBP molecule and (b) A single TBP molecule schematic taken from the simulations and visualized with VMD [8].](image)

At room temperature and atmospheric pressure, TBP is a liquid. It has a boiling point of \( 284^\circ \pm 5^\circ C \), a freezing point of about \(- 80^\circ C \) and a room temperature (\( 25^\circ C \)) density of \( 0.9708 \text{ g cm}^{-3} \) [95, 99].

It is the phosphoryl group mainly that gives TBP its extracting power - its oxygen atom forming coordinate links with cations. It holds quite a special place among other metal extractants not only due to its extensive use in the nuclear industry but also due to its other industrial applications such as a catalyst, an antifoaming agent, an antioxidant and as a corrosion inhibitor [95]. A simulation box filled with TBP molecules is shown in Figure 5.2. It is quite remarkable how the TBP - hydrocarbon diluent fits the requirements of nuclear reprocessing because of no precipitations and minimisation of corrosion (at suitable TBP and nitric acid concentrations). However there is a partial degradation (usually to dibutyl phosphate) by hydrolysis and this is the main reason why the solvent needs to be washed after use.
The other ingredient of the organic phase, in which TBP is mixed, is odourless kerosene. This is a mixture of alkanes, primarily consisting of dodecane. In the simulations that will follow linear dodecane (n-dodecane) was used as the organic diluent. This organic diluent is vital to the extraction powers of TBP due to two main reasons. The first one is that it reduces undiluted TBP’s extracting power which if too strong could create difficulties in the completion of the extraction cycle by back-extracting (stripping) the desired metals back to the aqueous phase. For most fuel reprocessing purposes, a 30% by volume TBP in hydrocarbon provides a solvent of suitable extracting strength. The second reason is that it actually improves TBP’s physical properties by shifting its density and viscosity towards those of the diluent itself [95], thus optimising the transfer kinetics and flow properties. Another advantage of dodecane (and other paraffinic hydrocarbons) is its low density and high resistance to oxidation which would probably come from nitric acid. Therefore this normal paraffinic hydrocarbon, usually taken and purified from paraffin petroleum stock and largely consisting of n-dodecane, became the standard for the PUREX process [95, 96].
5.2 Methodology

All the simulations present were performed in Gromacs 4.5.4 and Gromacs 4.6.1 [74]. This simulation package was selected mainly due to its ease of use, the experience our simulation group has on this software and also because of the availability of relevant force fields. The Assisted Model Building with Energy Refinement (AMBER) force field was used [100] and the charges for the TBP atoms were taken from the OPLS (optimised potentials for liquid simulations) developed by Cui et al [101]. The bond length stretching, bond angle bending and dihedral torsion energy and angle parameters for the complete characterization of the TBP molecule are given in the tables 5.1 - 5.3 below. The n-dodecane and the three butyl chains were modelled as united atom beads, using the force field parameters provided by Yang et al [102]. The united atom was preferred rather than an explicit one because the results from using both models are for very similar hydrocarbons [103] and grouping each carbon with its bonded hydrogen atoms to form a united atom saves a significant amount of computational time. Hence the united atom is used not only because of its computational efficiency but also and more importantly because the results provided by this model are in reasonable agreement with available experimental data.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>$K_r$[kcal/(mol Å$^2$)]</th>
<th>$r_{eq}$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS-P</td>
<td>230</td>
<td>1.610</td>
</tr>
<tr>
<td>OS-C</td>
<td>320</td>
<td>1.410</td>
</tr>
<tr>
<td>O2-P</td>
<td>525</td>
<td>1.480</td>
</tr>
<tr>
<td>C-H</td>
<td>340</td>
<td>1.090</td>
</tr>
<tr>
<td>C-C</td>
<td>310</td>
<td>1.526</td>
</tr>
</tbody>
</table>

Here O$_2$ is the oxygen connected to the phosphorus by a double bond, OS is the ester bonded oxygen, P is the phosphorus, H is hydrogen and C are the carbon atoms.
### Table 5.2: Bond angle bending energy and angle parameters

<table>
<thead>
<tr>
<th>Angle type</th>
<th>$K_\theta$ [kcal/(mol deg$^2$)]</th>
<th>$\theta_{eq}$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-OS-P</td>
<td>100</td>
<td>120.5</td>
</tr>
<tr>
<td>OS-P-O2</td>
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<td>108.23</td>
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<tr>
<td>OS-P-OS</td>
<td>45</td>
<td>102.6</td>
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<tr>
<td>OS-C-H</td>
<td>50</td>
<td>109.5</td>
</tr>
<tr>
<td>OS-C-C</td>
<td>50</td>
<td>109.5</td>
</tr>
<tr>
<td>H-C-H</td>
<td>35</td>
<td>109.5</td>
</tr>
<tr>
<td>C-C-H</td>
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<td>109.5</td>
</tr>
<tr>
<td>C-C-C</td>
<td>40</td>
<td>109.5</td>
</tr>
</tbody>
</table>

### Table 5.3: Dihedral torsion energy and angle parameters

<table>
<thead>
<tr>
<th>dihedral type</th>
<th>$V_n$ (kcal mol$^{-1}$), $\gamma_n$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n=1</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
</tr>
<tr>
<td></td>
<td>n=3</td>
</tr>
<tr>
<td>C-OS-P-O2</td>
<td>0</td>
</tr>
<tr>
<td>C-OS P-OS</td>
<td>0</td>
</tr>
<tr>
<td>H-C-OS-P</td>
<td>0</td>
</tr>
<tr>
<td>C-C-OS-P</td>
<td>0</td>
</tr>
<tr>
<td>OS-C-C-H</td>
<td>0.25</td>
</tr>
<tr>
<td>OS-C-C-C</td>
<td>0</td>
</tr>
<tr>
<td>H-C-C-H</td>
<td>0</td>
</tr>
<tr>
<td>C-C-C-H</td>
<td>0</td>
</tr>
<tr>
<td>C-C-C-C</td>
<td>0.2</td>
</tr>
</tbody>
</table>

87
To clarify, the angle bending energy expression that the numbers in Table 5.2 refer to is the cosine of the angle. Also for Table 5.3 to make sense to the reader the expression for the total interaction potential energy is provided although the study will not go in further detail on this[101].

\[ E := \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedrals} \sum_n V_n (1 + \cos(n\varphi - \gamma_n)) + \sum_{a<b} [\epsilon_{ab} (\frac{R_{ab}}{r_{ab}})^{12} - 2\epsilon_{ab} (\frac{R_{ab}}{r_{ab}})^{6} + \frac{C_{q_a q_b}}{r_{ab}}] \]  

(5.1)

With the above data, molecular dynamics simulations were performed for a number of tributyl phosphate - dodecane compositions and temperatures at a constant number of molecules. The very first simulations were carried out for pure tributyl phosphate using the NPT ensemble in a simulation box containing 500 TBP molecules with a cut-off distance of 15 Å [101] for the Lennard-Jones interactions. The molecules were randomly inserted into the simulation box and then the system was energy minimised by using the method of steepest descents, so that the molecule configurations (bond lengths) can be relaxed. Then by using the constant volume and temperature (NVT) ensemble with the Berendsen thermostat [75], the system was left to equilibrate. The final configuration from this NVT run was used to perform a constant pressure and temperature (NPT) ensemble run at 1 atm and 298 K respectively by using the Nosé-Hoover barostat and thermostat[77]. From this run the density of the system was calculated and compared to experimental data where a reasonable agreement was found[96, 99].

Following simulations were performed, at first on small system sizes, with the addition of dodecane. Consisting of a maximum of 40 tributyl phosphate and 140 dodecane molecules, NPT runs were carried out to see how the system interacts and to have an idea of the length scales of the molecules and their intermolecular correlations. Dodecane molecules were emplaced randomly into the simulation box, like the TBP ones. To allow the system to equilibrate, a 1 ns NPT simulation was performed, at 1 bar and 298 K. After equilibration, a 10 ns NVT simulation was performed with a constant number of molecules, pressure and temperature (298 K). The timestep used for all simulations was defined at 0.2 fs.
After this, bigger systems were created, of different tributyl phosphate to dodecane compositions and temperatures as will be shown in the Results section below. All systems were visualised using VMD [8].
5.3 Results and Discussion

5.3.1 Mass density

The simulations for measuring the density of pure TBP and pure dodecane were performed at a constant temperature of 298 K. This was done to further validate the accuracy of the characterisation of the molecules used in these simulations and the results were obtained from a $NPT$ run, after the energy minimisation and a $NVT$ run for equilibration, as described above. The density value found from simulations performed on pure TBP was $0.9755 \text{ g cm}^{-3}$ compared with the experimental value of $0.9708 \text{ cm}^{-3}$ reported previously[96, 99].

5.3.2 30% volume TBP in dodecane at various temperatures

The first set of simulations of tributyl phosphate was done for a range of temperatures (298 K - 800 K). The composition of the mixture, 30% volume of TBP in dodecane, was chosen as it is the composition used in reprocessing plants since it was found to be the more efficient for metal extraction.
Figure 5.3: The first two snapshots of the 30% TBP-dodecane temperature range investigation. The picture on the top is at 298 K and the picture at the bottom at 350K. Dodecane was removed from the simulation box for further clarification. The golden-yellow coloured atoms represent the phosphorus atoms, the red ones are for oxygen atoms and the light green ones for the hydrocarbon chains.
Chapter 5. Tributyl Phosphate (TBP) in organic diluent

Figure 5.4: The picture at the top is at 400 K and the picture at the bottom at 500 K. Dodecane was removed from the simulation box for further clarification.
Figure 5.5: The picture at the top is at 600 K and the picture at the bottom at 800K. Dodecane was removed from the simulation box for further clarification.
Figures 5.3-5.5 show a mixture of TBP in dodecane (30% by volume of TBP in dodecane) under a range of temperatures (from 298 K to 800K). Dodecane was removed from the screenshots for clarity. All simulations were performed under an NPT ensemble for 2 ns. The screenshots were taken at the end of the simulation time and their purpose was to show the effect that change in temperature might or might not have on this kind of mixture. In Figure 5.3 the screenshot on the left was performed under a temperature of 298 K and the one on the right under 350 K. In Figure 5.4 the left screenshot is at 400 K and the right at a temperature of 500 K and lastly in Figure 5.5 the left screenshot is of a simulation run at 600 K and the right one at 800 K.

Unfortunately, as can be seen from these Figures, it is not clear whether temperature has any effect on the mixture of TBP-dodecane. It cannot be observed if the behaviour of TBP molecules acts differently under various temperatures; if for example a filament structure is formed. It seems rather that TBP molecules continue to move freely within the mixture without forming any kind of specific structure. Further simulations were performed in the next section of Chapter 5 where other variables were tested (like TBP concentration in section 5.3.4) in order to further examine the behaviour of TBP molecules.


5.3.3 Radial distribution function

The radial distribution function (RDF) is an example of a pair correlation function which describes how density varies as a function of distance from a reference particle; how, on average, the atoms in the system under investigation are radially packed around each other.

This is a quite effective way to describe the average structure of systems where there is continual movement such as liquids. Due to the fact that a single snapshot of a system at a specific moment in time would provide an instantaneous structure of the atoms and not the whole ‘story’, it is extremely useful to be able to calculate and study the average structure. In more simple terms, the RDF is proportional to the probability of finding an atom/particle/molecule at a distance $r$ from the reference atom/particle/molecule.

The construction of an RDF is made possible by picking a reference atom in the system and determining how many atoms are within a distance of $r$ and $r + dr$ from that atom (see Figure 5.6).

Figure 5.6: A schematic representation of the radial distribution function evaluation.
A snapshot of the system is taken at regular (user defined) time intervals and the number of atoms found in each shell around the reference atom is counted and stored. At the end of the simulation the average number of atoms in each shell is calculated and is then divided by the volume of each shell and the average density of the atoms in the system. The formula is given below in equation 5.1.

\[
g(r) = \frac{n(r)}{4\pi r^2 \rho \Delta r}
\]  

(5.2)

where \( g(r) \) is the radial distribution function, \( n(r) \) is the average number of atoms in a shell of width \( \Delta r \), at a distance of \( r \) from the reference atom with \( \rho \) as the number density \( (= N/V) \).

The radial distribution functions (RDFs) between atoms belonging to different tributyl phosphate molecules were calculated. Notably, the interest lies on the polar head group of TBP and therefore the pair-correlation functions between phosphorus - phosphorus, phosphorus and the two different types of oxygen and also between the sp\(^2\) double bonded oxygens were investigated to help with understanding the coordination and arrangement of these atoms. All simulations were performed at 298K and 1 atm pressure using an NPT ensemble in a simulation box of 6 nm. Table 5.4 shows the number of TBP and dodecane molecules used in the different TBP-dodecane solution concentrations. Graphs are presented in the next page.

**Table 5.4: TBP and dodecane number of molecules (N) in RDF simulations**

<table>
<thead>
<tr>
<th>TBP/dodecane concentration (by % volume)</th>
<th>( N ) TBP</th>
<th>( N ) dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>49</td>
<td>515</td>
</tr>
<tr>
<td>30</td>
<td>146</td>
<td>401</td>
</tr>
<tr>
<td>60</td>
<td>291</td>
<td>229</td>
</tr>
</tbody>
</table>
5.3.3.1 Phosphorus-phosphorus radial distribution function

Figure 5.7: Intermolecular radial distribution function between pairs of phosphorus atoms of two TBP molecules at 1 bar and 298 K in a) 10%, b) 30% and c) 60% TBP/dodecane solution respectively.
5.3.3.2 Phosphorus-sp\(^2\) oxygen (P-O\(^2\)) radial distribution function

**Figure 5.8:** Intermolecular radial distribution function between phosphorus and sp\(^2\) oxygen atoms of two TBP molecules in a) 10\%, b) 30\% and c) 60\% TBP/dodecane solution respectively.
5.3.3.3 Phosphorus-$sp^3$ oxygen (P-OS) radial distribution function

Figure 5.9: Intermolecular radial distribution function between phosphorus and $sp^3$ oxygen atoms of two TBP molecules in a) 10%, b) 30% and c) 60% TBP/dodecane solution respectively.
5.3.3.4 \( \text{sp}^2 \text{ oxygen-sp}^2 \text{ oxygen (O2-O2) radial distribution function} \)

**Figure 5.10:** Intermolecular radial distribution function between two \( \text{sp}^2 \text{ oxygen atoms of two TBP molecules in a) 10\%, b) 30\% and c) 60\% TBP/dodecane solution respectively.} \)
A calculation of radial distribution functions has been done to show the distribution of atoms of interest between two tributyl phosphate molecules and how this is affected by changing the TBP concentration. It is also a quantity that can be checked experimentally with, for example, X-ray neutron scattering[104].

It can be seen, from all the figures, that they follow the same sequence; the radial distribution function peak heights are gradually reduced with increased TBP concentration.

The phosphorus-phosphorus (P-P) radial distribution function (Figure 5.7) shows a broad low-intensity peak starting at around 14 Å with a sharper one at 9.5 Å. The highest, most intense, peak is at 4.5 to 5 Å. Because of the presence of butyl groups, an assumption was made that phosphorus atoms between two different TBP molecules cannot come close to each other from the hydrophobic side. If they do approach each other it would probably be from the phosphorus-sp$^2$ oxygen (P=O) bond side.

The peaks decrease because the coordination number (area under graph), $n(r)$, of phosphorus-phosphorus atoms $\approx 2$ at all TBP-consisting concentrations. Therefore because $g(r)$ is analogous to $n(r) / \rho$ (where $\rho$ is density), as can be seen in Equation 5.1, then the RDF peaks should decrease at increasing TBP concentrations.

Figure 5.8 shows the phosphorus-sp$^2$ oxygen (P-O2) radial distribution function. As shown with the peaks in the P-P radial distribution function, the closest distance that they can get is at 4.5 Å as indicated by the RDF figure. Hence the following assumption was made: since the bond length of P=O is 1.48 Å, a shoulder for the P-O2 RDF was thought to be present at around 3 Å. In point of this assumption, a peak at around 3 Å is indeed present in the figure. The second peak is observed at 6 Å, whereas a third, broader one, is present at around 8 to 8.5 Å. A fourth peak is present in all three configurations, and is the least intense one at around 11.5 Å.

The phosphorus-sp$^3$ oxygen (P-OS) radial distribution function figures give an idea of how the sp$^3$ oxygen atoms distribute themselves around phosphorus, between two
TBP molecules. At larger distances rather than the P=O arrangements, the first peak is observed at 5 Å. A second peak is observed at 9.5 to 10 Å and a third one at 14.5 Å. One would expect that as the P=O groups come close to each other, the single-bonded oxygens (OS), attached to the butyl chains, would remain separated by a large distance. The butyl chains are free to rotate and are thought to fold onto themselves as well, in various arrangements.

Lastly, the sp$^2$-sp$^2$ oxygen (O$_2$-O$_2$) RDFs are calculated and look very similar to the P-P RDFs, with peaks at 5, 10 and 14.5 Å.

From the digest of these observations, one can make the assumption that TBP molecules can self-associate in TBP-dodecane solutions. All neutral organophosphorus compounds exhibit a tendency to self-associate and TBP is expected to follow this trend \[105, 106, 107, 108, 109\].
5.3.4 Tributyl phosphate/dodecane mixture filament formation and structure

The tributyl phosphate/dodecane mixture has been investigated under a series of NPT-MD simulations for various TBP concentrations. This was done in order to strengthen and add to the findings of the previous section, on the RDFs of this mixture. On the next page a series of simulations are presented which were completed in Gromacs v4.6.1 [74] under 1 bar of pressure and a temperature of 298 K using the NPT ensemble for 2 ns, in a simulation box of 6 nm on each side.

As with previous simulations of the bulk organic phase, the molecules of TBP and dodecane were randomly inserted into the simulation box, of originally 12 nm size on each side. This was done in order to ensure no overlapping between molecules. After this, scaling of the box was implemented, by a factor of 0.5, to have a final simulation box of 6 nm. After the scaling, by using the method of steepest descents, the whole system was energy minimised to relax bond lengths and have a starting, random, configuration to begin the simulations with.

The numbers presented in Table 5.5 below were found to accurately represent the system in question under these conditions (1 bar and 298 K). They are compared with other studies which performed similar simulations on various properties of tributyl phosphate [109, 110, 111, 112].

<table>
<thead>
<tr>
<th>TBP/dodecane concentration (by TBP% volume)</th>
<th>N TBP</th>
<th>N dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>24</td>
<td>544</td>
</tr>
<tr>
<td>10</td>
<td>49</td>
<td>515</td>
</tr>
<tr>
<td>30</td>
<td>146</td>
<td>401</td>
</tr>
<tr>
<td>60</td>
<td>291</td>
<td>229</td>
</tr>
<tr>
<td>100</td>
<td>500</td>
<td>0</td>
</tr>
</tbody>
</table>
5.3.4.1 10% TBP in dodecane

Figure 5.11: The general structure of TBP in the organic diluent (dodecane). The figure here represents the 10% TBP by volume in dodecane, where dodecane has been excluded for clarity. The first figure is taken at 95 ps where the red circle shows filament alignment of TBP molecules.
Figure 5.12: Snapshots of TBP in the organic diluent (dodecane) from the same simulation. The figures here represent the 10% TBP by volume in dodecane, in various snapshots throughout a 2 ns NPT simulation where dodecane has been excluded for clarity. Figure 5.11 snapshot is taken at 95 ps whilst on this figure snapshots are taken at 1 and 2 ns respectively where the changing of filament arrangement is shown.
The simulations performed on TBP in organic diluent showed the TBP molecules forming filaments throughout the dodecane solution. In the 2 ns simulations performed, filaments started to form only after 50 to 100 ps and remained throughout the whole of the simulation. After about a quarter of the simulation time (0.5 ns) most of the TBP molecules were a part of filament with only a few moving around in diluent.

The orientation of the TBP molecules is seen to be as follows: the sp\(^2\) oxygen of one TBP molecule comes and sits close to the phosphorus atom of another TBP molecule which in turn has its sp\(^2\) oxygen turned towards the phosphorus atom of the next closest TBP molecule. This sequence can be clearly seen in figure 5.11 and especially in the first simulation snapshot, where it is magnified. The organic branches (butyl chains) on the other hand are seen to be stretched out into the diluent. There are areas where the filaments come together and the structural order of these filaments is lost. An assumption for this is that various adjacent TBP molecules compete for a place close to the phosphorus atom of another TBP molecule to align with, and the filament structure turns into a ‘tangle’ of TBP molecules.

This seems to happen throughout the simulation, after the first filaments are formed, as can be seen in the second and third snapshot of the simulation in figure 5.11. Relatively mobile filaments move around the diluent, forming ‘knots’ and then new filaments are formed, also from the few remaining TBP molecules which were before dangling in dodecane, leaving the ends of the previous filaments to take their place.
Figure 5.13: A 30% TBP by volume in dodecane mixture in a 2 ns NPT simulation run. Dodecane has been removed for clarity. One can see how more distorted the filament structure is now compared to a 10% TBP mixture in Figure 5.11.

It is also worth noting that, in agreement with the RDF data collected, with increasing TBP concentration the number of TBP molecules in filament alignment (and hence the filament length) is decreased. This is considered to be due to the fact that with increasing number of TBP molecules, more filaments can be formed but can also come to contact with one another more easily, creating more nodes. So more filaments can be formed with increasing TBP concentration but they can be disconnected much more easily when they come into contact with one another and also because more TBP molecules are now competing to align. As figure 5.12 shows, there is a more ‘distorted’ image of TBP molecules without the clear filament structure seen in figure 5.11. Although filament structuring can also be seen in this configuration, it is not as consistent and more nodes (areas where filaments meet and lose their lengthy structure) are now present. Simulations were also run in various temperatures other than 298 K (see section 5.3.2), but no clear variation of the overall structure can be seen.
5.3.5 Structure factor $S(q)$

The radial distribution function is directly related, via a Fourier transform, to the structure factor $S(q)$ of the system. This is commonly used for comparison of simulated systems with experimental data taken, for example, from X-ray scattering experiments.

The simulated structure factors for phosphorus atoms, sp$^2$ double-bonded oxygen atoms, sp$^3$ oxygen and of the whole tributyl phosphate molecule were carried out using the software Gromacs v4.6.1 [74]. These calculations were performed on 10%, 30% and 60% by volume of TBP in dodecane solutions. To calculate these, the software implemented the Fourier transform on the radial distribution function [113], which was calculated previously.

\[
S(q) = 1 + \rho \int [g(r) - 1] \exp^{iq \cdot r} dr \\
= 1 + \rho \int [g(r) - 1] \exp^{iqr \cos \theta} r^2 \cos \theta d\theta d\phi \\
= 1 + \rho 4\pi \int_0^\infty [g(r) - 1] (\frac{Snqr}{qr}) r^2 dr
\]

where $\rho$ is the density, $g(r)$ is the radial distribution function and $q$ is the scattering wave vector. $S(q)$ is proportional to the scattering intensity of the particles that have been scattered by a wave-vector $q = q_{\text{initial}} - q_{\text{final}}$. Note that this equation is only applicable to isotropic fluids.
5.3.5.1 Phosphorus atom structure factor $S(q)$

**Figure 5.14:** Structure factor of phosphorus atoms of a TBP molecule in a) 10%, b) 30% and c) 60% TBP/dodecane solution respectively.
5.3.5.2 $sp^2$ oxygen (O2) structure factor $S(q)$

**Figure 5.15:** Structure factor of double-bonded (O2) oxygen atoms of a TBP molecule in a a) 10%, b) 30% and c) 60% TBP/dodecane solution respectively.
5.3.5.3 $sp^3$ oxygen (OS) structure factor $S(q)$

**Figure 5.16:** Structure factor of single-bonded (OS) oxygen atoms of a TBP molecule in a) 10\%, b) 30\% and c) 60\% TBP/dodecane solution respectively.
5.3.5.4 Tributyl phosphate structure factor $S(q)$

![Graph a) 10% TBP in DDC](image)

![Graph b) 30% TBP in DDC](image)

![Graph c) 60% TBP in DDC](image)

**Figure 5.17:** Structure factor of TBP molecules in a) 10%, b) 30% and c) 60% TBP/dodecane solution respectively.
Chapter 5. Tributyl Phosphate (TBP) in organic diluent

The structure factor figures in the previous pages can point the reader to the direction in which the range of the various atom group lengths lie. They can also indicate how the tested atoms, and therefore the TBP molecules come close to each other and align. No numerical smoothing of the data has been applied nor any truncation of data. After discussion with Prof. A.J. Masters it was thought unnecessary to do so because of the results being focused on low $q$; numerical smoothing generally corrects for high $q$.

One has to note however that by looking at the $S(q)$ figures, the graphs should not start at the point of origin i.e. (0, 0). There should not be a value of $q$ that is equal to zero, but instead the starting point should be at a very low $q$ value. Therefore the peak of the first shoulder in the $S(q)$ graphs might not be very reliable because of this fact; instead the peak might be somewhere around that area that the current peak that is shown in the figures is now. This is due to the fact that there are very few values of intensity at low $q$ and the line drawn to join these points might not be as accurate as desired.

On the TBP structure factor figures, if the equation of $L = 2\pi / q_o$ is used, where $q_o$ is the value of the maximum of the first peak in the figure, the value of the length of TBP molecules can be calculated. This can be explained as the length of the filaments of stacking TBP molecules in the TBP/dodecane mixture. The value of $q_o$ from the $S(q)$ figures above is around $1.2 \text{ nm}^{-1}$; incorporating this into the equation above gives an average length of about 5-5.2 Å. Again, this value cannot be considered as extremely accurate due to reasons stated above, that the initial peak is around the area of $1.2 \text{ l/nm}$ but may not be exactly $1.2 \text{ l/nm}$. There is clearly a peak at low $q$ but it could be anywhere between $q = 0$ and $2\pi / L$. 

113
5.3.6 Enthalpy of system

![Enthalpy](image)

**Figure 5.18:** Enthalpy as a function of concentration in \% vol of TBP in dodecane, at 1 bar and 298 K. The red line is a straight line representing the enthalpy of pure components.

The simulations of various TBP concentrations in Gromacs have allowed the calculation of the average enthalpy of the mixture of TBP and dodecane with the software. Taking the average of the total energy of the system over time provides the internal energy of the system. Pressure and volume are known and therefore the enthalpy of the system can be calculated. The units of these calculated enthalpies when taken directly from Gromacs were kJ per mole of simulation box and were of the order of magnitude of $10^4$. To evaluate the data in usual enthalpy units of kJ per mole, the initial numbers were divided by the number of molecules of the simulation box in each TBP concentration. The simulations for Figure 5.17 were performed under the $NPT$ ensemble at 1 bar and 298 K. It has to be noted that the same simulations were also run in the $NVT$ ensemble, where by using the $g$-energy function with Gromacs, the average enthalpy values were recorded. $g$-energy is an in-built algorithm in Gromacs.
which extracts information from the .edr file of the simulation (the file that contains all the energy terms that are saved in a simulation). The output is printed on a .xvg file which can then be used for plotting/analysis. The \textit{NVT} runs produced larger enthalpy values.

The enthalpy of an ideal mixture is also plotted in Figure 5.17 to compare with the TBP/dodecane mixture. For an ideal mixture under constant temperature and pressure, the line joining the enthalpy of pure component A to the enthalpy point of pure component B is a straight line. Given TBP’s nature and behaviour in the systems examined, significant deviation from this line was expected.

Nevertheless the measured enthalpies of TBP/dodecane do not deviate much from the trend exhibited by an ideal solution. There is the possibility of the system needing more time to equilibrate and therefore much longer simulations need to be run for the values to be statistically significant. Still, the values received correspond closely to the ideal solution model and since the TBP/dodecane mixture does not exhibit random mixing, it can be said that it is more proof on the TBP forming structural ordering of some type at most concentrations.

The enthalpies of mixing were attempted to be calculated by using the following equation

\[ \Delta_{\text{mix}}H = H_{x_1,x_2} - x_1H_m(1) - x_2H_m(2) \]  \hfill (5.6)

where \( H_{x_1,x_2} \) are the enthalpy values calculated, and \( x_1H_m(1) \) and \( x_2H_m(2) \) are the enthalpies of pure TBP and pure dodecane respectively. Unfortunately this did not give the desired shape expected nor was it close to values found experimentally in the literature[105], probably due to noise and non negligible error margins in the data received and hence the results are not presented in the study because they will not be of any use.
5.4 Summary

With the use of molecular dynamics simulations with Gromacs[74] and VMD[8] software, various properties of tributyl phosphate - an important extractant and a major component in the PUREX process, have been investigated. The united atom force field (which does not include explicit representation of non-polar hydrogen atoms) alongside the AMBER force field have been successfully tested for the characterisation of the tributyl phosphate and dodecane molecules. The density of TBP has been calculated and was found to be a close match with experimental data and simulations of the extractant with dodecane have been performed at various temperatures.

From the temperature simulations, one can see that TBP molecules tend to come closer together, although the data are not clear enough to support the premise of cluster formation. They did not show any clear alteration to the whole structure. The radial distribution functions and structure factors of various TBP atoms were also investigated and important values for the distance between two TBP molecules in an organic diluent were received. For example, the radial distribution function of two phosphorus atoms of two different TBP molecules can give an idea of how close two molecules can get in the given solution. Also by checking the P-O2 and the O2 - O2 distances, assumptions can be made about the orientation of the packing of approaching TBP molecules; that TBP molecules approach each other from the P=O side rather than from the hydrophobic (butyl-chain) side. Intermolecular electrostatic interactions between the two phosphorus groups might also play a role in this. This was confirmed by the snapshots in Figure 5.11, of a 10% TBP in dodecane simulation where filaments are clearly seen to form with the said TBP orientation.

The data also indicate that with decreasing TBP concentration the peak features of the RDF graphs increase. This makes one think that with increasing concentration (more number of TBP molecules) the TBP stacking is probably disturbed leaving more TBP molecules moving around, coming quickly into a stacking structure which is then disrupted by other TBP molecules. This was the case with other TBP/dodecane simulations performed, where with increasing TBP concentration it was observed that the number of filaments was increasing but their length was decreasing and nodes were formed more easily and in more numbers, disrupting the filament structure. Also more TBP molecules were now members of a node, rather
than a filament, or are seen to be moving near such structures without being part of them. Furthermore to the RDFs, by using the Fourier transform in the Gromacs software, the structure factors of phosphorus, sp$^2$ and sp$^3$ oxygen atoms and of the whole TBP molecule were calculated. The results suggest that TBP-TBP association is present upon dilution by n-dodecane.
Chapter 6

Uranyl nitrate in aqueous nitric acid (UO$_2$(NO$_3$)$_2$/HNO$_3$/H$_2$O) and tributyl phosphate in aqueous nitric acid (TBP/HNO$_3$/H$_2$O) ternary mixtures

Further to the previous chapter, where various TBP characteristics were studied when the molecule comes into contact with an organic diluent, an investigation on the interactions of TBP and uranyl nitrate in aqueous solutions of nitric acid were thought to be of value to the project. Since all these are components of the third phase forming in the PUREX process, it is of high importance to study their interactions and properties so as to give an insight of what is happening when these compounds come into contact with one another in various nitric acid concentrations.

Whilst the molecular dynamics simulations are continued with the addition of aqueous nitric acid as a diluent, the SAFT program has been modified to include a second salt and hence calculate the mean activity coefficients of uranyl nitrate in a ternary mixture, now containing nitric acid.
6.1 Uranyl nitrate in aqueous nitric acid with SAFT

Further to Chapter 4 and the use of Statistical Associating Fluid Theory on determining the mean activity coefficients of single strong electrolyte solutions and aqueous uranyl nitrate, a modification to the code has led to the calculation of mean activity coefficients in ternary mixtures such as uranyl nitrate in nitric acid and water. A mixture such as this was chosen because it was thought important to calculate the chemical potentials of uranyl nitrate, and the density of the solution, by varying the nitric acid concentration. It is important to know any thermodynamic properties of PUREX process compounds in order to enlarge the current knowledge around the process. It will also be interesting to see the effect on the uranyl nitrate’s activity coefficients with the addition of various concentrations of nitric acid in comparison with the results obtained in Chapter 4 for the uranyl nitrate aqueous solution.

6.1.1 Uranyl nitrate in 1-3m aqueous nitric acid

Activity coefficients in ternary mixtures (like this two-salt in aqueous solution mixture) cannot be calculated experimentally but there are equations developed that can calculate these by inputing experimental data (like activity coefficient values) taken from binary mixtures of these salts [114, 115].

To calculate the mean activity coefficient of uranyl nitrate, the activity coefficient values of single ions $\text{UO}_2^{2+}$ and $\text{NO}_3^-$ are recorded. Then, if say the salt is $\text{M}_{n_1}\text{X}_{n_2}$, with cation M charge $z_1$ and anion X charge $z_2$ then

$$n_1z_1 = -n_2z_2$$  \hspace{1cm} (6.1)

and to find the mean activity coefficient of the salt, the following equation will be used[116]

$$\gamma^\pm = (\gamma_1^{n_1}\gamma_2^{n_2})^{1/n}$$  \hspace{1cm} (6.2)

where $\gamma^\pm$ is the mean activity coefficient and $n$ is the sum of stoichiometric coeffici-
cients $n_1$ and $n_2$ of the cation and anion respectively.

Figure 6.1 on the next page shows the mean activity coefficients of uranyl nitrate in a ternary mixture $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$, under three different aqueous nitric acid concentrations (molalities); 1, 2 and 3 m.
6.1.1.1 $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}$

**Figure 6.1:** Uranyl nitrate mean activity coefficients in 1-3 aqueous nitric acid molalities
The uranyl nitrate mean activity coefficients were calculated for a range of 0.05 up to 4 molality of uranyl nitrate in three mixtures. The mixtures also consisted of water and 1, 2 and 3 molality concentrations of nitric acid. The results are presented in figure 6.1 and a distinct difference can be seen from the mean activity coefficients of uranyl nitrate calculated in Chapter 4. The graphs here do not exhibit any minimum and the numbers continue to increase until they reach very high activity coefficient values and have to be considered unreliable at high molalities. A reason for the way the model is behaving at high molalities, by predicting quite high activity coefficient values which seem unreliable, is that it is not very accurate at high concentrations of ternary mixtures. Although the mean spherical approximation (MSA) model gives activity coefficients of single electrolyte solutions with high accuracy up to saturation[117], it is less reliable at high concentrations of mixed electrolyte solutions because of no additional mixing parameters are included.

The matter of the difference in the results of activity coefficients of aqueous uranyl nitrate and uranyl nitrate in aqueous nitric acid can be explained by the presence of nitrate ions in the ternary solution. In the aqueous uranyl nitrate binary solution, the salt is introduced slowly into the mixture whilst in the ternary mixture even before the introduction of the uranyl nitrate, nitric acid is already present in the solution. The presence of nitrate ions will have an affect on the calculation of the activity coefficients of uranyl nitrate since it also contains the same group. So, in a sense, the mean activity coefficients figures can be seen like the figures of the binary mixture, but at an already initial salt concentration present. Hence their graphs will be expected to start at some point further than the minimum present in the binary mixture figures.

Data presented in Figure 6.2 were calculated by starting off the model with no nitric acid present. As explained in the paragraph above, because this is now a ternary mixture and not a binary one, when the program tries to calculate the presence of nitrate ions in order to calculate the mean activity coefficients of uranyl nitrate it also inadvertently reads in the nitrate ions of the nitric acid already present. Therefore the initial values calculated for the mean activity coefficients of uranyl nitrate will not be as accurate and will exceed the numerical values that the program is expected to give. Hence it was though logical to start off the model with no nitric acid present so as to see if the model would behave as expected, presenting a minimum like in the binary...
mixtures. Although it might not be clear in Figure 6.2, the first data point was taken at a zero nitric acid molality and at a very small uranyl nitrate molality. From the second data point and onwards, the molality of uranyl nitrate was slowly increased in a now 1 molal HNO$_3$/H$_2$O solution. The first value of the mean activity coefficient is almost unity (0.99411) when a minute quantity of uranyl nitrate is introduced in the mixture ($1 \times 10^{-6}$ mol/kg). Then from the second reading onwards, where the nitric acid concentration rises from zero to a molality of 1, the model starts behaving as in figure 6.1 where the calculated mean activity coefficients are always increasing.

**Figure 6.2:** Uranyl nitrate mean activity coefficients from molalities of $1 \times 10^6$ to 1 mol/kg in aqueous nitric acid of molality 1 mol/kg. The starting value is at zero HNO$_3$ molality. The same trend is also observed in the calculations of uranyl nitrate mean activity coefficients in mixtures of 2 and 3 $m$ of nitric acid.
6.1.1.2 \( \text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O} \) solution densities

As can be seen from Figure 6.3 the density of the solution increases with increasing nitric acid concentration, as expected. The quantities calculated could be a good indicator for the validity of the model, when compared to experimental measurements of density which will be made for the same system. As noted before, in section 4.4.2.4, the scarcity of experimental data available for these systems did not allow for the comparison between model and experiment. However these data may be useful in the sense that they can be used in flowsheet modelling or can provide a good indication for future experiments on similar mixtures. A software program which implements flowsheet modelling, gProms[93], combined with a version of SAFT (gSAFT) can use the data from these plots for examining solution densities in ternary mixtures.
6.1.2 Suggestions for comparison with SAFT model

In the absence of any experimental data to compare the accuracy of SAFT for the \(\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}\) ternary mixture, it might be useful if it can be compared with a different activity coefficient model. One such model is the Pitzer’s model\[56, 57\]. It can provide activities and enthalpies provided that the variation of parameters with temperature are known. Pitzer’s ternary interaction parameters can be found by experiment and then inputed into the model to calculate activity coefficients. Enthalpy of mixing data at several temperatures in aqueous electrolyte solutions allow the determination of the variation of the Pitzer’s parameters with respect to temperature.

Unfortunately it was not achievable in this thesis, to compare SAFT with Pitzer’s model due to lack of ternary parameters needed in the Pitzer’s equations to calculate the activity coefficients for the \(\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O}\) ternary mixture.

Extended Debye-Hückel model

An extension of the initial Debye-Hückel model (mentioned in sections 3.1 and 4.2.1) has improved the model’s concentration range. By taking into consideration the size of the ions, the equation for an ion \(i\) of charge \(z_i\) now becomes\[118\]

\[
-\log_{10}\gamma_i = \frac{A \sqrt{I_m} z_i}{1 + B a_i \sqrt{I_m}} + c_i I_m
\]  

(6.3)

where \(\gamma_i\) is the activity coefficient, \(I_m\) is the ionic strength and \(a_i\) is the size of the ions. The quantities \(A\) and \(B\) can be found from the following equations

\[
A = 1.82483 \times 10^6 \rho_o^{0.5} (\epsilon_o T)^{-1.5}
\]  

(6.4)

\[
B = 50.2916 \rho_o^{0.5} (\epsilon_o T)^{-0.5}
\]  

(6.5)

where \(\rho_o\) is the density (g/cm\(^3\)), \(\epsilon_o\) is the dielectric constant of pure water and \(T\)
is the temperature (K). The ionic parameter $c_i$ depends on composition of medium and temperature (as $A$ and $B$) but it also depends on the nature of the $i$ species. Frequently the term in $c_i$ is neglected.

With this improvement, the extended Debye-Hückel model can now predict activity coefficients up to $I=0.1$ mol/kg in contrast with its predecessor, which would only accurately calculate activity coefficients in solutions of ionic strength up to $I=0.005$ mol/kg[118].

A reason why the extended Debye-Hückel model might not be as accurate as SAFT is because of the ion size, $a_i$. It is introduced as the “distance of closest approach” which essentially means that it is the sum of the ions effective radii in solution. It is implicitly assumed that $a_i$ is the same for all pairs of ions, which means that they are all taken as spheres of diameter $a_i$. This is a rather drastic approach, especially when involving electrolytes where the sizes of the ions differ considerably. It is quite important for the accuracy of the model’s predictions, to describe the size of the ions befittingly and have an accurate description of the dielectric constant[119].

There has been an attempt to compare SAFT and the extended Debye-Hückel model in this study for molalities up to 0.1-0.2 mol/kg, but the results were erroneous and not presentable. Therefore it was not possible to perform a comparison between them. It would have been interesting to see how close the Debye-Hückel model comes to the more advanced SAFT method. It is proposed to test this (and perhaps alongside a Pitzer model comparison as well) in the Future work section of Chapter 7.
6.2 Tributyl phosphate/nitric acid/water and tributyl phosphate/nitric acid/dodecane/water mixtures

6.2.1 TBP/HNO$_3$/H$_2$O mixture

The TBP/HNO$_3$/H$_2$O mixture was investigated with molecular dynamics simulations with Gromacs v4.6.1[74], under various nitric acid concentrations. This was done under 1 bar of pressure and a temperature of 298 K. The simulation was run for 2 ns with a timestep of 0.2 fs. Each simulation was initially populated with all the molecules inserted randomly and allowed to distribute inside the simulation box. TBP has been simulated using charges[101] as in Chapter 5 and nitric acid using charges from Baaden et al.[110]

<table>
<thead>
<tr>
<th>Nitric acid concentration (Molarity)</th>
<th>$N$ TBP</th>
<th>$N$ HNO$_3$</th>
<th>$N$ H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M</td>
<td>72</td>
<td>51</td>
<td>950</td>
</tr>
<tr>
<td>10M</td>
<td>72</td>
<td>136</td>
<td>754</td>
</tr>
<tr>
<td>16M</td>
<td>72</td>
<td>184</td>
<td>640</td>
</tr>
</tbody>
</table>

Figure 6.4 in the following page provides the simulation screenshots of a TBP/HNO$_3$/H$_2$O mixture after a 2 ns NPT run. Screenshots were taken at the end of the simulation. As stated in Table 6.1 above, the three screenshots have the same number of TBP molecules but each is run at a different nitric acid concentration (3, 10 and 16 M respectively, from top left to right). Discussion on these simulations is on the page following Figure 6.4.
Figure 6.4: Simulation screenshots of a TBP/HNO$_3$/H$_2$O mixture after an NPT run for 2 ns. The TBP molecule number is left constant (72) whilst the nitric acid concentration is varied from 3 M to 10 M to 16 M (from top left to right respectively). The bigger molecules are TBP where the green color represents the butyl chains. The red colour is for the oxygen molecules and the blue is for the nitrogen. Hydrogen is removed from the figure (for a more clear image). Nitric acid is red and blue and water molecules are red.
The simulations shown in Figure 6.4 represent 72 TBP molecules in a variety of aqueous nitric acid concentrations (molarities of 3, 10 and 16 M). As can be seen from the figures above each system is clearly phase separated, with the nitric acid distributed throughout the TBP molecules.

At 3 M the overwhelming majority of nitric acid molecules appear to be located close to the P=O group of the TBP molecules, many of them possibly forming hydrogen bonds. The TBP/water interface is very well defined and no nitric acid molecules seem to have migrated towards water molecules.

At 10 M the TBP/water interface is less well defined and one can see that a small number of water molecules have moved into the TBP phase. Similarly a few nitric acid molecules can be seen in the water phase. Note that at this concentration, the nitric acid molecules (136 in number) are in excess of the TBP molecules. Again though, as in the 3 M figure, the TBP molecules seem to be surrounded by water molecules.

At the 16 M simulation there is a significant amount of water molecules present in the TBP phase. The nitric acid molecules apart from coming into contact with TBP, now seem to be everywhere in the mixture, moving alongside water and TBP molecules. The structure of the mixture is quite abstract which comes into contrast with the layering seen in the simulations with lower nitric acid concentration.
With regards to the previous simulations performed with TBP and dodecane molecules, now it can be observed that there is no structural order to the TBP at any nitric acid concentration. No filaments or any other ordered structure can be seen to form with TBP in the absence of dodecane from the solution. The following screenshots in Figure 6.5 show the same simulations as in Figure 6.4, but with only TBP present to show the above observation.

**Figure 6.5:** Simulation screenshots of a TBP/HNO$_3$/H$_2$O mixture after an NPT run for 2 ns at 1 bar and 298 K, taken at the end of the simulation. The screenshots are of 3, 10 and 16 M of nitric acid respectively. Only TBP molecules are shown for clarity. No clear TBP structure pattern can be seen in the absence of dodecane.
6.2.2 TBP/HNO₃/C₁₂H₂₆/H₂O system

With the same test parameters as with the TBP/HNO₃/H₂O mixture, a mixture of TBP/HNO₃/C₁₂H₂₆/H₂O was also investigated with NPT-MD simulations in order to see how the addition of dodecane affects the solution, particularly TBP and nitric acid. The molecule numbers used were set up in order to try and simulate the concentrations of third phase.

<table>
<thead>
<tr>
<th>N</th>
<th>TBP</th>
<th>N HNO₃</th>
<th>N C₁₂H₂₆</th>
<th>N H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>551</td>
<td>411</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

Water molecules were described as flexible, using the single point charge model Transferable Intermolecular Potential with 3 Point charges (TIP3P)[112].
Figure 6.6: MD simulation of the TBP/HNO$_3$/C$_{12}$H$_{26}$/H$_2$O system. Number of molecules in system is given in Table 6.2. The system was run for 2 ns with a 2 fs timestep at 1 bar and 298 K. The size of the box was 6 nm per side. The bigger molecules are TBP where the green colour represents the butyl chains. The all-green molecules are dodecane, the red colour is for the oxygen molecules and the blue is for the nitrogen. Nitric acid is red and blue and water molecules are red.
Chapter 6. Uranyl nitrate in aqueous nitric acid
\((\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3/\text{H}_2\text{O})\) and tributyl phosphate in aqueous nitric acid \((\text{TBP}/\text{HNO}_3/\text{H}_2\text{O})\) ternary mixtures

Figure 6.7: Same simulation as in Figure 6.6 but with only TBP molecules shown for clarity.

Figure 6.8: Same simulation as in Figure 6.6 but with only HNO\(_3\) molecules shown for clarity. Note how the HNO\(_3\) molecules follow the same pattern in the mixture as with TBP above.
The chain-like structures formed by TBP seem to persist in the simulations. Just like in Chapter 5, where TBP/dodecane mixtures were simulated, the extractant seems to insist on forming these filament-like structures throughout the simulation albeit at a lesser extend. This might be due to the presence of nitric acid which seems to hinder the head-to-tail stacking of the TBP molecules, one of the reasons being that it forms hydrogen bonds with TBP. It can be noticed from Figures 6.7 and 6.8 that both these molecules follow very similar pathways in the mixture. Both TBP and HNO₃ seem to be around the same area in the simulation box at any given snapshot which led to the conceptualisation of the idea that the polar phosphorus group of TBP has some kind of interaction with the nitric acid.

One can also see, after visually examining various timesteps in the 2 ns simulation, that nitric acid can also move around within the mixture leading to the suggestion that it can move along the TBP chain-like structuring.

The nitric acid often seems to be in contact with dodecane molecules. A test simulation with only dodecane and nitric acid showed complete separation of the two in the mixture/simulation box which leads to the belief that the charges and generally the simulation parameters used were not the cause of this.
RDFs of phosphorus and nitrogen in the TBP/HNO$_3$/C$_{12}$H$_{26}$/H$_2$O system

**Figure 6.9:** Intermolecular radial distribution function between a phosphorus atom of TBP and a nitrogen atom of a nitric acid molecule in a TBP/HNO$_3$/C$_{12}$H$_{26}$/H$_2$O system. Number of molecules in system is given in Table 6.2.

**Figure 6.10:** Intermolecular radial distribution function between a nitrogen atom of nitric acid and the oxygen atom of the P=O group of a TBP molecule in a TBP/HNO$_3$/C$_{12}$H$_{26}$/H$_2$O system.
The RDFs show that there is a strong correlation between the nitrogen in the nitric acid and the phosphorus and oxygen in TBP molecules. This reinforces the observation made with the simulation results, where nitric acid was said to frustrate the TBP molecules and their filament-stacking structuring by trying to interact and to create hydrogen bonds with the P=O group.
6.3 Summary

A lightly-modified version of the SAFT-VRE equations of state has allowed for the calculations of mean ionic activity coefficients and solution densities in ternary mixtures. The calculated data do not exhibit the same initial trend with the activity coefficient data from binary mixtures and this is thought to be because of the presence of a second salt in the system before the presence of the compound in question, uranyl nitrate in this case.

Molecular dynamics simulations continued on the footsteps of Chapter 5 by adding more third phase components alongside TBP, the PUREX solvent extractant. They have shown that TBP does not continue to form the filament-like structuring when dodecane is not present (as in the TBP/HNO$_3$/H$_2$O system). Another conclusion from the results is that TBP filaments remain throughout the third phase concentration, although at a much lesser extent than in the TBP/dodecane mixtures. This points the finger towards nitric acid and its interactions with TBP. In the simulation screenshots and also in the calculated radial distribution functions it can be seen that nitric acid clearly has some form of interaction with the P=O group of TBP, thus hindering its preferred orientation towards the polar head (P=O) of an adjacent TBP molecule.
Chapter 7

Discussion

This study was set to explore various components and their interactions, which are consisting the third phase, a major issue in the PUREX process of recycling spent nuclear fuel, through the use of computational methods. In doing so, a gap in knowledge was identified; that the thermodynamic data for third phase components were scarce and also that the behaviour of the solvent extractant in the process, tributyl phosphate, is not fully understood albeit that in recent years more studies were conducted on the matter.

In this chapter the computational work and the conclusions drawn from it will be summarised. Furthermore, the limitations experienced during this project will be discussed along with suggested future work to expand upon the material presented.
7.1 Conclusions

SAFT and electrolyte solutions

Most of the ionic solutions studied are relatively new compounds and as a result there are not enough experimental data on their thermodynamic properties, such as vapour pressures, densities and activity coefficients in mixtures. Therefore prediction of these values would be essential and useful for engineering applications. The mean ionic activity coefficient is also the most common data type used in the description of the electrolyte solution behaviour.

In this study, the electrolyte SAFT-VRE has been applied to describe thermodynamic properties of aqueous ionic solutions. In the first step, it has been applied to single strong electrolyte solutions and the model responded positively by calculating the mean ionic activity coefficients of eight aqueous ionic solutions, providing very good agreement with experimental data. It was also tested with divalent salts such as calcium nitrate and it corresponded adequately. After composing a proper model and parameters for uranyl and nitrate ions, we have calculated the mean ionic activity coefficients, vapour pressures and densities of uranyl nitrate in aqueous solution. Our model parameters for nitrate allowed us to also calculate the same properties for nitric acid, another important component of the third phase.

Furthermore, the same properties were calculated for the ternary mixture of uranyl nitrate, nitric acid and water, hence providing a reliable model for activity calculation of these components without the need of further parameter testing. This model could also be used in calculating mean ionic activity coefficients, vapour pressures and densities of solution of a two-salt mixture under the same conditions (1 bar and 298 K).
Tributyl phosphate behaviour

With the use of molecular dynamics simulations and the Gromacs[74] v4.5.4 and v4.6.1 software we were able to replicate various TBP-consisting systems for examination. Our findings have shown that TBP has the tendency to self-assemble in filaments, the length and number of TBP molecules within to be dependant of the TBP concentration in the mixture. TBP, as well as other organophosphorus compounds was theorised to be able to self-associate[105, 106, 107, 108, 109] and through our simulations we have found that this is the case, as long as an organic diluent is present. The preferred orientation of TBP in an organic mixture was seen to be as follows: the sp\(^2\) oxygen of one TBP molecule attaches via intermolecular forces to the phosphorus atom of another TBP molecule which in turn has its sp\(^2\) oxygen turned towards the phosphorus atom of the next closest TBP molecule. Also from our temperature-range simulations this was not found to be altered, although not seen as clear. These filaments are found to be more distinct and longer in low TBP concentrations (best results at 10-20% by vol of TBP in dodecane), whereas at higher TBP concentrations the filaments are persistent throughout the system but can break off more easily and are shorter (although more in number). The calculation of radial distribution functions and of structure factors have indicated the presence of aggregates in these systems, hence reinforcing our position (through our findings) that TBP forms aggregates.

Further analysis on the system was performed, first by adding nitric acid and water and removing dodecane. The filament formation of TBP cannot be seen now which leads to the conclusion that without an organic diluent, TBP cannot move as freely in the mixture and thus cannot form these filament structures. Adding back the dodecane into the system and some filament formation can be seen although not as evident as with the TBP/dodecane systems. Through our findings we believe that the main reason for this is the presence of nitric acid into the mixture. In the simulation screenshots it can be seen that nitric acid clearly has some form of interaction with the P=O group of TBP, thus hindering its preferred orientation towards the polar head (P=O) of an adjacent TBP molecule. The calculated RDFs for the phosphorus - nitrogen and nitrogen - (O=P) show that there is a strong correlation between the nitrogen in the nitric acid and the phosphorus and oxygen in TBP molecules. This reinforces the observation made with the simulation results, where nitric acid was said to frustrate the TBP molecules and their filament-stacking structuring by trying...
to interact and to create hydrogen bonds with the P=O group.

7.2 Limitations and Future work

On SAFT

If no ion-ion association is considered, because of the assumption of full dissociation of strong electrolytes in solution, better calculated results on mean ionic activity coefficients, liquid densities and water activities are obtained[120]. Also, the programming implementation of such models becomes easier and the computational time is reduced. However, preliminary tests and simulations in this study, as well as studies in the literature [5, 120, 121] have shown that this exclusion of ion-pairing leads to unsatisfactory and unreliable mean ionic activity coefficient calculations when higher temperatures (>298 K) are used. This effect is more obvious at higher salt concentrations (>2.5-3 m) especially in ternary mixtures.

Also, for ternary mixtures, the mean spherical approximation (MSA) model can be improved because it lacks accuracy of predicting mean ionic activity coefficients at high molalities[117]. Due to the lack of experimental data, it might be proven useful if a comparison is done between the SAFT model for ternary mixtures and the extended Debye-Hückel model, or the Pitzer’s model, at low molalities, in search of an indication of how succesful SAFT is compared to competing models.

On molecular dynamics simulations and TBP

An analysis of the hydrogen bonds or further investigation by using different techniques, on the structural properties and internal organisation of TBP and other organophosphorus compounds might reveal more on the behaviour of TBP in organic diluent. Another matter for consideration is the extent of simulation time. While the size of the system used (6nm per side of simulation box) seems sufficient for the number of TBP molecules used, to be able to move freely and unconstricted, the increase of simulation time (more than 2ns, which was the time used for the majority of simulations of this study) might reveal more on the TBP behaviour and movement.
and also on the stability of the solutions tested. One has to consider however that the current set up uses a considerable amount of computational time (around 16-20 hours for the TBP/C_{12}H_{26} systems, depending on the number of molecules and the size of the simulation box, and as long as 6 days for bigger systems with more compounds such as the TBP/HNO_{3}/C_{12}H_{26}/H_{2}O system).

For possible longer term future work that may have a substantial impact on spent nuclear reprocessing, and specifically on the third phase formation, extra simulations can be suggested for further examining these systems. For example, calculation of the inertia tensor and diagonalising it to give eigenvectors and eigenvalues. These can be used to describe the size and shape of the filaments that are observed in this study. From these, one can plot the root mean square radius of gyration as a function of time.

Measuring the shape of the molecular clusters and how that changes with time might also be useful in helping to understand third phase structuring. Also self diffusion coefficients can be measured in order to give some insight on the mobility of species at equilibrium.

There is support in literature that at the water-oil interface of such systems there is an increased concentration of TBP molecules[43, 47, 110, 122, 123]. If these filaments persist, which is what our findings have shown, then this might be a possible pathway for the transport of uranium and plutonium from the aqueous phase to the organic phase, without meeting the non-polar dodecane in the process. Further analysis on the transport properties of TBP is suggested, where with simulations of said systems this premise can be examined.
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