Computer Simulation Study of Third Phase Formation in a Nuclear Extraction Process

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<td>BAR</td>
<td>Bennett Acceptance Ratio</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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<td>FTIR</td>
<td>Fourier Transformed Infrared</td>
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<td>GEMC</td>
<td>Gibbs Ensemble Monte Carlo</td>
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<td>GROMACS</td>
<td>GROningen MAchine for Chemical Simulations</td>
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<td>Limiting Organic Concentration</td>
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<td>PUREX</td>
<td>Plutonium Uranium Reduction EXtraction</td>
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<td>Small-Angle Neutron Scattering</td>
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<td>SAXS</td>
<td>Small-Angle X-ray Scattering</td>
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<td>TBP</td>
<td>Tri-\textit{n}-Butyl Phosphate</td>
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Abstract

The University of Manchester


Third phase formation is an undesirable phenomenon during the PUREX process, which is a continuous liquid-liquid extraction approach for the reprocessing of uranium and plutonium from spent nuclear fuel. When third phase formation occurs, the organic extraction solution splits into two layers. The light upper layer, which is commonly named the light organic phase, contains a lower concentration of metal ions, tri-\textit{n}-butyl phosphate (TBP) and nitric acids but is rich in the organic diluent. The heavy lower layer, which is commonly named the third phase, contains high concentrations of metal ions, TBP and nitric acids. As the third phase contains high concentrations of the uranium and plutonium complexes it can thus cause processing and safety concerns. Therefore, a comprehensive understanding of the mechanism of third phase formation is needed so as to improve the PUREX flowsheet.

To investigate third phase formation through molecular simulations, one should first obtain reliable molecular models. A refined model for TBP, which uses a new set of partial charges generated from our density functional theory calculations, was proposed in this study. To compare its performance with other available TBP models, molecular dynamics simulations were conducted to calculate the thermodynamic properties, transport properties and the microscopic structures of liquid TBP, TBP/water mixtures and TBP/\textit{n}-alkane mixtures. To our knowledge, it is only TBP model that has been validated to show a good prediction of the microscopic structure of systems that consist of both hydrophobic and hydrophilic species.

This thesis also presents evidence that the light-organic/third phase transition in the TBP/\textit{n}-dodecane/HNO\textsubscript{3}/H\textsubscript{2}O systems, which is relevant to the PUREX process, is an unusual transition between two isotropic, bi-continuous micro-emulsion phases. The light-organic/third phase coexistence was first observed using Gibbs Ensemble Monte Carlo (GEMC) simulations and then validated through Gibbs free energy calculations. Snapshots from the simulations as well as the cluster analysis of the light organic and third phases reveal structures akin to bi-continuous micro-emulsion phases, where the polar species reside within a mesh whose surface consists of amphiphilic TBP molecules. The non-polar \textit{n}-dodecane molecules are outside this mesh. The large-scale structural differences between the two phases lie solely in the dimensions of the mesh. To our knowledge, the observation of the light-organic/third phase coexistence through simulation approaches and a phase transition of this nature have not previously been reported.

Finally, this thesis presents evidence that the microscopic structure of the light organic phase of the Zr(IV)/TBP/\textit{n}-octane/HNO\textsubscript{3}/H\textsubscript{2}O system, which is also related to the PUREX process, is different from that of the common hypothesis, where such system is consisted of large ellipsoidal reverse micelles. Snapshots from simulations, hydrogen bonding analysis and cluster analysis showed that the Zr\textsuperscript{4+}, nitrate, TBP and H\textsubscript{2}O form extended aggregated networks. Thus, as above, we observe a bi-continuous structure but this time with embedded local clusters centred around the Zr\textsuperscript{4+} ions. The local clusters were found to consist primarily of Zr(NO\textsubscript{3})\textsubscript{4}.3TBP complexes. This finding provides a new view of the structure of the Zr(IV)/TBP/\textit{n}-octane/HNO\textsubscript{3}/H\textsubscript{2}O system.
Declaration

The University of Manchester

Candidate Name: Junju Mu

Faculty: Science and Engineering

Thesis Title: Computer Simulation Study of Third Phase Formation in a Nuclear Extraction Process

Declaration to be completed by the candidate:

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1 Introduction

1.1 Motivation

It is well known that nuclear waste, which contains high-level radioactive elements, needs to be treated carefully before disposal. The Plutonium Uranium Reduction EXtraction (PUREX) process, which was invented by Anderson and Asprey\textsuperscript{1} in the 1940s, is one of the most commonly used processes in the world to reprocess and recycle the radioactive elements, most importantly uranium and plutonium, from nuclear waste.

The standard PUREX flowsheet involves firstly dissolving the waste nuclear fuel in a nitric acid solution so as to give a nitrate solution of plutonium, uranium, minor actinides and fission products. Secondly, the dissolved species are conditioned to the required uranium concentration, acidity and, in the case of plutonium, valency. Thirdly, the conditioned solution is fed to the liquid-liquid extraction process and mixed extensively with an organic extraction solution. The organic extraction solution consists of tri-\textit{n}-butyl phosphate (TBP) and a hydrocarbon diluent, usually kerosene, which is rich in \textit{n}-dodecane. During the mixing, the TBP molecules selectively form complexes with the metal-nitrate complexes, especially uranyl nitrate and plutonium nitrate, and move back into the bulk organic solution after a short period, achieving the separation of those from the other metals present. Usually more than 99\% of U and Pu are separated from the nitrate solution and extracted into the organic extraction solution during this process. Finally, the extracted uranium and plutonium are converted to storage as solid products through post-processing processes.

The PUREX flowsheet, especially the liquid-liquid extraction process, is not foolproof, as undesirable phenomena, such as the formation of the third phase, may occur during the process. In the liquid-liquid extraction process, third phase formation occurs when the concentration of the metal-nitrate complexes exceeds the solubility limit of the organic phase, resulting in the organic phase splitting into two layers.\textsuperscript{2} The light upper layer, which is commonly named the light organic phase, contains a lower concentration of metal ions, TBP and nitric acids but is rich in the organic diluent. The heavy lower layer, which is commonly named the third phase, contains high concentrations of the metal-nitrate-TBP complexes and nitric acids. As the third phase contains high concentrations of the uranium and plutonium complexes it can thus cause processing and safety concerns such as an increased potential for nuclear criticality or runaway decomposition reactions.\textsuperscript{3} This undesirable phase separation may also cause phase inversion, where the concentration of
polar aqueous molecules exceeds the concentration of organic compounds in the heavy third phase, and create difficulty in the stripping process. Therefore, a comprehensive understanding of the mechanism of third phase formation as well as new flow sheet models for safely improving the efficiency without cause third phase formation are needed. This is because that the procedures of the PUREX process, i.e. analytical monitoring and reaction kinetics control, are dependent on the assumptions of molecular geometries, such as the structure of the molecular aggregates, and intermediates such as the metal complexes. Molecular simulations provide a powerful method for investigating the microscopic structure and thermodynamic properties of the systems that correspond to the PUREX process.

1.2 Research background

1.2.1 Experimental work

The formation of the third phase in PUREX process has long been investigated since the 1950s. Many experiments investigated the effects of different variables, i.e. temperature, concentration of nitric acid, the species of the extractant and diluent, as well as chemical modifiers, on the solubility limitation of the metal-acid complexes in the organic extraction solution, which is usually called the limiting organic concentration (LOC). These experimental studies provided insights into the effects of variables on the formation of the third phase and subsequently helped improve the PUREX flowsheet. Much attention was paid to the mechanism of the third phase formation, such as the speciation of the metal-acid complexes, the role of the molecular species during the extraction and the microscopic structure of the light organic and third phases. This is because that, as mentioned earlier, the procedures of the PUREX process are dependent on the assumptions of molecular geometries and intermediates. Hence, understanding the mechanism of third phase formation is the key to improve the PUREX flowsheet and run the PUREX process more efficiently without the formation of the third phase.

The mechanism of the third phase formation has been widely explored by experiments. The behaviour of TBP and nitric acid in systems that are relevant to PUREX process (PUREX-related systems) was first investigated by Alcock et al. in 1955. They studied the metal-free TBP/kerosene/HNO₃/H₂O systems through experiments. Their most interesting finding was that the nitric acid can be extracted, without the contribution of
metal, by TBP from nitric solution into the organic extraction solution. In addition, they found that both TBP and HNO\(_3\) also have solubility limitation in the organic phase and, the values of these are affected by temperature as well as the concentration of TBP and HNO\(_3\). In 1956, Healy et al.\(^{24}\) carried out electrical conductivity measurements on TBP/kerosene/HNO\(_3\)/H\(_2\)O systems, which contain a variety of metal species including U(VI), Pu(IV), Th(IV) and Zr(IV), and found that the nitrates were extracted by TBP in the neutral, unionised form and were always solvated by a definite number of TBP molecules.

One of the most popular hypotheses on the microscopic structures of the phases is that metal ions, mineral acids, water and TBP aggregate into reverse micelles in both the light organic and third phases. A typical reverse micelle is an aggregate of water and surfactant, where the hydrophobic “tail” regions of the surfactant are in contact with the surrounding solvent and the hydrophilic “head” regions and water molecules are in the centre. In PUREX-related systems, however, reverse micelles are usually regarded as the large aggregates formed by metal ions, nitrates, water and TBP, where the hydrophobic tails of TBP form spherical or ellipsoidal shells that shelter all the ions and polar molecules, such as water and nitrates, in the centre.

In 1990, Osseo-Asare\(^{25,26}\) first proposed the reverse micelle structure to describe the metal-acid-extractant complexes based on an extensive analysis of existing experimental data such as nuclear magnetic resonance (NMR)\(^{27}\), infrared spectroscopy\(^{28}\), vapour pressure osmometry\(^{29}\), liquid-liquid distribution\(^{30}\) and calorimetry\(^{31-33}\). Osseo-Asare suggested that the light organic and third phases are both micro-emulsions with reverse micelles that consist of dozens of molecules. Between 1998 and 1999, Chiarizia et al.\(^{34-36}\) studied the extraction of metal by various P,P-di-alkane-di-phosphonic acids using small-angle neutron scattering (SANS) measurements and reported the formation of large cylindrical aggregates, which may contain dozens of molecules, when gradually increasing the concentration of metal ions in the organic phase. This hypothesis by Osseo-Asare and Chiarizia et al., however, was disputed by Jensen et al.\(^{37}\), who conducted a comprehensive study on the U(VI)/TBP/n-dodecane/HNO\(_3\) system using chemical analysis, SANS and extended X-ray absorption fine structure (EXAFS) measurements. Jensen et al. compared the U(VI)/TBP/n-dodecane/HNO\(_3\) system with the metal-free TBP/n-dodecane/HNO\(_3\) system and, suggested that third phase formation was not caused by the extensive aggregation of the metal-TBP complexes, as the aggregation of the species in the organic phase still occurs upon HNO\(_3\) extraction in the absence of metal, while co-extraction of U(VI) only contributed to a modest additional growth of the aggregation. Jensen also
proposed that, according to the EXAFS data, U(VI) was extracted into the light organic phase as a $\text{UO}_2(\text{NO}_3)_2\cdot2\text{TBP}$ complex from the aqueous solution but in the third phase the complex was instead $\text{UO}_2(\text{NO}_3)_2\cdot2\text{TBP}\cdot\text{HNO}_3$. These complexes are small clusters rather than large reverse micelles. What is more, they thought that the addition of one HNO$_3$ molecule to $\text{UO}_2(\text{NO}_3)_2\cdot2\text{TBP}$ is the key to third phase formation, as the $\text{UO}_2(\text{NO}_3)_2\cdot2\text{TBP}\cdot\text{HNO}_3$ complex may be too polar to exist in the alkane diluent.

Between 2003 and 2004, Chiarizia et al. studied U(VI)/TBP/n-dodecane/HNO$_3$ and Th(IV)/TBP/n-octane/HNO$_3$ systems by fitting to their SANS data using a sticky sphere model, where the potential of the sticky spheres consists of a repulsive hard core and a rectangular attractive well. According to this study, third phase formation results from the attractive interactions among the swollen reverse micelles in the organic phase rather than the increasing size of the aggregates. They also suggested that the attractive potential energy between the polar cores of the small micelles significantly increased when more uranyl nitrate or HNO$_3$ are extracted into the organic phase, thereby giving rise to third phase formation. In the meantime, Nave et al. studied the metal-free TBP/n-dodecane/HNO$_3$ systems using small-angle X-ray scattering (SAXS) measurements and compared the data with the results of the calculations using sticky sphere model. They reported that the calculated results using the sticky sphere model agreed well with SAXS data and thus the aggregates formed by TBP were akin to reverse micelles at low nitric acid content.

The appropriateness of the sticky sphere model, however, was disputed by Motokawa et al., who carried out both SAXS and SANS experiments to study the structure of a TBP/n-octane mixture at different concentrations of TBP. They reported that the sticky sphere model failed to fit the SANS and SAXS data and that the reverse micellar structure based on the sticky sphere model may not be accurate. In addition, they proposed that the TBP molecules forms dimers in their systems where the P=O bonds from TBP are in an anti-parallel arrangement and an ellipsoidal model can be used to represent the TBP dimers. The calculated structure factors using the ellipsoidal model agreed with their SANS data well and, they suggested that the attraction between TBP reverse micelles is not the cause of third phase formation. More recently, evidence from NMR measurements, infrared spectroscopy measurements and molecular dynamics (MD) simulations, which agreed with each other well, indicated that there are no reverse micelles in either the light organic or third phases of the metal-free TBP/n-dodecane/HNO$_3$/H$_2$O systems. This disagrees with the mechanism proposed by Nave et al. and the hypothesis of reverse micellar structure.
in PUREX-related systems. In addition, Ivanov et al. showed experimentally that third phase formation occurs when the initial concentration of nitric acid in the aqueous phase exceeds 14.7 M, regardless of the presence of metal ions. This indicate that the nitric acid and TBP may be the main cause of third phase formation and the third phase in the metal-free system shares great similarity with the PUREX system.

1.2.2 Computer simulation studies

In addition to the experimental studies described above, computational simulation studies were also performed, especially in the last two decades, to investigate the behaviour of molecules in PUREX-related systems. Molecular simulations studies were pioneered by Guilbaud and Wipff\textsuperscript{45,46} who performed MD simulations to study the uranyl/nitrate aqueous systems in the 1990s. Later on, in 2001, Baaden \textit{et al.}\textsuperscript{47} first studied the behaviour of TBP at the water-oil interface through MD simulation method. In their systems, nearly all TBP molecules, along with many HNO\textsubscript{3}, H\textsubscript{2}O and a small amount of chloroform, aggregated at the interfaces. They suggested that this phenomenon was related to the formation of the third phase. However, this may only be an interfacial phenomenon as the total number of TBP molecules simulated, which was at most 60, is quite low and the layer formed by TBP aggregates is too thin to be regarded as a phase. Baaden \textit{et al.}\textsuperscript{48} then studied the formation of metal-nitrate-TBP complexes by simulating the phase separation of uranyl/TBP/oil/HNO\textsubscript{3}/H\textsubscript{2}O systems using MD simulations. Their systems, which contained up to 60 TBP and five UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} complexes, were initially set up in a randomly mixed configuration. The de-mixing processes were then simulated for up to 6 ns. During the de-mixing simulations, they observed the formation of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}:TBP and UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}:2TBP at the interface. However, because of the size of the simulation, all the uranyl nitrates ended up at the interface, leaving none within the bulk organic phase. Hence, further validation is required to reach a convincing conclusion.

Between 2006 and 2007, Bühl \textit{et al.}\textsuperscript{49,50} studied the complexation of some typical uranyl complexes such as [UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{4}]\textsuperscript{2−}, [UO\textsubscript{2}(OH\textsubscript{2})\textsubscript{4}(NO\textsubscript{3})]\textsuperscript{+}, [UO\textsubscript{2}(OH\textsubscript{2})\textsubscript{3}]\textsuperscript{2+}, and [UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}]\textsuperscript{−} in both the gas phase and bulk aqueous solutions using Car-Parrinello MD simulations\textsuperscript{51}. They reported that the solvent can elongate the U−O (nitrite) bond and thus weaken the bonds between uranyl and NO\textsubscript{3}− ligand. In addition, they compared different conformations of the NO\textsubscript{3}− ligand, namely, the mono-dentate and bidentate nitrates. They calculated the U−O (nitrate) bond length and, by calculating the free energy change,
showed that, in aqueous solution, the mono-dentate nitrate is more stable than the bi-dentate nitrate. In addition, between 2009 and 2010, Ye et al.\textsuperscript{52,53} investigated the formation of uranyl complexes at the interface between the aqueous and organic phases using MD simulations. They used united-atom models where the methyl and methylene groups on TBP and \textit{n}-dodecane were treated as single particles. By estimating the interaction energy between different molecular conformations, such as mono-dentate \textit{UO$_2$$^-$NO$_3$}, bidentate \textit{UO$_2$$^-$NO$_3$} and \textit{NO$_3^-$H$_2$O}, they proposed that nitrates are more likely to co-ordinate with uranyl ions in a mono-dentate conformation which had lower energy in the aqueous solution. This was supported by the atomic pair correlation functions, which showed that the coordination number of nitrate oxygen around uranyl ion favours the mono-nitrate conformation.

Later, in 2010, in order to improve the accuracy of their molecular models, Ye et al.\textsuperscript{54} re-parametrised the TBP model by performing quantum mechanics (QM) calculations. They performed Density Functional Theory (DFT)\textsuperscript{55,56} calculations, which used the B3LYP functional\textsuperscript{57-59} and the small-core Stuttgart RECP and associated Stuttgart orbital basis set\textsuperscript{60}, to determine the partial charges on uranyl, nitrate and water and, applied these new charges to their models to investigate the uranyl/TBP/\textit{n}-dodecane/HNO$_3$/H$_2$O systems. Based on their simulation results they reported that the number of NO$_3^-$, TBP and H$_2$O that coordinated with a uranyl ion is always five and, they proposed a possible scenario for the transformation of uranyl complex in the process. Firstly, the five coordinated uranyl complex is extracted into the organic phase in the form \textit{UO$_2$(NO$_3$)$_2$$^-$2TBP$\cdot$H$_2$O} or \textit{UO$_2$(NO$_3$)$_2$$^-$3TBP}. Secondly, the organic phase is a neutral environment and is unfavourable to the mono-dentate conformation of the nitrate. Thus, the two mono-dentate nitrates would finally transform into bidentate nitrates and crowd out the water molecule or the extra TBP. However, according to their figures, most of the uranyl complexes were still at the interface or within the aqueous phase while no uranyl complexes migrated deep into the organic phase. What is more, the authors did not observe the “final” transform of the uranyl, namely, from a five coordinated complex to \textit{UO$_2$(NO$_3$)$_2$$^-$2TBP}. Hence, further validations, especially testing the accuracy of the molecular models that were used, should be carried out to reach a convincing conclusion.

A systematic comparison of the molecular models of TBP was then carried out by Cui et al.\textsuperscript{61} in 2012. They performed MD simulation and compared the performances of two set of Lennard-Jones (LJ) parameters – the Assisted Model Building with Energy Refinement (AMBER)\textsuperscript{62,63} or Optimized Potential for Liquid Simulation (OPLS)\textsuperscript{64,65} force fields, in
combination with two sets of partial charges for the TBP model. One partial charge set calculated using the Modified Neglect of Differential Overlap (MNDO) semi-empirical quantum mechanical methodology, was taken from Baaden et al. and was denoted as the MNDO charge set. The other charge set, which was denoted as the DFT charge set, was obtained by performing DFT calculations using the B3LYP functional and the TZVP basis set. They reported that the electric dipole moment of TBP was overestimated by both the DFT and MNDO charges and that a scaling factor of 70% and 60% should be applied to the DFT and MNDO charges respectively. They then reported that the calculated self-diffusion coefficients of TBP from the models which used the scaled charge sets were closer to the experimental data than that used unscaled charges. However, the best value of the calculated self-diffusion coefficient was still 2.7 times smaller than the experimental value. In addition, the calculated densities of TBP also showed that the TBP models which used the scaled charges were more accurate as compared to experimental results. What is more, by comparing atomic pair correlation functions, they reported that different partial charges had strong effects on the structure of TBP liquid, but different LJ parameters did not. Overall, they suggested that the best TBP model available was the one which used the OPLS form of LJ parameters and 70% scaled DFT partial charges.

The accuracy issue of the molecular models was not restricted to TBP, as Ye et al. reported that, when simulating $n$-dodecane liquid using the OPLS-AA force field at ambient condition through MD, a liquid-to-gel phase transition occurred where the $n$-dodecane liquid slowly turned into a gel-like solid. They proposed that this was caused by the 1-4 intra-molecular forces in the force field, which made the torsional potential of the carbon chains too high and thus over-estimated the stiffness of the carbon chains. They tested different scaling factors for the 1-4 intra-molecular forces and reported that a lower scaling factor resulted in a lower torsional potential for gauche dihedrals. They proposed an $n$-dodecane model which used the original OPLS-AA parameters, but recommended a scaling factor as low as 0 for the 1-4 intra-molecular potential of interaction. With a more reliable $n$-dodecane model, Ye et al. then investigated the extraction of water into a solution of 30% TBP in $n$-dodecane using MD simulations. However, they found that the well tested TBP model, which was recommended by Cui et al., dramatically overestimated the solvation free energy of water in TBP, which caused the water molecules to be almost completely immiscible with TBP molecules. This phenomenon, however, is contrary to experiment which show that water is miscible with TBP up to a molar ratio of 1.05 at ambient conditions. Cui et al. then calculated the solubility of water in TBP using a variety of partial charge sets for TBP and found that a scaling factor of 90% for the DFT
partial charges\textsuperscript{61} was most appropriate for reproducing the solubility of water in TBP as measured by experiment, but at the cost of sacrificing the accuracy of TBP model in an \textit{n}-dodecane diluent.

To guarantee accuracy of the TBP model in both organic diluent and aqueous solution, Benay and Wipff\textsuperscript{71} attempted to use united-atom polarisable force field models\textsuperscript{72} for the molecular models in 2014. Polarisable models, in theory, should be able to catch the electrostatics of the molecules more accurately than non-polarisable force-fields, as they take into account induction effects. However, one should be wary that the polarizability parameters need to be carefully fitted to experimental data in order to achieve an accurate polarisable model. In addition, for the same systems, the computational cost for simulating polarisable models is several times more than for simulating non-polarisable models. By comparing a variety of united-atom TBP models, Benay and Wipff found that the performance of the polarisable models are no better than their corresponding non-polarisable models, as polarization effects reduced the surface activity of TBP molecules although the interfacial behaviour of TBP complexes was not severely affected. Apart from this, it is seen that the densities of pure TBP liquid predicted by all of the TBP models were around 1.03 kg·m\textsuperscript{-1} at ambient condition, which is 6 \% higher than the experimental measured 0.9725 kg·m\textsuperscript{-1} and, is even higher than the density of water.\textsuperscript{73} This is because that the unit-atom models treated methyl and methylene groups on TBP as single particles and omitted the hydrogen atoms. Hence, the structure of the TBP molecules was changed and the density of the TBP liquid was affected.

Later, in 2014, the microscopic structure of TBP aggregates in \textit{n}-alkane solutions was investigated using MD simulations by Leay \textit{et al.}\textsuperscript{74} and Cui \textit{et al.}\textsuperscript{75} Leay used the unscaled DFT charge set\textsuperscript{61} for a TBP model using the OPLS-UA force field\textsuperscript{65} and, observed filament TBP structures in a variety of \textit{n}-alkane diluents at a variety of TBP concentrations. Cui and co-workers, however, used the 70 \% scaled DFT charges\textsuperscript{61} for a TBP model using the OPLS-AA force field\textsuperscript{64} and reported much small TBP clusters. Based on the atom-atom radial distribution functions and angle distribution profiles, Cui proposed that the TBP molecules mainly formed dimers with the two P=O bonds from phosphate groups antiparallel to each other in the \textit{n}-dodecane diluent. Obviously the aggregation behaviour of TBP and the microscopic structure of TBP in \textit{n}-alkane are highly model dependent and molecular models, especially for TBP, should be validated before use.

Our research\textsuperscript{5} showed that all of the TBP models, which were recommended by Baaden \textit{et al.}\textsuperscript{47}, Cui \textit{et al.}\textsuperscript{61,75}, Ye \textit{et al.}\textsuperscript{54,69}, Leay \textit{et al.}\textsuperscript{74}, and Benay and Wipff\textsuperscript{71}, were not able to
reproduce the correct microscopic structure of TBP aggregates in n-dodecane diluent as well as the thermodynamic properties of TBP in both organic and aqueous solutions. Hence, their simulation results and conclusions, which were introduced above, should be treated with caution.

In the last three years, since the start of our study on this project\textsuperscript{76}, researchers have continued to investigate PUREX-related systems using molecular simulation approaches. In 2015, Vo \textit{et al.}\textsuperscript{77} re-parametrised the TBP and \textit{n}-dodecane models and investigated the association behaviour of TBP in \textit{n}-dodecane. They took the non-polarisable all-atom general AMBER force field (GAFF)\textsuperscript{78} force field for TBP and \textit{n}-dodecane and, reparametrized the models by fitting to experimentally measured densities and enthalpies of vaporisation. The fitting was achieved by varying the LJ parameters for the double bond oxygen from TBP and the carbon atoms from \textit{n}-dodecane. They reported that the optimised TBP and \textit{n}-dodecane model can give good predictions of many properties such as density, dipole moment, heat of vaporisation and tagged particle diffusion. In addition to model fitting, their potential of mean force\textsuperscript{79} calculations showed that for two TBP molecules the anti-parallel dimer conformation, where the P=O bonds from TBP were in an anti-parallel arrangement, had the lowest free energy in the TBP/\textit{n}-dodecane mixtures. The dimerisation constant, which corresponded to this conformation, was estimated to be around 2.2 M\textsuperscript{-1} from their MD simulations, while around 65% of TBP molecules in the systems are observed to be monomers. Later, in 2016, Vo. \textit{et al.}\textsuperscript{80,81} corrected their results on dimerisation constant as they claimed that their earlier result was restricted to low TBP concentration in \textit{n}-dodecane. They carried out more extensive investigations on the TBP/\textit{n}-dodecane systems using both MD and Fourier Transformed Infrared (FTIR) spectroscopy methods. They reported that TBP primary formed dimers and trimers in \textit{n}-dodecane diluent and may exist in the form of oligomers at high TBP concentration. In addition, they reported that their calculated dimerisation and trimerisation constants of TBP in \textit{n}-dodecane are 1.54 and 0.56 M\textsuperscript{-1} respectively, which agreed well with their FTIR data. Their results show that the TBP molecules are not likely to form reverse micelles as the average number of TBP in a TBP cluster, which was no greater than 3, is too low to form proper reverse micellar structure.

Servis \textit{et al.}\textsuperscript{82} have recently investigated the self-aggregation of TBP and di-amyl amyl phosphonate (DAAP) in \textit{n}-dodecane and \textit{n}-octane. In their work, they proposed a new optimisation method for the all-atom TBP model, which is to increase the torsional potentials that contain phosphorus atoms such that the carbon tail orientations are then
more extended. The aim of this approach was to fit the calculated dipole moment of TBP to the experimental data. They reported that the optimised TBP model gave accurate predictions of bulk density, heat of vaporisation and dipole moment of TBP. By conducting molecular dynamics simulations using the optimised TBP model, they gave a prediction of the equilibrium constant of TBP polymers in both \( n \)-dodecane and \( n \)-octane. In addition, they reported that the number of TBP in a TBP aggregate can reach up to 7 in both \( n \)-dodecane and \( n \)-octane and, they proposed that such extensive aggregations of TBP may have implications for third phase formation. However, it is noted that their investigation and models were confined within the scope of extractant/\( n \)-alkane solutions, where the effect of polar molecules, such as HNO\(_3\) and H\(_2\)O that play important roles in third phase formation, was not taken into account. In our recent research\(^{44}\), where the HNO\(_3\) and H\(_2\)O molecules that diffused into the organic phase were taken into consideration, the microscopic structure of the aggregations showed significant differences as compared to that in TBP/\( n \)-alkane binary mixtures. Hence, it is still early to correlate the self-aggregation of TBP in organic diluent and the third phase formation in the PUREX process without investigating the roles of mineral acid and H\(_2\)O. This year, Servis et al.\(^{83}\) published their new results on the network analysis in hydrogen bonded clusters in TBP/\( n \)-dodecane/HNO\(_3\)/H\(_2\)O systems. They performed both MD simulations and infrared spectroscopy to investigate the sizes of the hydrogen bonded clusters, which was defined as the number of molecules in a cluster, as well as the detailed species of the clusters. They suggested that hydrogen bonded dimers such as TBP–HNO\(_3\) and TBP–H\(_2\)O as well as small molecular chains such as TBP–HNO\(_3\)–HNO\(_3\), TBP–HNO\(_3\)–H\(_2\)O and TBP–H\(_2\)O–TBP are the most common hydrogen bonded clusters in the TBP/\( n \)-dodecane/HNO\(_3\)/H\(_2\)O systems. However, the system sizes in their simulations were limited to a few thousand atoms in total and the system size dependence in their simulations was not properly checked. What is more, due to the small system sizes they did not observe coexisting light organic and third phases in their simulations. Hence, proper simulation evidence that show the coexisting light organic and third phases and their microscopic structures is yet to be reported.

1.2.3 Summary

To sum up, there are divergent opinions, especially from experimental studies, on the microscopic structures and speciation of metal-acid-extractant complexes in PUREX-related systems. The major problem here is that a SANS or SAXS profile can be
reproduced by several, different structural models. Considerable care is required to arrive at a correct, unique structure. NMR and infrared spectroscopy can help determining the topology of molecules and species of bonds that are formed respectively, but model fitting is still required to obtain the structure of molecule clusters.

Until the start of our study on this project, there was lack of accurate molecular models, especially for TBP for the simulation studies on PUREX-related systems, i.e. the TBP/n-alkane, TBP/n-alkane/HNO₃, uranyl/TBP/n-alkane/HNO₃ systems. Simulation results that were generated using inaccurate molecular models should be treated with caution. In the last two years, although a few accurate and validated TBP models have been developed, proper simulation evidence that shows co-existing light organic and third phases and their microscopic structures are yet to be reported and the mechanism of third phase formation is yet to be revealed.

1.3 Thesis overview and a note on the format

This thesis is presented as an Alternative Format thesis according to the submission guidelines issued by The University of Manchester. Peer reviewed scientific publications have long been the medium of exchange in scientific research, and these have become instantly available globally with the advent of the internet, thereby increasing the pace of scientific discourses. The author believes that the Alternative Format thesis most accurately captures the contribution to the field made by this work.

The thesis consists of two main parts. The first part consists of Chapters 1 and 2. In Chapter 1 the motivation is introduced and relevant research background is reviewed. Chapter 2 introduces the fundamentals of computational molecular simulations and, the details of the computational approaches used throughout the research, including MD and GEMC simulations, are explained.

The second part of this thesis (Chapters 3 to 5) consists of the results and discussions which are written in the form of journal articles. We started our research by re-parametrisng and testing molecular models that are capable of reproducing the microscopic structures of PUREX-related systems. This is because, as reviewed in Section 1.2.2, accurate models are essential in order to investigate the microscopic structure of the light organic and third phases and the mechanism of third phase formation. The details of this work are given in Chapter 3. Using the re-parameterised models we then explored the
co-existence of the light organic and third phases, which correspond to a TBP/n-dodecane/HNO₃/H₂O system, through MD and Gibbs Ensemble Monte Carlo (GEMC) simulations with the guidance of experiments. The microscopic structures of the light organic and third phases as well as possible driving forces of third phase formation of that system were also explored and discussed. The details of this work are given in Chapter 4.

We then turned to a more complicated system that is relevant to the PUREX process, namely, the Zr(IV)/TBP/n-octane/HNO₃/H₂O system. The microscopic structures of the light organic phases at a variety of Zr(IV) concentrations were extensively explored and, the driving forces of the aggregation behaviour of the molecules in that system were discussed. The details of this work are given in Chapter 5.

In Chapter 6, the overall outcome of this study and its contribution to this field is discussed. The research directions that could be pursued in the future are also discussed.

Finally, the description of a few analysis techniques which were used in this study but are not described in detail in Sections 3, 4 and 5, are provided in the Appendices. These include pair correlation function analysis, the calculation of excess free energy, the periodic shear flow method for viscosity calculation and the connectivity matrix method for cluster analysis.

1.4 References


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2 Fundamentals of molecular simulations

2.1 Introduction to molecular simulations

2.1.1 What is a molecular simulation?

Molecular simulation is an approach that mimics the behaviour of a system using physical or mathematical models that represent molecular systems. It is a useful tool to explore and gain new insights of systems at nanometre scale, which is still a challenge for experiments. Molecular simulation was first seen in 1930s where Morrell and Hildebrand\(^1\) used gelatine balls to mimic the packing and movement of the molecules. However, such molecular simulations are slow and inaccurate as the physical models are too coarse to reproduce the actual behaviour of atomic systems. In the early 1950s, electronic computers became partly available for non-military use.\(^2\) This marks the starting point of computational molecular simulations which, based on assumptions, uses mathematical expression to describe the molecular models and molecular interactions. With the advent of modern computers, especially the fast growth of computational power in recent decades, molecular simulations that are performed on computers using molecular models are getting increasingly popular.\(^3\) In the meantime, the molecular models that represent different molecular systems are being continuously developed and optimised.

2.1.2 Why molecular simulation?

It is known from Statistical Mechanics, which is briefly introduced in Section 2.2, that the macroscopic quantities of a system, such as temperature, free energy and viscosity, are directly related to the microscopic motion of the particles in that system.\(^4\) For given microscopic details of a system, i.e. the geometry and the mass of the particles and the interactions between them, molecular simulations can predict the microscopic structures, energies and motions of the particles in that system. While Statistical Mechanics, which is the tool to bridge microscopic quantities and macroscopic quantities, can conveniently convert these predicted microscopic quantities to macroscopic quantities that can be measured from experiments. Hence, molecular simulations, together with statistical mechanics, not only provide a new approach to study the macroscopic quantities and behaviour of interested systems from a microscopic point of view, but also are able to conveniently study the microscopic structure of systems at nanometre scale. What is more, as molecular simulations are usually performed on modern computers, it is a cheaper and
safer alternative approach to experiments that need precise instruments or hazardous chemicals, but at the cost of accuracy due to the assumptions made.

2.2 Statistical mechanics

As mentioned in Section 2.1.2, Statistical Mechanics is the bridge between macroscopic and microscopic quantities. With Statistical Mechanics one can not only predict the behaviour of bulk systems from known microscopic molecular properties but also extract microscopic properties from known bulk behaviour.

2.2.1 Partition function

We consider a simple one-component atomic system which contains \( N \) atoms at a temperature, \( T \), and in a volume \( V \). The system, according to the Boltzmann distribution law, can exist in many possible states, where the probability of observing the system in a particular state, \( i \), is given by

\[
p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}},
\]

where \( p_i \) is the probability of observing state \( i \), \( \beta = 1/(k_B T) \) and \( k_B \) is the Boltzmann constant and, \( E_i \) is the energy of state \( i \). The denominator of Eq. 2.1 is usually called the partition function, \( Q \), and is given by

\[
Q = \sum_i e^{-\beta E_i}.
\]

According to Statistical Mechanics, the thermodynamic state of such a system is defined by the given variables, namely, \( N, V \) and \( T \). Most of other thermodynamic properties of that system, i.e. the density, \( \rho \), pressure, \( P \), or constant volume heat capacity, \( C_V \), can be derived through knowledge of the fundamental equations of thermodynamics or equation of state approaches. For example, the internal energy of the system, \( U \), pressure, \( P \), chemical potential, \( \mu \), and constant volume heat capacity, \( C_V \), are given by Eq. 2.3 to 2.6, respectively.

\[
U = \sum_i p_i E_i = \frac{1}{Q} \sum_i E_i e^{-\beta E_i} = -\left( \frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}
\]
\[ P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \]  
(2.4)

\[ \mu = -k_B T \left( \frac{\partial \ln Q}{\partial N} \right)_{V,T} \]  
(2.5)

\[ C_V = 2k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B T^2 \left( \frac{\partial^2 \ln Q}{\partial T^2} \right)_{N,V} \]  
(2.6)

### 2.2.2 Ensembles

Based on Statistical Mechanics, the macroscopic property of a system is obtained by averaging an infinite number of microscopic configurations of that system while each of the microscopic configurations can exist with a certain probability. In classical Statistical Mechanics, the microscopic configurations a system are usually regarded as the arrangements of positions, \( r \), and momenta, \( p \), of all the atoms in that system. These atomic \( r \) and \( p \) can be thought as the coordinates in a multidimensional space, which is usually called a phase space. For a system that consists of \( N \) atoms, its phase space has \( 6N \) dimensions where the atomic positions and momenta each contribute \( 3N \). Each particular point in a phase space is called a phase point. This corresponds to a particular state of the microscopic system, defined as a micro-state, \( \Gamma \). Each micro-state is a particular configuration of \( r \) and \( p \) of all the atoms in the microscopic system. A collection of \( \Gamma \) in phase space is defined as an ensemble. The micro-states are distributed according to a probability density \( \rho(\Gamma) \), which is determined by the macroscopic thermodynamic state of the system.

In Statistical Mechanics, the macroscopic property \( A_{\text{obs}} \) that is observed experimentally can be assumed to be the time average, \( \langle A \rangle_{\text{time}} \), over a number of instantaneous micro-states, \( \Gamma \), in an equilibrium phase space within a long time interval, \( \tau_{\text{obs}} \), and is given by

\[ A_{\text{obs}} = \langle A \rangle_{\text{time}} = \lim_{\tau_{\text{obs}} \to \infty} \frac{1}{\tau_{\text{obs}}} \int_0^{\tau_{\text{obs}}} A(\Gamma(\tau)) d\tau . \]  
(2.7)

This is of particular important for the molecular simulations, i.e. molecular dynamics (MD), which deal with time evolution of the microscopic systems.

Gibbs suggested the ergodic hypothesis that the time average of the quantity is the same as the ensemble average, \( \langle A \rangle_{\text{ens}} \), of a number of instantaneous micro-states in phase space
that are distributed according to a probability density, $\rho(\Gamma)$, of the micro-states.\(^3\) This is given by

$$A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \int A(\Gamma)\rho(\Gamma)d\Gamma.$$ \hspace{1cm} (2.8)

This is of particular important for the molecular simulations, i.e. Monte Carlo (MC) simulation, which deal with the probability distribution of micro-states of the microscopic systems. The probability distribution of the micro-states is constant in an ensemble at equilibrium.

To sum up, time averaging over micro-states generated by an equilibrium MD, or ensemble averaging over micro-states generated by an equilibrium MC, yields thermodynamic properties. As illustrated in Section 2.2.1, the thermodynamic state of the system is usually defined by a small set of variables such as $NVT$ or $NPT$. Hence, ensemble can be defined from a real life experimental condition with particular rules. This allows each ensemble of states to be connected with a thermodynamic property, which can be calculated as a function of the partition function, $Q$. In molecular simulations, the most commonly used ensembles are listed below:

- The canonical ensemble, which describes a closed system that cannot exchange mass (i.e. number of molecules $N$) or volume $V$ with the outside world, but exchanges energy such that the temperature $T$ of the system is uniform and constant. This ensemble is usually called the $NVT$ ensemble.
- The grand-canonical ensemble, which describes an open system that has constant temperature and volume and can pass energy into and out of the system. Additionally however, a grand-canonical system may pass mass into and out of the system to keep the chemical potential, $\mu$, constant. This ensemble is usually called the $\mu VT$ ensemble.
- The micro-canonical ensemble, which describes an isolated system that the mass, volume and energy of the system are kept constant. This ensemble is usually called the $NVE$ ensemble.
- The isothermal-isobaric ensemble, which is used to describe a system in which the temperature and number of molecules are constant as in the canonical ensemble. However, the important feature of the isothermal-isobaric ensemble is that the pressure of the system is maintained to a constant value by allowing the volume of the system to fluctuate. This ensemble is usually called the $NPT$ ensemble.
In this study, due to need of comparing simulation results to experimental data, the majority of molecular simulations were performed using the NPT ensemble.

2.3 Classical force field and molecular models

Molecules influence each other when they get close. These influences involve attractive and repulsive forces between molecules that have different distance dependences. The intra-molecular and inter-molecular interactions have long been investigated since the introduction of concepts of molecules and atoms. Thus most common theory about the atomic interactions is that atoms have strong repulsion at short distance but have weak attractions at long range.

2.3.1 Classical force field

In this study a classical force field is used, where the following assumptions are made. Firstly, the nuclei and electrons are not explicitly represented. The electron clouds are averaged into point charges on atoms and their effects are represented by specific interactions such as Coulomb interaction. The atoms are represented by spheres and are assumed to represent the smallest level of description of the molecular system. A sphere usually can vary in softness and has a radius and a constant charge. Secondly, the covalent bonds between atoms are assumed to be represented by springs and the springs can vary in stiffness and have equilibrium lengths. Breaking or forming of the springs is not allowed during simulations. Thirdly, the potential energy of a molecular system is assumed to be the sum over all pairs of atoms and depends only on the distance between pairs of atoms. The classical molecular force field, which is based on the assumptions mentioned above, is the mathematical description of the interactions between these spheres. These interactions are usually described by equations and pre-assigned parameters which can be derived from higher level simulations, such as quantum mechanical calculations, or through fitting to experimental data. The benefit of this assumption is that it dramatically reduces the complexity of the simulated system and thus allows for much more particles to be simulated as the same computational cost. However, one has to be wary that these assumptions ignored many effects of the electrons, i.e. polarisability of the molecules and covalency effect of highly charged ions. In addition, as breaking or forming of the covalent bonds is not allowed, there are no chemical reactions such as dissociation.
For a molecular system in a simulation, the sum of all the interactions is defined as the total potential energy, $E_{\text{tot}}$, and consists of a variety of terms. A typical total potential of a molecular system, based on the pairwise additivity assumption mentioned above, may be written as

$$E_{\text{tot}} = E_{\text{str}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{VdW}} + E_{\text{ele}}, \tag{2.9}$$

where $E_{\text{str}}$ is the energy for stretching a covalent bond between two atoms, $E_{\text{bend}}$ is the energy for bending an angle between two covalent bonds which involve three atoms, $E_{\text{tors}}$ is the torsional energy for rotation around a covalent bond which involves four atoms, $E_{\text{VdW}}$ is the Van der Waals energy between atom pairs, and $E_{\text{ele}}$ is the electrostatic energy between atom pairs. Among these five energy terms the first three represent the interactions that involve covalent bonds, which are usually called as bonded potentials. The Van der Waals and electrostatic energies do not involve covalent bonds and thus are called as non-bonded potentials. Note that the $E_{\text{tot}}$ in Eq. 2.9 still ignores many terms, for example, coupling between bond stretch and bond bending.

Due to the nature of the potentials it is obvious that the efficiency of calculating the total potential energy is dominated by the number of non-bonded potentials. This is because that the time required for calculating the bonded potentials increase on the order of $N$, but the time required for the calculation of non-bonded potentials increase on the order of $N^2$. Hence, proper approaches, which increase the efficiency of the calculations of non-bonded potentials, are essential to the molecular simulations. This aspect will be discussed in detail in Section 2.4.

2.3.2 Bonded interactions

In classical molecular simulations, a molecule is regarded as a group of atoms that are connected by covalent bonds. Thus, the bonded potentials, namely, $E_{\text{str}}, E_{\text{bend}}$ and $E_{\text{tors}}$, are classified as the energies that are contributed by bonded interactions. The typical bonded potentials are introduced below.

**Stretching energy**

For an atomic model, the stretching energy is the energy for the extension or compression of the spring that bonds two atoms. The stretching of a covalent bond is shown in Figure 2.1. A typical equation for the stretching energy, $E_{\text{str}}$, is given by
\[ E_{str} = \sum_{\text{bonds}} \frac{K_r}{2} (r_{ij} - r_{eq})^2, \] 

(2.10)

where \( K_r \) is the force constant for stretching or compressing the bond between atoms \( i \) and \( j \), \( r_{ij} \) is the distance between atoms \( i \) and \( j \). At \( r_{ij} = r_{eq} \) the stretching energy is zero.

![Figure 2.1. Stretching of a covalent bond.](image)

**Bending energy**

Typically, for the classical force field, the bending energy between two covalent bonds can be approximated to harmonic potential and is given by

\[ E_{bend} = \sum_{\text{angles}} \frac{K_\theta}{2} (\theta_{ijk} - \theta_{eq})^2, \] 

(2.11)

where \( K_\theta \) is the force constant for bending the bond angle between atoms \( i, j \) and \( k \), \( \theta_{ijk} \) is the bond angle between atoms \( i, j \) and \( k \), and \( \theta_{eq} \) is the equilibrium bond angle. At \( \theta_{ijk} = \theta_{eq} \) the bending energy is zero. The illustration of bond bending is shown in Figure 2.2.

![Figure 2.2. Bending between two covalent bonds.](image)

**Torsional energy**

It is known that, for four adjacent bonded atoms, the central covalent bond can frequently rotate and change the confirmation of the four aligned atoms, i.e. from trans to cis. Figure 2.3 show the torsional angle of four linearly bonded atoms.
For the torsional term, the bond can rotate continuously. Hence, the torsional energy should be a periodic function with a period of $2\pi$. The typical torsional potential is well represented by a Fourier series, given by

$$E_{tor} = \sum_{n} V_n \cos(n\Phi_{ijkl} + \Phi_0),$$ \hspace{1cm} (2.12)

where rotation function, $V_n$ is a constant that determines the energy barrier for the bond rotation, $\Phi_{ijkl}$ is the torsional angle of the four linearly bonded atoms $i, j, k$ and $l$, and $\Phi_0$ is the reference torsional angle, and $n$ is an integer with a minimum value of 1. It is noted here that the torsional potential in trans and gauche conformations are assumed to be the same in Eq. 2.12.

![Figure 2.3. Torsional/dihedral angle of four linearly bonded atoms (in trans form)](image)

2.3.3 Non-bonded interactions

Apart from the bonded interactions introduced in Section 2.3.2, there are also interactions that exist between atom pairs. These interactions are usually, in a classical force field, described by Van der Waals and electrostatic interactions, where the corresponding energies are called Van der Waals and electrostatic potentials, respectively.

**Van der Waals energy**

The Van der Waals interaction describes the sum of repulsive and attractive dispersion interactions between atoms that are not covalently bonded. When two non-bonded atoms are at short distances the Van der Waals interaction exhibits strong repulsion, which mimics the overlap of negatively charged electronic clouds of atoms. At intermediate distances the Van der Waals interaction turns from strong repulsive to mildly attractive and this mimics the electron–electron correlations, i.e. dipole – dipole, dipole – induced dipole and dispersion interactions. The Van der Waals interaction goes from mildly attractive to zero at large distances.
For a classical force field, the most commonly used mathematical expressions to represent Van der Waals potential are the Buckingham potential and the Lennard-Jones (LJ) potential. In this work, the LJ 12-6 potential is used to describe all the energies that correspond to dispersion interactions in our simulated molecular systems. The LJ 12-6 potential, $E_{LJ}$, is given by Eq. 2.13 and its schematic illustration is shown in Figure 2.4.

$$E_{LJ} = \sum_i \sum_j \left[ 4\varepsilon_{ij} \left( \frac{\sigma_{12}^{12}}{r_{ij}^{12}} - \frac{\sigma_{6}^{6}}{r_{ij}^{6}} \right) \right].$$  \hfill (2.13)

In Eq. 2.13, $r_{ij}$ is the distance between atoms $i$ and $j$, $\sigma_{ij}$ is the distance between atoms $i$ and $j$ where the LJ potential is zero, and $\varepsilon_{ij}$ is the minimum of the LJ potential. Typically, for a classical force field, the $\sigma_{ij}$ and $\varepsilon_{ij}$ values for same types of atoms are optimised and provided but, for different types of atoms, the $\sigma_{ij}$ and $\varepsilon_{ij}$ values are usually calculated using mixing rules based on the known $\sigma_{ii}$ and $\varepsilon_{ii}$ values.

Two kinds of mixing rule are commonly used for LJ potentials, namely, the Lorentz-Berthelot rules and the geometric rules. For both of the mixing rules the equation for calculating the mixed $\varepsilon_{ij}$ is the same, which is given by

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}},$$  \hfill (2.14)

![Figure 2.4](image). Schematic illustration of the Lennard-Jones 12-6 potential against atomic distance, which is shown as red solid line. The repulsive and attractive contributions are shown as blue dashed lines. This figure is adapted from Zhang et al.
where \(i\) and \(j\) represents atom types \(i\) and \(j\), respectively.

For the calculation of mixed \(\sigma_{ij}\) the equations used for Lorentz-Berthelot rules and the geometric rules are given by Eq. 2.15 and 2.16, respectively.

\[
\sigma_{ij} = \sigma_{ii} + \sigma_{jj} - \frac{\sigma_{ij}}{2} \quad (2.15)
\]
\[
\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}} \quad (2.16)
\]

In Eq. 2.15 and 2.16, again, \(i\) and \(j\) represents atom types \(i\) and \(j\), respectively.

### Electrostatic energy

The classical force field assumes that the uneven internal distribution of electrons in a molecule is represented by positive or negative partial charges on the atoms. The electrostatic energy corresponds to the interactions between the charged atoms, which are usually takes the form of the law of point-charge interaction by Charles Augustin Coulomb. Hence, the electrostatic potential is given by

\[
E_{ele} = \sum_{i} \sum_{j} \left( \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \right), \quad (2.17)
\]

where \(q_i\) and \(q_j\) are the partial charges on atoms \(i\) and \(j\) respectively, \(\varepsilon_0\) is the vacuum permittivity and \(r_{ij}\) is the distance between atoms \(i\) and \(j\).

Typically, the partial charges on the atoms of a molecule are acquired by fitting to experimental data or more directly from quantum mechanical calculations.

### 2.3.4 Choice of classical force field

In order to perform simulations with satisfactory accuracy it is of vital importance to choose the correct force field. Over the last few decades a large number of classical force fields have been developed. Ideally force fields are designed to be transferable between a number of molecular systems. However, some of the force fields are more suitable for particular systems and states, than others. Hence, it is essential that, for each molecular simulation study, comparison of the performance of the force field should be done at the beginning of the study. Typically, the performance tests include the comparison to the
experimental thermodynamic and kinetic properties, i.e. densities, viscosities, excess energy terms and microscopic structures etc.

The most commonly used force field are listed below:

- Optimised Potentials for Liquid Simulations (OPLS)\textsuperscript{9,10}. This was developed by Jorgensen \textit{et al.} and is continuously being developed\textsuperscript{11-13}. This force field contains both all-atom and united-atom form of parameters and was optimised for biomolecular systems and organic liquids.
- Assisted Model Building with Energy Refinement (AMBER)\textsuperscript{14,15}. This was originally parametrised for biomolecular simulations and has been extended to a wider range of systems through the development of the general AMBER force field (GAFF)\textsuperscript{16}.
- Chemistry at HARvard Molecular Mechanics (CHARMM)\textsuperscript{17}. The total potential function used by CHARMM is the same as AMBER but the detailed parameters used are different. CHARMM is also parametrised for biomolecular simulations and is continuously being developed\textsuperscript{18,19}.
- GROningen MOlecular Simulation (GROMOS)\textsuperscript{20}. This is a united-atom force field aimed at biomolecular simulations and parametrised for proteins. It is also continuously being developed with ongoing improvements\textsuperscript{21,22}.
- Transferable Potentials for Phase Equilibria (TraPPE)\textsuperscript{23-25}. This is aimed at molecular simulations of \textit{n}-alkanes which are the main components in fuels. It is also good at simulating aromatics and compounds that contain sulphur or nitrogen. This force field mainly consists of united-atom models and takes the same functional from that of AMBER.

In this study, as the systems are organic and the major components are small molecules or ions, the OPLS force field is most suitable. However, due to the fact that our systems contain many polar aqueous molecules such as H\textsubscript{2}O and HNO\textsubscript{3}, the OPLS force field models may require re-parametrisation and testing before the investigation. The details of the re-parametrisation and testing work are reported in Chapter 3.

2.4 Improving the efficiency of simulations

As was already mentioned in Section 2.3.1, for a molecular system that contains \textit{N} atoms, the time required for the calculation of non-bonded potentials is proportional to \textit{N}^2. Hence,
to reduce the computational cost of the calculations, various techniques, such as truncating the non-bonded potentials and Fourier transforming the long range Coulombic interactions, are required. In this section, the concept of periodic boundary conditions and approaches, such as those mentioned above, are introduced.

2.4.1 Periodic boundary conditions

In order to perform molecular simulations with satisfactory efficiency the size of the simulated systems are usually no more than thousands of atoms. In rare cases the system sizes can reach up to millions of atoms. Nevertheless, if we assume the simulation boxes are cubic in shape, these system sizes typically corresponds to a box with a side no more than 50 nm in length. Hence, the simulated molecular systems are quite small compared to real bulk systems and, the molecules near the surface of the simulation box will experience different forces compared to the ones in the centre. In other words, for such small molecular systems, the effects of the box boundaries are too strong, so that the behaviour of the system will not be the same as the molecules in bulk. In order to solve this problem, periodic boundary conditions are used, as shown in Figure 2.5.

![Figure 2.5](image_url)

**Figure 2.5.** Schematic 2D representation of the periodic boundary condition and cut-off.

The periodic boundary condition assumes that the simulation box is surrounded by ‘pseudo’ simulation boxes which are clones of the original box. When a molecule leaves the simulation box on one side it will enter the neighbouring ‘pseudo’ box, and thereby re-enter the original simulation box on the opposite side. In addition, the molecules that are
near one side of the simulation box can interact with the nearby molecules in the neighbouring ‘pseudo’ box. By doing so, all the molecules inside the simulation box will behave like molecules in bulk and thus the bulk properties can be estimated using relatively small system sizes. The periodic boundary conditions can work with boxes of many shapes, such as cubic, cuboidal, rhombic dodecahedron or truncated octahedron, but the most commonly used one is the cubic box.

However, one has to be aware of that while the periodic boundary condition helps solve the problem of box boundary effects, it can lead to severe, unphysical effects such as the fact that the molecules in the simulation box can interact with their clones in the neighbouring ‘pseudo’ boxes. In order to solve this problem a minimum image convention is introduced, where for an atom in the simulation box we only consider its interactions with the closest copy of each of the remaining atoms. For convenience, the minimum image convention usually corresponds to a spherical potential cut-off that, if we assume that the simulation box is cubic, has a maximum radius of half of box size. Each atom has same minimum image convention and, for each atom, its interactions with any atoms that are outside the potential cut-off are excluded and regarded as zero. An illustration of the potential cut-off, $r_{cut}$, is shown in Figure 2.5. The minimum image convention and potential cut-off can not only solve the unphysical problem introduced by the periodic boundary condition but also reduce the number of interactions to be calculated, especially when the potential cut-off is small compared with the box sizes.

### 2.4.2 Truncating short-range potential

As mentioned in Section 2.4.1, the combination of periodic boundary conditions and the potential cut-off are extremely useful to simulate the bulk properties of molecule systems and improve the efficiency of the simulations. The potential cut-offs are usually applied for non-bonded potentials, i.e. the LJ and electrostatic potentials. It is known from Eq. 2.13 that the LJ potential decays as $1/r^{12}$ and $-1/r^6$, where $r$ is the distance between two atoms. Hence the LJ potential decays rapidly as $r$ increases and thus can be regarded as a short-range potential. However, from Eq. 2.17 we know that the electrostatic potential decays slowly as $1/r$, so the electrostatic potential is regarded as being a long range potential. Hence, the application of a cut-off for the LJ potential should not seriously affect the behaviour of the atoms that are more than $r_{cut}$ away, but such a cut-off for an electrostatic potential would lead to a poor description of the system. Special approaches must be used
to deal with the problem of truncating long-range electrostatic potentials and this will be introduced in Section 2.4.3.

Figure 2.6. Schematic illustration of the shifted and switched LJ potentials.

Although the use of cut-offs for the short range LJ potential dramatically reduces the number of interactions to be calculated, it can result in energy conservation problems as the LJ force at the cut-off is infinite, leading to numerical errors. This problem, however, can be easily solved by using a potential shift or a potential switch approach.

The potential shift approach is to add a shift function to the LJ potential, $E_{LJ}$, so that the value of the shifted potential at $r_{cut}$ equals zero. The potential switch approach is to multiply the LJ potential by a switch function from $r_{switch}$ to $r_{cut}$ so that $E_{LJ}$ is gradually switched to zero from $r_{switch}$ to $r_{cut}$. In the potential switch approach $r_{switch}$ is the cut-off radius where the switch functions begins. A schematic illustration of the shifted and switched LJ potentials, $E_{LJ}$, is shown in Figure 2.6. There is a finite discontinuity in the force at the cut-off for the potential shift and no discontinuity in the force at all for the potential switch. This helps overcome the numerical problems noted above for a straightforward potential truncation. However, long-range corrections should be applied to compensate for the missing long-range part of the potential in order to calculate the correct potential energy and pressure.\textsuperscript{3}
2.4.3 Treating long-range forces

As mentioned in Section 2.4.3 the long-range electrostatic potential should not be simply truncated at the cut-off without further treatment. In this section, the Ewald summation\(^{26}\) and Particle-Mesh Ewald (PME)\(^{27,28}\) is introduced, which solves the problem raised by the application of a cut-off.

As given by Eq. 2.17, the total electrostatic potential can be written as

\[ E_{ele} = \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \left( \frac{q_i q_j}{r_{ij}} \right) = \frac{1}{8\pi\varepsilon_0} \sum_{i \neq j} \left( \frac{q_i q_j}{r_{ij}} \right), \tag{2.18} \]

where the first form explicitly counts all point charge pairs, while the second form counts all interactions and divides by 2 to compensate for double counting. Ewald\(^{26}\) suggested that, for a charge neutral system, the electrostatic interaction can be transformed by

\[ E_{ele} = \frac{1}{8\pi\varepsilon_0} \left[ \sum_{i \neq j} \left( \frac{q_i q_j \cdot \text{erfc} \left( \frac{1}{2\sqrt{\zeta r_{ij}}} \right)}{r_{ij}} \right) + \sum_{i \neq j} \left( \frac{q_i q_j \cdot \text{erf} \left( \frac{1}{2\sqrt{\zeta r_{ij}}} \right)}{r_{ij}} \right) \right], \tag{2.19} \]

where \(\zeta\) is a parameter that determines the relative weight between the direct space sum and the reciprocal space sum and, \(\text{erf}(x)\) and \(\text{erfc}(x)\) are the error function and the complementary error function respectively, which are given by

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt, \tag{2.20} \]

and

\[ \text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-t^2) dt. \tag{2.21} \]

In other words, the Ewald summation method divides the original problem space (Eq. 2.18), which is the space of the electrostatic point charges, into two separate problem spaces (Eq. 2.19). The first problem space, which corresponds to the first term in Eq. 2.19, is designated as the ‘real’ space which contains the original point charges plus proportional charge distributions that have the same magnitude but with the opposite charge. These proportional charge distributions are centred at the same locations in space as each point charge. The second problem space, which corresponds to the second term in Eq. 2.19, is
designated as the ‘reciprocal’ space which contains only the opposite of the charge distributions from the ‘real’ space. Figure 2.7 illustrates a schematic representation of the original point charge space, the ‘real’ space and the ‘reciprocal’ space, where $q_j$ is the magnitude of point charge $j$. The summation of the ‘real’ and the ‘reciprocal’ spaces yields the original point charge distribution.

To solve the problem in the ‘real’ space one only evaluates the electrostatic interactions between all atoms within each atom’s cut-off radius. However, to solve the problem in the ‘reciprocal’ space one needs to evaluate the electrostatic interactions of the particles in the simulation box with all their clones in an infinite array of periodic replications of the simulation box within an infinite sphere. Here we assume the so-called “tin-foil” boundary conditions, where the infinite sphere is immersed in a perfectly conducting medium and hence the dipole term on the surface of the infinite sphere is zero. The infinite periodic functions should converge rapidly when reciprocal sum is solved in the Fourier domain using fast Fourier transform (FFT). The results is then converted back into ‘real’ space through inverse FFT and summed with the results from the ‘real’ space to yield the electrostatic potential of the original point charge space, namely, the simulation box.

Figure 2.7. Schematic illustration of the original point charge space, the ‘real’ space and the ‘reciprocal’ space, where $q_j$ is the magnitude of point charge $j$.

The PME approach was derived from the Ewald summation approach and, has the same form of charge functions in the ‘real’ space. However, when solving the problem in the ‘reciprocal’ space, PME approach first discretises the original charge space into a 3D mesh,
where the charge functions are interpolated onto the mesh. The 3D mesh is then Fourier transformed into the ‘reciprocal’ space where the electrostatic potential is calculated. The results of the calculation is then transformed into the ‘real’ space using inverse FFT and finally the electrostatic potential of the original point charge space is estimated according to the values of the 3D mesh. It is noted that in the PME approach the “tin-foil” boundary conditions \(^{29}\) are also applied. The PME approach is dramatically faster than the Ewald summation approach and thus is most commonly used in molecular simulations.

2.5 Molecular dynamics

As mentioned in Section 2.2.2, MD simulations deal with the time evolution of microscopic systems. In this section, the fundamental concepts and techniques used in MD simulations in this study are introduced.

2.5.1 Finite difference approach

To deal with the time evolution the MD simulation solves Newton’s equations of motion for all the atoms in a system, where the configuration of the system, i.e. positions and momenta of all the atoms, changes with time. In this section, the finite difference approach which calculates the positions and momenta of each atom along time is introduced. The force, \(\mathbf{f}_j\), acting on a certain atom \(j\), is given by

\[
\mathbf{f}_j = -\frac{\partial E}{\partial \mathbf{r}_j},
\]

(2.22)

where \(\mathbf{r}_j\) is the position of the atom \(j\) in the Cartesian coordinate and \(E\) is the total potential energy of the system, depending on all atomic positions. With the known forces the new momenta and positions of the atoms can then be calculated by solving the Newton’s second law of motion.

For MD simulations it is only feasible to solve the Newton’s equations of motion on a step-by-step basis. In other words, given the potentials and configuration of the system, i.e. atomic positions and momenta, at a time, \(t\), the configuration of the system at a later time, \(t + \delta t\), is obtained through numerically solving Newton’s equations of motion. Usually the increase of time, \(\delta t\), is defined as the time step in an MD simulation. Hence, efficient finite difference approaches are essential to MD simulations. The Verlet algorithm \(^{30}\) is one of the
most widely used finite difference approaches for integrating the equations of motion. It has become the basis for most algorithms in modern MD simulations. Modifications of the Verlet algorithm, namely, the leap-frog algorithm and velocity Verlet algorithm, improve the stability and accuracy of the scheme and are more popular nowadays. In this study, the leap-frog algorithm is used in all the MD simulations.

Given the position of an atom the force acting on that atom at time, \( t \), as well as its velocity at the previous time step, \( t - \delta t \), the leap-frog algorithm first calculate the velocity, \( \mathbf{v} \), at a half time step, \( \delta t/2 \), in advance. This is given by

\[
\mathbf{v}\left(t + \frac{\delta t}{2}\right) = \mathbf{v}\left(t - \frac{\delta t}{2}\right) + \mathbf{a}(t)\delta t,
\]

where \( \mathbf{a}(t) \) is the acceleration of the atom at time \( t \). The calculated velocity is then used to calculate the new position of that atom at the next time step, \( t + \delta t \), and is given by

\[
\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}\left(t + \frac{\delta t}{2}\right)\delta t.
\]

In the leap-frog algorithm the velocity leaps over the position and then in turn the position leaps over the velocity. The advantage of the leap-frog algorithm over the Verlet algorithm is that it can accurately estimate the velocity. However, the velocity is not calculated at the same time as the position. Thus one need to average the velocities at the former and latter time when the velocity at time, \( t \), is needed and, this is given by

\[
\mathbf{v}(t) = \frac{1}{2}[\mathbf{v}\left(t - \frac{\delta t}{2}\right) + \mathbf{v}\left(t + \frac{\delta t}{2}\right)].
\]

The velocity Verlet algorithm, as compared with the leap-frog algorithm, may be more stable with slightly longer time steps. However, this was not tested in this work.

2.5.2 Controlling the temperature

As discussed in Section 2.2.1, temperature is one of most important thermodynamic properties that define the state of a system. Hence, the temperature of the molecular systems should be continuously monitored using

\[
T(t) = \sum_{j=1}^{N} \frac{m_j |\mathbf{v}_j(t)|^2}{k_B N_f} = \frac{1}{(3N - 3 - N_c)k_B} \sum_{j=1}^{N} \frac{|\mathbf{p}_j(t)|^2}{m_j},
\]
where $T(t)$ is the temperature of the system at an instantaneous time $t$, $N$ is the total number of atoms in that system, $m_j$ is the mass of atom $j$, $\mathbf{v}_j(t)$ and $\mathbf{p}_j(t)$ is the velocity and momentum of atom $j$ at time $t$ respectively, $k_B$ is the Boltzmann constant, and $N_f$ and $N_c$ are the number of degrees of freedom and total number constraints of that system.

As noted in Section 2.2.2, molecular simulations can be performed using a variety of ensembles such as $NVE$, $NVT$ and $NPT$ ensembles. It is obvious that, for simulations using $NVT$ and $NPT$ ensembles, one need to control the temperature of the system in order to obtain the correct thermodynamic properties of the system. There are a variety of approaches to achieve this, of which the most commonly used are the velocity-rescaling thermostat\textsuperscript{33} and the Nosé-Hoover thermostat\textsuperscript{34,35}.

The velocity-rescaling thermostat is a modification of the Berendsen thermostat\textsuperscript{36} and, it rescales the velocities of all the atoms in the molecular system so that the kinetic energy gives the desired target temperature. The idea of the velocity-rescaling thermostat is given by

$$v_i(t + \tau_T) = v_i(t) \sqrt{\frac{T}{T(t)}}.$$ \hspace{1cm} (2.27)

Here $\tau_T$ is the coupling time interval of the thermostat, $v_i(t)$ and $v_i(t + \tau_T)$ are the velocities of atom $i$ at time $t$ and $(t + \tau_T)$ respectively, $T(t)$ is the temperature of the system at time $t$, and $T_T$ is the target temperature of the simulation.

The velocity-rescaling thermostat is one of the most simple thermostat algorithms and is widely used for MD simulations. However, it does not generate the correct distribution of states in the canonical ensemble and thus cannot guarantee a correct prediction of properties. Hence, the velocity-rescaling thermostat is usually used at the early stage of MD simulations, where the molecular system approaches equilibrium from a non-equilibrium initial state. The Nosé-Hoover thermostat, however, has the advantage of reproducing the correct distribution of states of the molecular system and it is usually used at the final stage of MD simulations where the simulation data is used for post-analysis.
2.5.3 Controlling the pressure

Pressure, as noted in Section 2.2.1, is also an important thermodynamic property that define the status of a system and, the pressure of the molecular systems is monitored using the virial theorem which is given by

\[
P(t) = \frac{1}{3V(t)} \left[ \sum_{i=1}^{N} \left| \mathbf{p}_i(t) \right|^2 + \frac{1}{2} \sum_{i,j,i \neq j} \mathbf{r}_{ij}(t) \cdot \mathbf{F}_{ij}(t) \right],
\]

where \( P(t) \) and \( V(t) \) are the pressure and volume of the system at an instantaneous time \( t \) respectively, \( N \) is the total number of atoms in that system, \( m_i \) is the mass of atom \( i \), \( \mathbf{p}_i(t) \) is the momentum of atom \( i \) at time \( t \), and \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) and \( \mathbf{F}_{ij} = \mathbf{F}_i - \mathbf{F}_j \). Here \( \mathbf{r}_i \) and \( \mathbf{r}_j \) are the positions of atoms \( i \) and \( j \) respectively and, \( \mathbf{F}_i \) and \( \mathbf{F}_j \) are the forces acting on atoms \( i \) and \( j \) respectively.

Similar to the thermostat, the molecular system can be coupled to a pressure bath so that the internal pressure of the system is controlled to give the target value. This is especially relevant to MD simulations in the \( NPT \) ensemble. In this study, similar to that of the thermostat, two pressure coupling approaches are commonly used, namely, the Berendsen barostat\(^{37} \) and the Parrinello-Rahman barostat\(^{38,39} \).

The Berendsen barostat rescales the atom coordinates and box vectors to yield the target pressure, \( P_0 \). The scaling factor, \( \xi_{\alpha\beta} \), of the Berendsen barostat is a 3 by 3 matrix, where \( \alpha \) and \( \beta \) represent x, y, or z in the Cartesian coordinate, and it is obtained using

\[
\xi_{\alpha\beta} = \left[ 1 - \frac{\delta t}{\tau_P} Z_{\alpha\beta} \left( P_{0,\alpha\beta} - P_{\alpha\beta}(t) \right) \right]^{1/3},
\]

where \( \delta t \) is the time step, \( \tau_P \) is the pressure coupling interval, \( Z_{\alpha\beta} \) and \( P_{0,\alpha\beta} \) are the isothermal compressibility and target pressure tensor in the \( \alpha\beta \) direction respectively, and \( P_{\alpha\beta}(t) \) is the pressure tensor in the \( \alpha\beta \) direction at time \( t \). The box vector, \( \mathbf{L} \), and the atom coordinate, \( \mathbf{r} \), at time \( (t + \delta t) \) are given by

\[
L_\alpha(t + \delta t) = \xi_{\alpha\alpha} L_\alpha(t),
\]

and

\[
r_{i,\alpha}(t + \delta t) = \xi_{\alpha\alpha} r_{i,\alpha}(t),
\]
respectively, where \( L_\alpha \) is the component of box vector \( \mathbf{L} \) in the \( \alpha \) direction and \( r_{i,\alpha} \) is the component of coordinate \( \mathbf{r} \) of atom \( i \) in the \( \alpha \) direction, and \( \alpha \) represents \( x, y, \) or \( z \) in the Cartesian coordinate.

The Berendsen barostat is a fast algorithm but it does not generate the correct distribution of the states in the \( NPT \) ensemble. Hence, in this study, it is always used together with the velocity rescaling thermostat at the early stage of MD simulations. The Parrinello-Rahman barostat is similar to the Nosé-Hoover algorithm for temperature coupling and it can produce correct thermodynamics in the \( NPT \) ensemble.

2.6 Monte Carlo methods

The Monte Carlo method was first developed by von Neumann, Ulam and Metropolis\(^{40,41}\) who proposed the idea that the Boltzmann distribution of states can be sampled in a stochastic way. The total potential energy of a system can then be calculated by averaging the ensemble of micro-states of that system, where the probability of finding each micro-state is set. Such sampling method involves generating random numbers, performing arithmetic and logical operations, and changing the configuration of the molecular system. All these tasks are quite suitable to computers. In this section, the fundamental concepts and techniques used in Monte Carlo simulations in this study are introduced.

2.6.1 Monte Carlo algorithm

As shown in Section 2.2, for a microscopic system that contains \( N \) atoms, the observable thermodynamic property of its corresponding macroscopic system, \( A_{\text{obs}} \), can be calculated using Eq. 2.8. Combining Eq. 2.1 and 2.8 yields

\[
A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \frac{\int A(\Gamma) \exp[-\beta E(\Gamma)] d\Gamma}{\int \exp[-\beta E(\Gamma)] d\Gamma},
\]

where \( \Gamma \) is an instantaneous micro-state of the microscopic system which includes the positions and momenta of all the atoms, \( \beta = 1/(k_B T) \) and \( k_B \) is the Boltzmann constant, \( A(\Gamma) \) and \( E(\Gamma) \) are the property of interest and total energy of the micro-state \( \Gamma \) respectively, and the angle parentheses represent an average quantity.

For the Monte Carlo algorithm we only consider the positions of the atoms but not the momenta, hence Eq. 2.32 can be simplified to

\[
A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \frac{\int A(\Gamma) \exp[-\beta E(\Gamma)] d\Gamma}{\int \exp[-\beta E(\Gamma)] d\Gamma},
\]
\[ A_{\text{obs}} = \langle A \rangle_{\text{ens}} = \frac{\int A(r^N) \exp[-\beta E(r^N)] \, dr^N}{\int \exp[-\beta E(r^N)] \, dr^N}, \quad (2.33) \]

where \( r^N \) represents the positions of all the atoms in the \( N \)-atom system and \( A(r^N) \) and \( E(r^N) \) are the property of interest and potential energy of the instantaneous configuration \( r^N \) respectively. The probability density, \( \rho(r^N) \), of finding the system in a configuration around \( r^N \) can now be written as

\[ \rho(r^N) = \frac{\exp[-\beta E(r^N)]}{\int \exp[-\beta E(r^N)] \, dr^N}. \quad (2.34) \]

The Monte Carlo algorithm allow for randomly generating instantaneous configurations, \( r^N \), in the configuration space according to the probability distribution \( \rho(r^N) \). In this case, the number of instantaneous configurations, \( n_j \), generated around a particular configuration, \( r_j^N \), should approximately equal to \( n_{\text{tot}}\rho(r^N) \), where \( n_{\text{tot}} \) is the total number of instantaneous configurations that generated by Monte Carlo algorithm. This can be expressed as

\[ A_{\text{obs}} = \langle A \rangle_{\text{ens}} \approx \frac{1}{n_{\text{tot}}} \sum_{j=1}^{n_{\text{tot}}} n_j A(r_j^N), \quad (2.35) \]

where \( A(r_j^N) \) is the property of interest corresponding to that particular configuration \( r_j^N \). Compare Eq. 2.35 to Eq. 2.33 we can see that the calculation of \( A_{\text{obs}} \) has now been made feasible as we no longer have the incalculable denominator in Eq. 2.33.

Let us now turn to the actual Monte Carlo algorithm, which solves the problem of how to generate instantaneous configurations in the configuration space according to a relative probability proportional to the Boltzmann factor, \( \exp[-\beta E(r^N)] \). This can be done in three steps:

1. Assume we have a configuration, \( r^N \), of \( N \)-atom system which is denoted by “o” for old. The Boltzmann factor for this configuration is given by \( \exp[-\beta E(o)] \).
2. We then generate a new trial configuration, \( r^N \), which is denoted by “n” for new, by adding a small random displacement, \( \Delta \), to o. This random displacement can be a displacement of an atom or a rotation of an atom. The Boltzmann factor for this configuration is given by \( \exp[-\beta E(n)] \).
3. We should now decide whether to accept or reject the trial configuration according to the probability of the transition from o to n, which is given by \( p(o \rightarrow n) \). We now introduce two more quantities. Firstly we denote \( A(o \rightarrow n) \) as the transition matrix.
that determines the probability of performing a trial move from configuration \( o \) to \( n \). Secondly we denote \( \text{acc}(o \rightarrow n) \) as the probability of accepting a trial move from configuration \( o \) to \( n \). The relation given in Eq. 2.36 is followed and, \( \text{acc}(o \rightarrow n) \) should satisfy the criteria given by Eq. 2.37 where \( \rho(n) \) and \( \rho(o) \) are the probability density of finding the system in configurations \( n \) and \( o \) respectively.

\[
p(o \rightarrow n) = A(o \rightarrow n) \times \text{acc}(o \rightarrow n) \tag{2.36}
\]

\[
\text{acc}(o \rightarrow n) = \begin{cases} 
1 & \text{if } \rho(n) \geq \rho(o) \\
\frac{\rho(n)}{\rho(o)} & \text{if } \rho(n) < \rho(o)
\end{cases} \tag{2.37}
\]

In Monte Carlo simulations, the three steps are repeated for a sufficient number of cycles so that the system can reach proper equilibrium.

One problem, however, may occur in the Monte Carlo simulations when the simulated system contains large molecules or long-chain molecules rather than small atoms. This is because displacing a large molecule may result in large energy changes and thus the probability of accepting such transitions can be extremely low. One popular way to solve this is the configurational-bias approach, which was proposed by Siepmann \textit{et al}.\textsuperscript{42-45} The basic idea of the configurational-bias approach is that, instead of displacing entirely a large molecule, a small part of the large molecule is randomly chosen and the trial displacement is performed solely on that it, with careful treatment of the potential of the broken covalent bond. This approach, which moves a large molecule part by part, can increase the probability of acceptance of moving a large molecule in a dense system and, helps reduce the equilibration time needed and also allow a better sampling of configurations in the production run.

### 2.6.2 \textit{NPT} ensemble Monte Carlo

In this research, all Monte Carlo simulation were performed using the \textit{NPT} ensemble, where, in addition to the movement of the particles, the changes of volume \( V \) of the simulation box were also attempted and, were accepted or rejected according to an evaluation of the enthalpy change.

A schematic description of a Monte Carlo cycle that involves the change of \( V \) is as follows:
1. We firstly repeat the three-step procedure described in Section 2.6.1 for a number of particles. Usually all \( N \) particles are treated in sequence.

2. We now perform a trial volume change from \( V(o) \) to \( V(n) \), where, again, “o” denotes the old volume and “n” denotes the trial volume. The coordinates of all the particles, \( \mathbf{r}^i \), are then scaled by a scaling factor \( \xi = [V(n)/V(o)]^{1/3} \). This results in a change in the energy, \( U \), from \( U(o) \) to \( U(n) \), where \( U \) can be calculated using Eq. 2.3. The change in enthalpy, \( \Delta H \), is then calculated as

\[
\Delta H = U(n) - U(o) + P[V(n) - V(o)] - \frac{N}{\beta} \ln \left[ \frac{V(n)}{V(o)} \right].
\]  

(2.38)

3. We now decide whether to accept or reject the trial volume according to the probability of the transition from o to n, which is, again, given by \( p(o \rightarrow n) \). Again, we denote \( A(o \rightarrow n) \) as the transition matrix from volume o to n and, \( acc(o \rightarrow n) \) as the probability of accepting a trial volume from volume o to n. The relation given in Eq. 2.36 is, again, followed and, \( acc(o \rightarrow n) \) should satisfy the criteria given by

\[
acc(o \rightarrow n) = \begin{cases} 1 & \text{if } \exp(-\beta \Delta H) \geq 1 \\ \exp(-\beta \Delta H) & \text{if } \exp(-\beta \Delta H) < 1 \end{cases}.
\]  

(2.39)

2.6.3 Simulating phase equilibria

In this study, the Gibbs Ensemble Monte Carlo (GEMC)\(^{46}\) is used to simulate the phase equilibria of the system of interest. GEMC simulation is a powerful method to investigate phase co-existence. Unlike conventional Monte Carlo simulations, i.e. Monte Carlo simulations using canonical, micro-canonical or grand-canonical ensembles, which usually have only one simulation box, GEMC involves the simultaneous use of several simulation boxes. In a GEMC simulation, there are not only the displacements or rotations of molecules within a simulation box but also the exchange of molecules and volume between different simulations boxes. In the GEMC simulations in this study, there are two simulation boxes in a simulated system, where the simulation boxes are coupled to \( NPT \) ensemble.

As illustrated in Figure 2.8, if we assume a GEMC system contains two boxes, namely, box I and box II. Boxes I and II have volumes of \( V' \) and \( V'' \) as well as \( N' \) and \( N'' \) particles of the same type inside, respectively. In addition, the potential energy of boxes I and II are \( E' \) and \( E'' \) respectively. What is more, the particles inside one box do not interact with the particles inside the other box. There are three types of trial changes in such a GEMC
system. As shown in Figure 2.8a, the first type of trial change involves the displacement or rotation of a particle in the same box, where the resulting energy changes are $\Delta E^I$ and $\Delta E^{II}$ in boxes I and II, respectively. The corresponding enthalpy change, $\Delta H$, of the whole system can be written as

$$\Delta H = \Delta E^I + \Delta E^{II}. \quad (2.40)$$

The second type of trial change, as shown in Figure 2.8b, is the volume exchange, $\Delta V$, between the two boxes, where the resulting energy changes are $\Delta E^I$ and $\Delta E^{II}$ in boxes I and II, respectively. The corresponding enthalpy change, $\Delta H$, of the second type of trial change can be written as

$$\Delta H = \Delta E^I + \Delta E^{II} - \frac{N^I}{\beta} \ln \frac{V^I + \Delta V}{V^I} - \frac{N^{II}}{\beta} \ln \frac{V^{II} - \Delta V}{V^{II}}. \quad (2.41)$$

The third type of trial change is the swap of a particle between the two boxes. As shown in Figure 2.8c, the trial change of the system is that a particle from box II is swapped into box I. Hence, there are $(N^I + 1)$ and $(N^{II} - 1)$ particles in boxes I and II in the trial configuration respectively. The resulting energy changes are $\Delta E^I$ and $\Delta E^{II}$ in boxes I and II, respectively. The corresponding enthalpy change, $\Delta H$, of the third type of trial change can be written as

$$\Delta H = \Delta E^I + \Delta E^{II} + \frac{N^I}{\beta} \ln \frac{N^I + 1}{N^I} + \frac{N^{II}}{\beta} \ln \frac{N^{II} - 1}{N^{II}} + \frac{1}{\beta} \ln \frac{V^{II}}{V^{II-1}} - \frac{1}{\beta} \ln \frac{V^I}{N^I+1}. \quad (2.42)$$

Finally, following our notations in Section 2.6.2, the corresponding probability of accepting the trial change, $acc(o \rightarrow n)$, in a GEMC move is given by

$$acc(o \rightarrow n) = \begin{cases} 1 & \text{if} \quad \exp(-\beta \Delta H) \geq 1 \\ \exp(-\beta \Delta H) & \text{if} \quad \exp(-\beta \Delta H) < 1 \end{cases} \quad (2.43)$$
Figure 2.8. Illustration of the three types of trial changes in GEMC.

(a) Box I

$E^I + \Delta E^I, N^I, V^I$

$E^I + \Delta E^I, N^I, V^I$

(b) Box I

$E^I + \Delta E^I, N^I, V^I + \Delta V$

$E^I + \Delta E^I, N^I, V^I - \Delta V$

(c) Box I

$E^I + \Delta E^I, N^I + 1, V^I$

$E^I + \Delta E^I, N^I - 1, V^I$
2.7 References


3 A comparative molecular dynamics study on tri-\textit{n}-butyl phosphate in organic and aqueous environments and its relevance to nuclear extraction processes

3.1 Preface

This chapter presents part of some collaborative research with Dr. Ryuhei Motokawa and Dr. Christopher Williams, on the parameterisation and comparison of molecular models of tri-\textit{n}-butyl phosphate, \textit{n}-dodecane and \textit{n}-octane.

J. Mu carried out all the molecular dynamics simulations and analysis, Dr. Williams performed quantum mechanical calculations and Dr. Motokawa carried out the experiments.

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A Comparative Molecular Dynamics Study on Tri-$n$-butyl Phosphate in Organic and Aqueous Environments and its Relevance to Nuclear Extraction Processes

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![Graph](image)
Abstract

A refined model for tri-\textit{n}-butyl phosphate (TBP), which uses a new set of partial charges generated from our \textit{ab initio} density functional theory calculations, has been proposed in this study. Molecular dynamics simulations were conducted to calculate the thermodynamic properties, transport properties and the microscopic structures of liquid TBP, TBP/water mixtures and TBP/\textit{n}-alkane mixtures. These results were compared with those obtained from four other TBP models, previously described in the literature. We conclude that our refined TBP model appears to be the only TBP model from this set that, with reasonable accuracy, can simultaneously predict the properties of TBP in bulk TBP, in organic diluents and in aqueous solution. The other models only work well for two of the three systems mentioned above. This new TBP model is thus appropriate for the simulation of liquid-liquid extraction systems in the nuclear extraction process, where one needs to simultaneously model TBP in both aqueous and organic phases. It is also promising for the investigation of the microscopic structure of the organic phase in these processes and for the characterisation of third phase formation, where the TBP again interacts simultaneously with both polar and non-polar molecules. Because the proposed TBP model uses OPLS-2005 Lennard-Jones parameters, it may be used with confidence to model mixtures of TBP with other species whose parameters are given by the OPLS-2005 force field.
3.2 Introduction

Tri-\textit{n}-butyl phosphate (TBP) is commonly used as an extractant of hexavalent uranium and tetravalent plutonium in the Plutonium Uranium Reduction EXtraction (PUREX) process,\textsuperscript{1,2} where uranium and plutonium from irradiated nuclear fuel are reprocessed. In the PUREX process, the waste nuclear fuel is dissolved in nitric acid to form uranium and plutonium nitrates, and then mixed with an organic extraction solution consisting of TBP and a hydrocarbon diluent, usually kerosene, which is rich in \textit{n}-dodecane. The volume fraction of TBP in the organic solution is usually 30%. During the extensive mixing, the TBP molecules selectively form complexes with the actinide nitrates, and move back into the bulk organic solution after a short period, achieving the separation of those from the other metals present.

In the PUREX process, third phase formation occurs when the concentration of the actinide nitrates exceeds the solubility limit of the organic phase, resulting in the organic phase splitting into two layers\textsuperscript{3}. The heavy layer, which is the third phase, contains a high concentration of the uranium and plutonium complexes and thus can cause processing and safety concerns such as an increased potential for criticality or runaway decomposition reactions.\textsuperscript{4} This undesirable phase separation may also cause phase inversion and create difficulty in the stripping process.\textsuperscript{5} Therefore, a comprehensive understanding of the mechanism of third phase formation as well as new flow sheet models for improving the solubility of the organic phase is needed. Molecular dynamics (MD) simulations provide a powerful method for investigating the microscopic structure and thermodynamic properties of the PUREX system.

In the past few years, many computational studies have been carried out to investigate the cluster behaviour, interface mass transfer and microscopic structures of the PUREX system.\textsuperscript{6-11} However, the accuracy of the TBP models used in those simulations has been brought into question by some recent force field comparative studies. Cui and co-workers compared the Assisted Model Building with Energy Refinement (AMBER)\textsuperscript{12} force field with the Optimized Potentials for Liquid Simulations (OPLS)\textsuperscript{13} force field as well as investigating two sets of partial electric charges for the TBP model.\textsuperscript{14} According to their results, the microscopic structure of the pure TBP system is strongly affected by the different partial charges on the TBP molecules. Benay, Wipff and co-workers studied the effect of the partial charges on the thermodynamic properties and interfacial behaviour of TBP molecules using MD simulations.\textsuperscript{15} They also emphasised the important role of the
partial charges and proposed their favoured charge set. Recently, Vo and co-workers parameterised the AMBER force field for TBP and \(n\)-dodecane.\(^{16}\)

The association behaviour of TBP molecules in TBP/\(n\)-alkane organic solutions has also been widely investigated. The MD simulations of Leay \textit{et al.}, demonstrated that the polar TBP molecules stacked into filaments.\(^{17}\) They employed the AMBER99 force field\(^{12}\) and used charges obtained from density functional theory (DFT).\(^{14}\) On the other hand, recent simulations using the same charge set, scaled by 60\%, showed considerably less TBP aggregation.\(^{18}\) Thus it seems that the microscopic structure of the TBP molecules in \(n\)-alkanes is highly dependent on the distribution and magnitude of the partial charges used in the simulations.

At present, X-ray or neutron scattering may be the most appropriate experimental techniques for revealing the degree of TBP-aggregation. Motokawa \textit{et al.} have recently presented a variety of scattering intensity profiles for TBP/\(n\)-alkane binary systems through small-angle X-ray and neutron scattering (SAXS and SANS) experiments.\(^{19}\) The SAXS and SANS profiles, which can be compared to those obtained from simulation, provide a means of validation for the employed potentials. We find, however, neither Cui’s nor Wipff’s model predicts well the experimental scattering profiles at low scattering vectors. We have therefore re-parameterised the TBP partial charges to improve agreement with these experiments.

In this paper, we report an atomistic TBP model which makes use of a new partial charge set calculated by DFT.\(^{20,21}\) A comparative study has been carried out on five all-atom TBP models, including the TBP model we have reported. Specifically, we have computed various thermodynamic properties and the microscopic structures of liquid TBP, TBP/\(n\)-alkane organic mixtures, and TBP/water mixtures. For pure TBP systems, the mass densities, shear viscosities, self-diffusion coefficients and microscopic structure, as characterised by the SAXS intensity profiles have been computed and compared. For TBP/water mixtures, the solvation free energy of water in TBP and the densities have computed and compared; for TBP/\(n\)-alkane mixtures, the SAXS profiles of TBP/\(n\)-alkane systems, and the excess enthalpy of mixing between TBP and \(n\)-dodecane, were also calculated. Overall, our results showed that our recently developed TBP model is the most accurate model for the simulations where TBP molecules are involved in both the organic environment and aqueous environment. Polarisable TBP models have not been considered in this study as polarisable models are computationally much more costly when running relatively large systems. According to our simulations, it takes 8 times longer to simulate a
polarisable water model than the non-polarisable SPC/E water model under the same conditions using the GROMACS 4.6.7 simulation package. As a single TBP molecule contains 41 more atoms than a water molecule, it would be even more time consuming to simulate polarisable TBP models. United-atom models for TBP have also not been considered here. Our simulations indicate that the united-atom models for TBP typically show large inaccuracies in predicting the density, viscosity and the microscopic structure of the system, where details are given in Section 3.6.

3.3 Methodology

3.3.1 Force field parameterisation

In this work, force field parameters for bond stretching, bond angle bending, dihedral angle torsion and the non-bonded Lennard-Jones potential were taken from the OPLS-2005 parameter set which were obtained from DL_FIELD. The partial charges on the atoms of the TBP molecule were taken from models proposed in the literature, or the set generated by ourselves. The total potential energy of interaction, \(E\), takes the form

\[
E = \sum_{\text{bonds}} K_r (r_{ij} - r_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta_{ijk} - \theta_{eq})^2 \\
+ \sum_{\text{dihedrals}} \left[ \frac{V_1}{2} (1 + \cos \Phi_{ijkl}) + \frac{V_2}{2} (1 + \cos 2\Phi_{ijkl}) + \frac{V_3}{2} (1 + \cos 3\Phi_{ijkl}) \right] \\
+ \sum_{i} \sum_{j} \left[ \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij} \left( \frac{\sigma_{ij}^{12}}{r_{ij}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) \right],
\]  

(3.1)

where the terms, in order of appearance, are the bond length stretching between atoms \(i\) and \(j\), bond angle bending between atoms \(i, j\) and \(k\), bond torsion between atoms \(i, j, k\) and \(l\), electrostatic interactions between atoms \(i\) and \(j\) and Lennard-Jones interactions between atoms \(i\) and \(j\). Geometric mixing rules were used to calculate the cross terms in the Lennard-Jones potential. Five TBP models have been tested and compared in this study, where each of them uses the OPLS-2005 force field for the intramolecular and Lennard-Jones potentials, but different charge sets for the electrostatic potential. The detailed potential parameters for the five TBP models are listed in Tables 3.1–3.4, where the representations of atoms in TBP are shown in Figure 3.1. For the Lennard-Jones and Coulomb interactions between 1–4 atoms in the same molecule, the OPLS convention was followed, using a scaling factor of 0.5.
Figure 3.1. Schematic representation of the TBP model.

**Table 3.1.** Bond stretch force constant and equilibrium bond lengths for the OPLS-2005 force field.

<table>
<thead>
<tr>
<th>System</th>
<th>$i-j$</th>
<th>$K_i$ (kJ mol$^{-1}$ nm$^{-2}$)</th>
<th>$r_{eq}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>OS—P</td>
<td>96232</td>
<td>0.1697</td>
</tr>
<tr>
<td></td>
<td>OS—C</td>
<td>133888</td>
<td>0.1410</td>
</tr>
<tr>
<td></td>
<td>P—O2</td>
<td>219660</td>
<td>0.1480</td>
</tr>
<tr>
<td></td>
<td>C—H</td>
<td>142256</td>
<td>0.1090</td>
</tr>
<tr>
<td></td>
<td>C—C</td>
<td>129704</td>
<td>0.1529</td>
</tr>
<tr>
<td>$n$-Alkane</td>
<td>C—H</td>
<td>142256</td>
<td>0.1090</td>
</tr>
<tr>
<td></td>
<td>C—C</td>
<td>129704</td>
<td>0.1529</td>
</tr>
</tbody>
</table>

**Table 3.2.** Angle bending force constant and equilibrium angles for the OPLS-2005 force field.

<table>
<thead>
<tr>
<th>System</th>
<th>$i-j-k$</th>
<th>$K_\theta$ (kJ mol$^{-1}$ rad$^{-2}$)</th>
<th>$\theta_{eq}$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>C—OS—P</td>
<td>418.4</td>
<td>120.500</td>
</tr>
<tr>
<td></td>
<td>OS—P—O2</td>
<td>418.4</td>
<td>108.230</td>
</tr>
<tr>
<td></td>
<td>OS—P—OS</td>
<td>188.28</td>
<td>102.600</td>
</tr>
<tr>
<td></td>
<td>OS—C—H</td>
<td>146.44</td>
<td>109.500</td>
</tr>
<tr>
<td></td>
<td>OS—C—C</td>
<td>209.2</td>
<td>109.500</td>
</tr>
<tr>
<td></td>
<td>H—C—H</td>
<td>138.07</td>
<td>107.800</td>
</tr>
<tr>
<td></td>
<td>C—C—C</td>
<td>244.14</td>
<td>112.700</td>
</tr>
<tr>
<td>$n$-Alkane</td>
<td>H—C—H</td>
<td>138.07</td>
<td>107.800</td>
</tr>
<tr>
<td></td>
<td>C—C—H</td>
<td>156.9</td>
<td>110.700</td>
</tr>
<tr>
<td></td>
<td>C—C—C</td>
<td>244.14</td>
<td>112.700</td>
</tr>
</tbody>
</table>

**Table 3.3.** Dihedral torsion force constants for the OPLS-2005 force field.

<table>
<thead>
<tr>
<th>System</th>
<th>$i-j-k-l$</th>
<th>$V_1$ (kJ mol$^{-1}$)</th>
<th>$V_2$ (kJ mol$^{-1}$)</th>
<th>$V_3$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>C—OS—P—O2</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>C—OS—P—OS</td>
<td>0.42258</td>
<td>-10.93698</td>
<td>7.66090</td>
</tr>
<tr>
<td></td>
<td>H—C—OS—P</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.25104</td>
</tr>
<tr>
<td></td>
<td>C—C—OS—P</td>
<td>-22.22122</td>
<td>-1.87025</td>
<td>2.02087</td>
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<tr>
<td></td>
<td>OS—C—C—H</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.25520</td>
</tr>
<tr>
<td></td>
<td>OS—C—C—C</td>
<td>5.25092</td>
<td>-2.58990</td>
<td>2.28446</td>
</tr>
<tr>
<td></td>
<td>H—C—C—H</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.25520</td>
</tr>
<tr>
<td></td>
<td>C—C—C—H</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.25520</td>
</tr>
<tr>
<td></td>
<td>C—C—C—C</td>
<td>4.74884</td>
<td>-0.63178</td>
<td>1.67360</td>
</tr>
<tr>
<td>$n$-Alkane</td>
<td>H—C—C—H</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.25520</td>
</tr>
<tr>
<td></td>
<td>C—C—C—H</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.25520</td>
</tr>
<tr>
<td></td>
<td>C—C—C—C</td>
<td>4.74884</td>
<td>-0.63178</td>
<td>1.67360</td>
</tr>
</tbody>
</table>
Table 3.4. Partial electric charge sets used in five TBP models and Lennard-Jones parameters for the OPLS-2005 force field.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Refined</th>
<th>60% MNDO</th>
<th>70% DFT</th>
<th>90% DFT</th>
<th>OPLS2005</th>
<th>LJ parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$\varepsilon_{ii}$</td>
</tr>
<tr>
<td>O2</td>
<td>-0.7070</td>
<td>-0.522</td>
<td>-0.56581</td>
<td>-0.72747</td>
<td>-0.47</td>
<td>0.8368</td>
</tr>
<tr>
<td>P</td>
<td>1.3400</td>
<td>1.062</td>
<td>1.12672</td>
<td>1.44864</td>
<td>1.70</td>
<td>0.8368</td>
</tr>
<tr>
<td>OS</td>
<td>-0.5047</td>
<td>-0.336</td>
<td>-0.43106</td>
<td>-0.55422</td>
<td>-0.61</td>
<td>0.5858</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1222</td>
<td>0.12</td>
<td>0.25459</td>
<td>0.32733</td>
<td>0.08</td>
<td>0.2716</td>
</tr>
<tr>
<td>Cb</td>
<td>0.0297</td>
<td>0.036</td>
<td>0.01820</td>
<td>0.0234</td>
<td>-0.12</td>
<td>0.2716</td>
</tr>
<tr>
<td>Cc</td>
<td>0.1349</td>
<td>0.012</td>
<td>0.08491</td>
<td>0.10917</td>
<td>-0.12</td>
<td>0.2716</td>
</tr>
<tr>
<td>Cd</td>
<td>-0.2534</td>
<td>0.012</td>
<td>-0.02282</td>
<td>-0.02934</td>
<td>-0.18</td>
<td>0.2716</td>
</tr>
<tr>
<td>Ha</td>
<td>0.0361</td>
<td>-0.012</td>
<td>-0.01827</td>
<td>-0.02349</td>
<td>0.06</td>
<td>0.1255</td>
</tr>
<tr>
<td>Hb</td>
<td>0.0232</td>
<td>0</td>
<td>0.00049</td>
<td>0.00063</td>
<td>0.06</td>
<td>0.1255</td>
</tr>
<tr>
<td>Hc</td>
<td>-0.0175</td>
<td>0</td>
<td>-0.02709</td>
<td>-0.03483</td>
<td>0.06</td>
<td>0.1255</td>
</tr>
<tr>
<td>Hd</td>
<td>0.0589</td>
<td>0</td>
<td>-0.00035</td>
<td>-0.00045</td>
<td>0.06</td>
<td>0.1255</td>
</tr>
</tbody>
</table>

$^a$Unit in e. $^b$Units are kJ·mol$^{-1}$. $^c$Units are nm. $^d$A value of 0.3250 was used in the refined model in order to get better prediction of the density and self-diffusion coefficient of pure TBP liquid, where details are shown in Tables S3.2 and S3.3 in Section 3.6.

In this study, we refined the OPLS-2005 force field by re-calculating the partial charges on each atom of the TBP molecule, by performing a series of DFT calculations using the B3LYP functional$^{29-31}$ and the TZVP basis set.$^{32}$ We first performed a geometry optimisation calculation. Then, single point calculations were performed using the polarisable continuum model (PCM)$^{33}$ which mimicked the effect of the solvents, where relative dielectric constants of 8.1781, 2.0060 and 78.3553 were used for TBP, $n$-dodecane and water, respectively.$^{34}$ The solvent cavities in the single point calculations were built by using a series of overlapping atom-centred spheres with radii taken from the UFF force field.$^{35}$ The DFT charge sets were obtained by fitting to an electrostatic potential calculated at various points around the molecule, generated according to the Merz-Singh-Kollman (MSK) scheme.$^{36,37}$ Three different charge sets were obtained as the relative dielectric constant for each type of implicit solvent are different. The average value of the three DFT charge sets was used as the partial charges for our refined model. The details of the three DFT charge sets are shown in Table S3.1 in Section 3.6. All DFT calculations were performed using the Gaussian 09 software.$^{38}$

The partial charge set obtained from our DFT calculations not only took the liquid phase TBP into account, but also gave consideration to the status of the TBP within infinitely dilute $n$-dodecane and water solutions. Hence the partial charge set could be regarded as a good compromise for the charge distribution of TBP in organic or aqueous environment. In
addition to the charge calculations, the carbon-carbon Lennard-Jones interaction for our refined model was slightly adjusted to achieve better predictions of the density of TBP, where details are given in Tables S3.2 and S3.3 in Section 3.6. We designate our refined OPLS-2005 model as the refined model in this study.

Besides our new TBP model, we considered four TBP models proposed by previous researchers. The first two of these, which were proposed by Cui and co-workers,\textsuperscript{14} used two different partial charge sets. These were the 60\% scaled partial charges obtained from a Modified Neglect of Differential Overlap (MNDO) quantum chemistry calculation,\textsuperscript{39} and the 70\% scaled partial charges obtained from their \textit{ab initio} DFT calculation. In this study, we designate these two TBP models as the 60\% MNDO model and the 70\% DFT model respectively. The third TBP model was proposed by Ye and Cui, who changed the scaling factor from 70\% to 90\% for the DFT charge set to better model TBP-water interactions.\textsuperscript{40} In this study, we designate this model as the 90\% DFT model. The fourth TBP model uses the original OPLS-2005 charge set, which we designate as the OPLS2005 model.

### 3.3.2 Simulations

The MD simulations of the five TBP models were performed using the GROMACS 4.6.7 simulation package. The initial configurations for all of the simulations were generated by inserting the molecules into simulation boxes with a variety of dimensions ranging from 3 nm to 7 nm. All molecules were randomly distributed. The Verlet Leap Frog algorithm was used to integrate the equations of motion using a time step of 1 fs. Three-dimensional cubic periodic boundary conditions were employed and a non-bonded cut-off length of 1.2 nm was applied. The particle-mesh Ewald (PME) method was used to treat the long-range electrostatics, where switch functions\textsuperscript{41,42} were applied from 0.9 nm to 1.2 nm to shift the potential to zero at the real space cut-off. The switch functions were also applied from 0.9 nm to 1.2 nm to conserve the Lennard-Jones potentials at the cut-off. All bonds containing hydrogen atoms were constrained using the LINCS algorithm,\textsuperscript{43} with a LINCS order of 4. In all of the simulations, the steepest descent algorithm was used to minimise the energy of the initial configuration. The energy minimisation runs were followed by up to 20 ns equilibration runs using the NPT ensemble, using with the velocity-rescaling thermostat\textsuperscript{44} and the Berendsen barostat\textsuperscript{45} to converge the temperature, pressure and density of each system. Finally, 10 ns production runs, which used the Nosé-Hoover thermostat\textsuperscript{46,47} and
Parrinello-Rahman barostat,\textsuperscript{48,49} were performed at the same condition to generate the final simulation results.

3.3.3 Experimental section

3.3.3.1 Materials.

TBP was purchased from the Tokyo Chemical Industry (Tokyo, Japan) and dried overnight under molecular sieves (Wako Pure Chemical Industries, Osaka, Japan) before use. Both \textit{n}-octane and \textit{n}-dodecane were purchased from Wako and used without purification.

3.3.3.2 SAXS measurements.

SAXS measurements were performed to obtain the X-ray scattering intensity profiles, which can also be estimated based on atom pair radial distribution functions from simulations. Hence SAXS is a powerful tool that bridges the gap between simulation and experiment with regard to the microscopic structure of the systems.

An X-ray diffraction apparatus (NANO-Viewer, RIGAKU) was used in our SAXS experiment. The wavelength of the incident X-ray beam, $\lambda$, was 1.54 Å, where the incident beam was focused to a spot 450 µm in diameter at the sample position, using a pinhole slit collimator. The scattered X-rays from the sample were detected by a two dimensional position-sensitive detector (PILATAS 100K/R, RIGAKU), with 195 × 487 pixels (33.5 × 83.8 mm) and a spatial resolution of 0.172 mm, covering a $q$ range from 0.8 to 35 nm$^{-1}$ at two sample-to-detector distances of 64 and 337 mm. $q = (4\pi/\lambda)\sin \theta$ is the magnitude of the scattering vector, where $2\theta$ is the scattering angle. The scattering data recorded by the detector were corrected for counting efficiency, instrumental background and air scattering on a pixel-to-pixel basis. The X-ray scattering intensity distribution, $I(q)$, was circularly averaged, and converted to absolute unit of the scattering intensity of reciprocal centimetre (cm$^{-1}$) by calibration with water scattering.\textsuperscript{50} The sample solutions were loaded into glass capillary cells with 0.01-mm-thick walls and a 2.0 mm sample thickness. All of the X-ray scattering data were acquired at 25 °C.
3.4 Results and discussion

3.4.1 Prediction of pure TBP properties.

3.4.1.1 Mass density of pure TBP.

The pure TBP systems using different TBP models were simulated at a constant pressure of 1 bar and a variety of temperatures ranging from 288.15 K to 308.15 K to compare the calculated densities with the experimentally measured values. Each system contained 500 TBP molecules with a 6 nm/size cubic periodic boundary. The mass densities of the systems were computed as the average values from the production runs.

Mass density is an important thermodynamic property in the MD simulations as it is strongly related to all the intramolecular and intermolecular interactions between particles in a system. It is seen from Figure 3.2 that the predictions of the densities of the OPLS2005 model and the refined model show an averaged deviation from the experimental data of 0.4 % and 0.3 % respectively. The other three models are less accurate with averaged deviations larger than 0.7 %.

Figure 3.2. Calculated densities of pure TBP at different temperatures in comparison with experimental data. Trend lines are added for clarity and the experimental values were obtained from Fang et al. 51

3.4.1.2 Shear viscosity and self-diffusion coefficient of TBP.
Non-equilibrium MD (NEMD) simulations were carried out to compute the shear viscosity of the pure TBP systems at ambient conditions using the periodic shear flow method. In each of the NEMD simulations, an external force \( \mathbf{a} \) was applied, which caused a velocity field \( \mathbf{u} \) in the liquid according to the Navier-Stokes equation:

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u},
\]  

where \( \eta \) is the shear viscosity and \( \mathbf{a} \) is the external force per unit of mass and volume. For the NEMD simulations, each system contained 500 TBP molecules in a cubic periodic boundary box with a side length of around 6.1 nm. For each system, five NEMD simulations were performed with five different values of the external force \( \mathbf{a} \), from 0.01 to 0.1 nm ps\(^{-2}\) respectively. The shear viscosities of the systems at each value of external force were then calculated, and the shear viscosities were plotted as a function of the external force. The values of shear viscosity at \( |\mathbf{a}| = 0 \) were then extrapolated based on the viscosity-external force relation.

The self-diffusion coefficients of the pure TBP systems were calculated using the Einstein relation:

\[
\lim_{t \to \infty} \langle ||\mathbf{r}_i(t) - \mathbf{r}_i(0)||^2 \rangle_{i \in \text{TBP}} = 6 \ D \ t,
\]  

where \( D \) is the self-diffusion coefficient of a TBP molecule, \( \mathbf{r}_i(t) \) is the centre of mass of TBP molecule \( i \) at time \( t \), the angle brackets denote ensemble averaging over all TBP molecules and time origins. \( D \) was estimated by fitting a straight line to a plot of \( \langle ||\mathbf{r}_i(t) - \mathbf{r}_i(0)||^2 \rangle \) against \( t \), in the interval between 100 and 200 ps in the production run and dividing the gradient by 6. This time interval is long enough for the TBP molecules to decorrelate from their initial positions and short enough to avoid the large statistical uncertainties experienced at longer time intervals. In electrostatic-dominated systems such as water, diffusion coefficients are known to be sensitive to finite-size effects where \( D \) has been shown to increase linearly with the box size. Hence a variety of system sizes with 50, 148, 290, or 500 TBP molecules, which corresponding to a box length of 2.84 nm, 4.07 nm, 5.10 nm, and 6.10 nm respectively, have also been simulated in order to investigate the effect of system size.

The viscosities and self-diffusion coefficients of pure TBP systems at ambient condition using different TBP models are shown in Table 3.5. The dependence of the TBP self-diffusion coefficient on the length of the simulation cell is shown in Figure S3.1 in Section
3.6. The values of $D$ listed in Table 3.5 are the extrapolated self-diffusion coefficients at the infinite box size in Figure S3.1 in case of finite-size effect, although the self-diffusion coefficient of TBP does not have a clear finite-size effect as the slopes of the linear trend lines are zero to within the statistical errors.

Table 3.5. Calculated shear viscosities and self-diffusion coefficients of pure TBP at 298.15 K and 1 bar.

<table>
<thead>
<tr>
<th>TBP models</th>
<th>$\eta$ (mPa s)</th>
<th>$D$ ($\times 10^{-6}$ cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% MNDO</td>
<td>5.466 ± 0.052</td>
<td>1.167 ± 0.078</td>
</tr>
<tr>
<td>70% DFT</td>
<td>7.763 ± 0.086</td>
<td>0.832 ± 0.043</td>
</tr>
<tr>
<td>90% DFT</td>
<td>22.28 ± 1.78</td>
<td>0.404 ± 0.060</td>
</tr>
<tr>
<td>OPLS2005</td>
<td>3.897 ± 0.029</td>
<td>1.802 ± 0.070</td>
</tr>
<tr>
<td>refined</td>
<td>6.142 ± 0.043</td>
<td>1.082 ± 0.057</td>
</tr>
<tr>
<td>expt.</td>
<td>3.399$^a$</td>
<td>2.29$^b$</td>
</tr>
</tbody>
</table>

$^a$Experimental values were from Tian et al.$^{56}$ statistical errors were not given. $^b$Experimental values were from Tsimering et al.$^{57}$ statistical errors were not given.

The self-diffusion coefficient and shear viscosity are important properties that are commonly regarded as an indication of the accuracy of the molecular models in predicting transport behaviour. The results in Table 3.5 suggest that the OPLS2005 model best predicted both the self-diffusion constant and shear viscosity, although the deviations were still large (14.7% and 21.3%, respectively). All of the other models showed even lower accuracy in predicting the transport properties of TBP. Such discrepancies between the predictions of thermodynamic and transport properties have been reported previously.$^{14}$ This is an issue to be investigated in future work.

Compared with the 70% DFT model, the 90% DFT model excessively over-estimates the viscosity of pure liquid TBP, which indicates that lowering the charges of the DFT models will give better predictions of transport properties. It is also seen that the partial charge set is one of the main factors affecting the transport properties of TBP molecules.

Previously, Cui and co-workers$^{14}$ reported that the value of $D$ of the 70% DFT model can be increased by around 50% by reducing the 1-4 intramolecular scaling factor values from 0.5 to 0. However, in this study, the calculated $D$ using the OPLS2005 model was 117% higher than that using the 70% DFT model. This large difference only resulted from the difference of the partial charges, as all other force field parameters were identical. This indicates that the modification of the partial charges, instead of reducing the default 1-4 intramolecular scaling factor, is one of the key parameters in determining the transport
properties of the TBP molecules. In addition, according to Tables S3.2 and S3.3, the self-diffusion coefficients of TBP have also been shown to be sensitive to the parameters in the Lennard-Jones potential. In this paper, we have consistently used the OPLS-2005 parameters for the Lennard-Jones potentials and the bonded interactions, focusing on the effects of the partial charges alone. It may be the case, however, that to capture both equilibrium and transport properties satisfactorily, a full re-parameterisation of all the terms in the force field will be required. This is a big undertaking and is a possible avenue for future research.

3.4.1.3 SAXS profiles.

Pure TBP systems using different TBP models were simulated, where each system contained 500 TBP molecules. The $I(q)$ of the systems are estimated based on atom pair correlation functions using Eq. 3.4:

$$I(q) = I_e(q) \left\{ \left< F^2 \right> + \sum_{i=1}^{N} \sum_{j \neq i=1}^{N} f_i(q)f_j(q) \left( 1 + \int_{0}^{\infty} 4\pi r^2 \sqrt{\rho_i \rho_j} \left[ g_{ij}(r) - 1 \right] \frac{\sin(qr)}{qr} \, dr \right) \right\}. \quad (3.4)$$

Here $\rho_i$ and $\rho_j$ are the number densities of atoms $i$ and $j$ respectively, $g_{ij}(r)$ is the atomic pair correlation function between atom types $i$ and $j$, $f_i(q)$ is the atomic scattering factor of atom type $i$ calculated from the numerical Hartree-Fock wave functions, $\left< F^2 \right>$ is the scattering due to the averaged form factor of an isolated molecule and is given by Eq. 3.5, and $I_e(q)$ is the scattered X-ray intensity that crosses unit area perpendicular to the direction of propagation. It is given by Eq. 3.6.

$$\left< F^2 \right> = \sum_{i=1}^{N} \sum_{j \neq i=1}^{N} \left( f_i(q)f_j(q) \frac{\sin(qr)}{qr} \right). \quad (3.5)$$

$$I_e(q) = I_0 \left[ \frac{e^4}{R_0^2 m^2 c^2} \right] \left[ 1 + \cos^2(2\theta) \right]. \quad (3.6)$$

Here, $I_0$ is the intensity of the incident X-ray and $R_0$ is the sample-to-detector distance. These were set to be the same as in our experimental SAXS measurements. $e$ and $m$ are the charge and mass of the electron, respectively, and $c$ is the speed of propagation of radiation in the vacuum.

The calculated scattering intensities, $I(q)$, covered a $q$ range from 0.9 to 39 nm$^{-1}$. The minimum $q$ values that we could obtain were limited by the size of our simulation boxes. The smallest $q$ value attainable is given by $2\pi/d_{Box}$, where $d_{Box}$ is the length of the
simulation box. In order to achieve a $q$ value of 0.1 nm$^{-1}$, which would be comparable to the smallest values of $q$ observed experimentally, we would need to increase the number of particles simulated by a factor of roughly 700. Currently our system contains approximately 80,000 atoms. A 30 ns run, on our local computer, takes of the order of 12 days. It is therefore currently unfeasible to calculate scattering intensities at significantly smaller values of $q$.

Figure 3.3. Calculated and experimentally obtained SAXS profiles for pure TBP.

Figure 3.3 shows the calculated and experimentally obtained SAXS profiles for TBP. In Figure 3.3, two scattering peaks are observed at around $q = 6.4$ and 13.9 nm$^{-1}$. According to all the computational simulations for $I(q)$, one peak at $q = 6.4$ nm$^{-1}$ would be attributed to the interference between TBP molecules. Note that the average distance $d$, which is calculated as $d = 2\pi/q$, between TBP molecules can be estimated as 0.98 nm. The other peak at $q = 13.9$ nm$^{-1}$ is attributed to the intramolecular interactions of TBP, where the peak positions hardly change in all simulations and experiment. The value of $d$ was underestimated by three of the parameter sets in comparison with experiment (60% MNDO, 70% DFT and refined), and overestimated in case of the 90% DFT. These results indicate that $I(q)$ from the OPLS2005 model exhibits good agreement with experiment over a wide
The prediction of the microscopic structure of TBP by the refined model shows closer still agreement with the experiment. It is worth noting that the differences in the height of the peaks between the calculated and experimental SAXS profiles may be attributed to the effect on $q$-resolution of SAXS apparatus. The experimental errors of the peak heights are estimated to be ±20%.

3.4.2 Prediction of TBP/H$_2$O mixtures

Water is one of the major components in the nuclear extraction process and has strong interactions with both the actinides and the TBP molecules. The accuracy of the TBP-water interactions in the simulations may have a significant influence on the behaviour of TBP molecules at the interface, or the structure of the third phase. Hence, it is important for the TBP model to be able to accurately predict the interactions between the TBP and water molecules.

3.4.2.1 Free energy of solvation of water in TBP

In this study, we used Bennett’s acceptance ratio method (BAR)$^{61}$ to calculate the Gibbs free energy of solvation for a water molecule at infinite dilution in TBP solution under ambient conditions. Both the TIP3P$^{62}$ and the SPC/E$^{23}$ water models were tested. One water molecule was centred in a cubic box of 86 TBP molecules, with an approximate side length of 3 nm. The BAR method was performed using 16 intermediate states, $\zeta$, between 0 and 1 ($\zeta = 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.94, 0.98, 0.99, \text{and } 1.00$). At $\zeta = 0$ interactions between water and the surrounding TBP are switched off and at $\zeta = 1$ the water molecules fully interact with TBP. Both the Coulomb and Van der Waals interactions were coupled simultaneously by $\zeta$, and a soft-core potential$^{63}$ was used for water to prevent discontinuities when $\zeta$ approached either 0 or 1. The details of the soft-core potential are given in Section 3.6. The $\zeta$ points were chosen in order to get a smooth variation of the $\frac{dH}{d\zeta}$ profile. For each value of $\zeta$, the system was first equilibrated for 5 ns and the results were obtained from 2 ns production run (Table 3.6).

It is seen that the 90% DFT model yielded the closest $\Delta G_{\text{sol}}$ values for both the TIP3P and the SPC/E models, because it was optimised for TBP-water interactions. The refined TBP model correctly predicted $\Delta G_{\text{sol}}$ using SPC/E water but underestimates $\Delta G_{\text{sol}}$ with TIP3P water, which is again due to the universally applied partial charges on TBP. However, the
OPLS2005 model, which could be the best TBP model so far in terms of simulations of TBP in organic environment, significantly underestimated the value of $\Delta G_{\text{sol}}$.

**Table 3.6.** Free energies of solvation of water in TBP solution.

<table>
<thead>
<tr>
<th>Tested charge sets</th>
<th>$\Delta G_{\text{sol}}$ of H$_2$O in TBP (kJ mol$^{-1}$) using TIP3P water</th>
<th>using SPC/E water</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% MNDO</td>
<td>-6.12 ± 0.29</td>
<td>-6.52 ± 0.31</td>
</tr>
<tr>
<td>70% DFT</td>
<td>-10.20 ± 0.68</td>
<td>-10.71 ± 0.29</td>
</tr>
<tr>
<td>90% DFT</td>
<td>-18.27 ± 0.54</td>
<td>-20.30 ± 0.60</td>
</tr>
<tr>
<td>OPLS2005</td>
<td>-6.70 ± 0.48</td>
<td>-6.91 ± 0.52</td>
</tr>
<tr>
<td>refined</td>
<td>-17.42 ± 0.62</td>
<td>-19.23 ± 0.69</td>
</tr>
<tr>
<td>expt.</td>
<td>-19.58*</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental value from Peverati et al., where the statistical error was not given. The errors of the calculated $\Delta G_{\text{sol}}$ were estimated by splitting the data into blocks with respect to simulation time and determining the average variance of free energy differences over those blocks, assuming the blocks are independent.

### 3.4.2.2 Density of water saturated TBP solutions

The densities of water saturated TBP solutions were computed at a constant pressure of 1 bar and at a variety of temperatures ranging from 273.15 K to 328.15 K. These were then compared with the experimentally measured values, as shown in Figure 3.4. Each simulation system contained 1000 molecules in total and the molar ratio between water and TBP were set as 1.13, 1.05, 0.98 and 0.93 for systems at temperatures of 273.15 K, 298.15 K, 313.15 K and 328.15 K. A 5 ns equilibration run was performed for each system, followed by a 2 ns production run. Both the SPC/E and TIP3P water models were used in each simulation.

Figure 3.4 shows that the predicted densities from the refined model are closest to the experimental values, with less than 0.5% deviation compared to the experimental data. The 90% DFT model overestimated the densities of water saturated TBP solutions by 2% on average, despite its good prediction of $\Delta G_{\text{sol}}$. The other three TBP models, although showing reasonable density values, are not satisfactory because they predict that TBP is immiscible with water over a wide temperature range. The simulation results using TIP3P water model, which is shown in Figure S3.2 in Section 3.6, showed no significant difference to the results using SPC/E model. The final configurations of the water saturated TBP systems at 298.15 K are shown in Figure 3.5. It is seen from Figures 3.5a and d that
513 water molecules have aggregated into single large water clusters, with very few water molecules in the bulk, when the 60% MNDO and OPLS2005 models were used. In addition, Figure 3.5b shows a simulation snapshot of the 70% DFT model, where 513 water molecules have formed two large water clusters with no more than 20 water molecules in the bulk TBP. This shows that these three models show a much lower saturation concentration of water in TBP as compared with experimental data. Simulations using the 90% DFT and refined models, shown in Figures 3.5c and e, predict that the water molecules are evenly scattered in the bulk TBP to form homogeneous systems, in agreement with experiment.

**Figure 3.4.** Calculated densities of water saturated TBP solutions at different temperatures using SPC/E water; trend lines are added for clarity; experimental values were obtained from Hardy *et al.*\(^65\)

In conclusion, the refined model was the best among the five TBP models in predicting the properties relating to TBP-water interactions. The 90% DFT model, which was particularly optimised for TBP-water interactions, has also shown good accuracy. On the other hand, the remaining three models showed poor accuracy in predicting the TBP-water interactions, especially the mixing properties between TBP and water.
3.4.3 Prediction of the properties TBP/n-alkanes binary mixtures

The accuracy of the TBP model in an organic mixture environment, especially in the n-alkane diluent, is also of vital importance as the TBP molecules are active in the organic phase and the organic-aqueous interface in the PUREX process. Hence, a suitable TBP model should not only give accurate predictions of the properties of pure TBP and TBP/water mixtures, but also accurately predict the properties of TBP mixtures in the organic phase. In this study, SAXS profiles of TBP in n-octane or n-dodecane were measured and compared with simulation results, so as to study the microscopic structures of TBP/n-alkane systems. The excess enthalpies of mixing between TBP and n-dodecane molecules, which are strongly related to the interactions between TBP and n-dodecane molecules, were also calculated and compared to experimental data.
3.4.3.1 Validation of the \( n \)-Dodecane model using the OPLS-2005 force field.

The original \( n \)-dodecane models using ether the OPLS-AA or the AMBER force fields were reported to show an undesirable liquid-to-gel phase transition at ambient conditions.\(^{16,66}\) Hence, the long-chain alkane model must be validated before carrying out any simulation. In this study, we used the OPLS-2005 force field parameters for \( n \)-dodecane. The \( n \)-dodecane systems with different system sizes, with 50, 200 and 500 molecules respectively, were simulated in the NPT ensemble at 298.15 K and 1 bar. The densities were calculated and compared with experimental data.

The densities of the system that contains 500 \( n \)-dodecane molecules are shown in Figure S3.3 in Section 3.6. It is seen that the density, using the OPLS-2005 force field, does not show any sign of a liquid-to-gel phase transition as the density does not increases with time. The average density obtained was 751.7 kg m\(^{-3}\) from the simulation, which presents a 1% deviation compared with the experimental value of 745.8 kg m\(^{-3}\).\(^{56}\) In addition, the results obtained from different system sizes were extremely similar with a standard deviation of 0.13 kg m\(^{-3}\). Hence, the simulated densities were not affected by the finite size of the systems. Therefore the OPLS-2005 \( n \)-dodecane model was deemed suitable for the simulations of \( n \)-dodecane molecules at ambient conditions.

3.4.3.2 SAXS profiles.

Figure 3.6 shows the calculated and experimentally obtained SAXS profiles for \( n \)-octane and \( n \)-dodecane, where the OPLS-2005 force field parameters were used for both \( n \)-alkane models. Both the \( n \)-octane and \( n \)-dodecane models predicted the position of the scattering peak around \( q = 13.9 \) nm\(^{-1}\) as shown in Figures 3.6a and b, respectively. Furthermore, in both cases, the simulated profiles exhibited good agreements with experiment over a wide \( q \) region. This indicates that the \( n \)-octane and \( n \)-dodecane models using the OPLS-2005 force field give good predictions of the microscopic structure of \( n \)-octane and \( n \)-dodecane at ambient conditions. Again we note that the estimated error on the experimental peak height is ±20%.

The calculated and experimentally obtained SAXS profiles of TBP/\( n \)-alkane mixtures are shown in Figures 3.7-3.9. It is seen from Figures 3.7-3.9 that each model gives a good prediction of the position of the scattering peak around \( q = 13.9 \) nm\(^{-1}\), which corresponds to the internal structure interactions of the TBP and \( n \)-alkanes molecules. However, a large difference was observed at \( q < 10 \) nm\(^{-1}\), which was more likely to be related to the intermolecular structures.
Figure 3.6. Calculated and experimental SAXS profiles for (a) n-octane, (b) n-dodecane systems using the OPLS-2005 force field.

In Figure 3.7, none of the calculated profiles match the correct \( q \)-dependence for \( q < 10 \) \( \text{nm} \)^{-1}. All the calculated profiles show an increase between 3 and 10 \( \text{nm} \)^{-1}, while the SAXS profile is relatively flat. However, the profile obtained using the OPLS2005 model presents a tiny and broad characteristic peak at \( q \sim 7 \) \( \text{nm} \)^{-1} where the SAXS profile exhibits a tiny broad peak as well. This indicates that the OPLS2005 model is able to predict part of the intermolecular structure in the 30% TBP/n-octane solution, although none of the models are completely accurate.

Figure 3.7. Calculated and experimental SAXS profiles for systems of 30% TBP in n-octane.
This is not the case in Figure 3.8, where the volume fraction of TBP has been increased to 50%. In this case, the calculated profile from the OPLS2005 model shows good agreement with the SAXS profile over a wide $q$ region. Although it exhibits less agreement with the experiment, the refined model is able to accurately predict the position of the characteristic peak at $q \sim 6.5$ nm$^{-1}$ and the $q$-dependence at $q < 4$ nm$^{-1}$. The other three models, however, are not able to predict the correct position of the characteristic peak at $q \sim 6.5$ nm$^{-1}$, which indicates that they are not able to predict the intermolecular distances correctly in the 50% TBP/n-octane solution,

![Graph](image)

**Figure 3.8.** Calculated and experimental SAXS profiles for systems of 50% TBP in n-octane.

The simulation and experiment results for the 30% TBP in n-dodecane solution are shown in Figure 3.9. Both the OPLS2005 and the refined models show relatively good agreement with the experiment over a wide range of $q$ in terms of the $q$-dependence. The other three models, however, fail to predict the correct position of the characteristic peak at $q \sim 6.5$ nm$^{-1}$ in the TBP/n-dodecane mixture.

Based on the comparison between the calculated and experimental SAXS profiles, the OPLS2005 model is able to predict the microscopic structure and the aggregation behaviour of the molecules in the 30% TBP in n-dodecane and the 50% TBP in n-octane mixtures accurately. The refined model is accurate for the 30% TBP in n-dodecane mixture but less so for the TBP/n-octane mixtures. In addition, the performances of the other three
TBP models are much worse and are not able to predict the correct structures in TBP/n-alkane mixtures. Therefore, the OPLS2005 model is the best in the investigations of the microscopic structure and the aggregation behaviour of TBP molecules in the organic environment through simulations. The dielectric constant of \textit{n}-octane was not used in the DFT optimisation for the refined model, thus it is not surprising that it has better performance in the TBP/\textit{n}-dodecane mixture than the TBP/\textit{n}-octane mixtures. In the nuclear extraction process, \textit{n}-dodecane is the main component of the organic diluent. Thus, the refined model is an adequate one for simulating the nuclear extraction system.

![Figure 3.9. Calculated and experimental SAXS profiles for systems of 30% TBP in \textit{n}-dodecane.](image)

3.4.3.3 Excess enthalpy of mixing of TBP and \textit{n}-dodecane.

The excess enthalpy calculations were performed using relatively small simulation cells (approximately 7000 atoms). However, longer runs were performed with these systems in order to minimise statistical errors. These TBP/\textit{n}-dodecane systems with different TBP models were simulated for 50 ns during the equilibrium run and 5 ns during the production run.

The excess molar enthalpy of mixing, $\Delta H_{\text{ex}}$, which represents the heat released or taken up upon the mixing of TBP and \textit{n}-dodecane liquids, was calculated by subtracting the enthalpies of the pure components from the molar enthalpy of the mixture, using Eq. 3.7:
\[ \Delta H_{\text{ex}} = H_{\text{mix}} - x_1 H_1 - x_2 H_2, \]  

(3.7)

where \( x_1 \) and \( x_2 \) are the mole fractions of TBP and \( n \)-dodecane respectively, \( H_1 \) and \( H_2 \) are the molar enthalpies of the pure TBP and pure \( n \)-dodecane, respectively, \( H_{\text{mix}} \) is the molar enthalpy of the mixture. \( H \) is calculated as \( H = U + PV \), where \( U \) is the average internal energy of the system, \( P \) is the average pressure and \( V \) is the average volume of the simulation box. The calculated results were compared with the experimental values, as shown in Figure 3.10.

![Image](image_url)

**Figure 3.10.** Calculated excess enthalpy of mixing of different TBP/\( n \)-dodecane mixtures; trend lines are added for clarity.

All the models correctly predict the endothermic mixing of TBP and \( n \)-dodecane, as found experimentally. The 60% MNDO and the OPLS2005 models give the best predictions, though they slightly underestimate its value. The next best is the 70% DFT charge model, which gives good predictions at low mole fractions of TBP. The refined model overestimates \( \Delta H_{\text{ex}} \). This is unsurprising since the charges of the refined model were calculated by averaging the calculated TBP charges obtained in pure TBP, \( n \)-dodecane and water; the averaged charge set is approximately 4% more polar than the TBP surrounded by \( n \)-dodecane. Thus the TBP-TBP attractive interaction is somewhat higher and thus the
enthalpy of mixing is more endothermic. Nevertheless, in theory, the accuracy of the refined model in predicting the $\Delta H_{ex}$ could be improved by increasing the attraction between TBP and $n$-dodecane by accounting for the polarity of TBP. This could be achieved by abandoning the standard combining rules for the cross-terms $\varepsilon_{ij}$ and $\sigma_{ij}$ in Eq. 3.1 for specific pairs of atoms $i$ and $j$, while retaining the same parameters for other interactions. This could be a useful future investigation.

In conclusion, the OPLS2005 model is more appropriate for the simulations of TBP/$n$-alkane systems in terms of both the microscopic structure and thermodynamic properties. The refined model can predict the microscopic structure of the molecules in the TBP/$n$-alkane systems with moderate accuracy, but somewhat overestimates the enthalpies of mixing as a result of compromising on TBP-$H_2O$ potentials. The 60% MNDO model predicted the interactions between TBP and $n$-dodecane well, but cannot accurately predict the microscopic structure. The performance of the scaled DFT models is even less satisfactory.

3.5 Conclusions

The performance of five TBP models has been examined by comparing their predictions of the thermodynamic properties, transport properties and the microscopic structures of the pure TBP liquid, TBP/water mixture and TBP/$n$-alkane mixtures. Different models have shown different strengths and weaknesses in predicting thermodynamic, kinetic, and structural properties as the models were optimised based on different criteria. The general picture is that if one chooses the partial charges on the TBP to give good predictions for the properties of TBP-$n$-alkane mixtures, one fails badly in describing TBP-water interactions. If, instead, one chooses the atomic charges to give a good account of TBP-water systems, one gets poor results for TBP-$n$-dodecane mixtures. Thus the OPLS2005 TBP model is the best TBP model for MD simulations in organic environments, doing well, for example, in predicting the excess enthalpy of mixing of TBP and $n$-dodecane. It fails completely, however, in describing the behaviour of TBP in water, showing demixing for compositions that are shown to be homogeneous solutions under experimental conditions. On the other hand, other models, such as the 90% DFT model, give good predictions for TBP-$H_2O$ interactions, but they perform badly in predicting TBP-$n$-alkane interactions. Thus the predicted enthalpy of mixing for TBP-$n$-dodecane at a TBP mole fraction of 0.5 is too large by a factor of 2.5. Our refined TBP model, however, is a good compromise,
giving reasonable predictions for both TBP-$n$-alkane and TBP-water systems. Thus this model is a good candidate for use in situations where the TBP interacts simultaneously with both polar and non-polar molecules. An obvious example where such a model is necessary is in the modelling of the liquid-liquid nuclear extraction process. Here TBP acts as a ligand to certain actinide ions and transports them from an acidic aqueous phase to an organic phase, where the organic diluent is an $n$-alkane. The organic phase contains the $n$-alkane diluent, TBP, water, nitric acid and the actinide ions. To simulate this phase or, indeed, to simulate the interface between the aqueous and organic phases, one needs a TBP model that can interact correctly with both hydrophobic and hydrophilic species. We have used our refined model to study such systems and the results will be published in future articles.

Because the proposed TBP model uses OPLS-2005 Lennard-Jones parameters, it may be used with confidence to model mixtures of TBP with other species whose parameters are given by the OPLS-2005 force-field. This was indeed our motivation for varying only the atomic partial charges when considering TBP models. While we believe our refined model is a good candidate for modelling nuclear extraction, it is clearly far from perfect. The transport properties of TBP are not well predicted and the enthalpy of mixing of TBP and $n$-dodecane is significantly over-estimated. Improving on these predictions, while still retaining a good description of TBP-water interactions, will be a major enterprise. One may be able to make some progress by refining the Lennard-Jones parameters and the intra-molecular energy terms, but our suspicion is that what will eventually be needed is a polarisable force-field. Until such a development, however, we believe our model will prove to be a useful tool for gaining insight into how TBP interacts with both the polar and non-polar molecules present in nuclear extraction processes.
### 3.6 Supporting information

#### Table S3.1. Calculated DFT charges.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Gas phase</th>
<th>TBP in water</th>
<th>TBP in dodecane</th>
<th>TBP in bulk</th>
<th>Average of the three liquid state charge sets</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$q_i$</td>
<td>$q_i$</td>
<td></td>
</tr>
<tr>
<td>O2</td>
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<td>-0.7070</td>
</tr>
<tr>
<td>P</td>
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<td>-0.5047</td>
</tr>
<tr>
<td>C_a</td>
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<td>0.1222</td>
</tr>
<tr>
<td>C_b</td>
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<td>0.029911</td>
<td>0.029336</td>
<td>0.029716</td>
<td>0.0297</td>
</tr>
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<td>C_d</td>
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<td>-0.248128</td>
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<td>H_a</td>
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<td>0.036507</td>
<td>0.035510</td>
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<tr>
<td>H_b</td>
<td>0.022533</td>
<td>0.023173</td>
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<td>0.0232</td>
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<tr>
<td>H_c</td>
<td>-0.018835</td>
<td>-0.017147</td>
<td>-0.017974</td>
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<tr>
<td>H_d</td>
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<td>0.059689</td>
<td>0.057780</td>
<td>0.059170</td>
<td>0.0589</td>
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</tbody>
</table>

*This charge set was obtained by fitting to the optimised geometry of a single TBP. °This charge set was obtained by fitting to the optimised geometry of TBP in bulk water, where the water solvent is represented by polarisable continuum model (PCM). †This charge set was obtained by fitting to the optimised geometry of TBP in bulk dodecane, where the dodecane solvent is represented by PCM. ‡This charge set was obtained by fitting to the optimised geometry of a single TBP. §This charge set is the average of the three charge sets obtained from liquid state TBP and these were the charges used for the ‘refined’ model. ‖Unit in e.

#### Table S3.2. Optimisation of carbon-carbon Lennard-Jones parameter for the refined TBP model by varying the $\sigma$ value at ambient condition.

<table>
<thead>
<tr>
<th>$\varepsilon_i$ (kJ mol$^{-1}$)</th>
<th>$\sigma_i$ (nm)</th>
<th>Density (kg m$^{-3}$)</th>
<th>Diffusion coefficient (10$^{-6}$ cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3100</td>
<td>943.91 ± 0.66</td>
<td>1.971 ± 0.082</td>
<td></td>
</tr>
<tr>
<td>0.3150</td>
<td>953.71 ± 0.64</td>
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<td>0.3400</td>
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<td>997.00 ± 0.77</td>
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<td>0.3700</td>
<td>994.90 ± 0.75</td>
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<tr>
<td>0.3800</td>
<td>988.94 ± 0.80</td>
<td>0.124 ± 0.005</td>
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</tr>
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</table>

*Experimental value is 972.7 kg m$^{-3}$ from Fang et al.$^{51}$ °Experimental value is 2.29 × 10$^{-6}$ cm$^2$ s$^{-1}$ from Tian et al.$^{56}$
Table S3.3. Optimisation of carbon-carbon Lennard-Jones parameter for the refined TBP model by varying the $\varepsilon$ value at ambient condition.

<table>
<thead>
<tr>
<th>$\sigma_{ij}$ (nm)</th>
<th>$\varepsilon_{ij}$ (kJ mol$^{-1}$)</th>
<th>Density (kg m$^{-3}$)$^a$</th>
<th>Diffusion coefficient ($10^6$ cm$^2$ s$^{-1}$)$^b$</th>
</tr>
</thead>
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<tr>
<td>0.3100</td>
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<td>813.49 ± 0.64</td>
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</tr>
<tr>
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<td>0.2716</td>
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<td>1.971 ± 0.082</td>
</tr>
<tr>
<td></td>
<td>0.4074</td>
<td>1016.40 ± 0.67</td>
<td>0.458 ± 0.046</td>
</tr>
<tr>
<td>0.3250</td>
<td>0.1358</td>
<td>850.53 ± 0.47</td>
<td>4.724 ± 0.319</td>
</tr>
<tr>
<td></td>
<td>0.2716</td>
<td>970.74 ± 0.60</td>
<td>1.082 ± 0.057</td>
</tr>
<tr>
<td></td>
<td>0.4074</td>
<td>1034.70 ± 0.75</td>
<td>0.175 ± 0.014</td>
</tr>
<tr>
<td>0.3500</td>
<td>0.1358</td>
<td>887.44 ± 0.55</td>
<td>2.523 ± 0.182</td>
</tr>
<tr>
<td></td>
<td>0.2716</td>
<td>994.77 ± 0.82</td>
<td>0.341 ± 0.032</td>
</tr>
<tr>
<td></td>
<td>0.4074</td>
<td>1051.52 ± 0.49</td>
<td>0.044 ± 0.006</td>
</tr>
<tr>
<td>0.3700</td>
<td>0.1358</td>
<td>899.45 ± 0.52</td>
<td>1.988 ± 0.148</td>
</tr>
<tr>
<td></td>
<td>0.2716</td>
<td>997.90 ± 0.75</td>
<td>0.146 ± 0.013</td>
</tr>
<tr>
<td></td>
<td>0.4074</td>
<td>1060.24 ± 0.77</td>
<td>0.032 ± 0.005</td>
</tr>
</tbody>
</table>

$^a$Experimental value is 972.7 kg m$^{-3}$ from Fang et al.$^{51}$ $^b$Experimental value is $2.29 \times 10^{-6}$ cm$^2$ s$^{-1}$ from Tian et al.$^{56}$

Figure S3.1. Diffusion coefficients of TBP for different simulation box side lengths, $D$, using the five TBP models; the experimental data for the self-diffusion coefficient of TBP is $2.29 \times 10^{-6}$ cm$^2$ s$^{-1}$. $^{57}$
Figure S3.2. Calculated densities of water saturated TBP solutions at different temperatures using TIP3P water; trend lines are added for clarity; experimental values were obtained from Hardy et al.65

Figure S3.3. Calculated densities of n-dodecane as a function of time using the OPLS-2005 force field.
Table S3.4. Calculated density, self-diffusion constant and shear viscosity values of united-atom TBP at 298.15 K and 1 bar.

<table>
<thead>
<tr>
<th>Tested charge sets</th>
<th>ρ (kg m⁻³)</th>
<th>D (x10⁻⁶ cm² s⁻¹)</th>
<th>η (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA</td>
<td>1132.1 ± 0.2</td>
<td>3.704 ± 0.047</td>
<td>1.839 ± 0.095</td>
</tr>
<tr>
<td>expt.</td>
<td>970.83b</td>
<td>2.29c</td>
<td>3.399b</td>
</tr>
</tbody>
</table>

*United atom model taken from the SET-5 model from Benay et al.\textsuperscript{4} Experimental values are from Tian et al.\textsuperscript{56} Experimental values are from Tsimering et al.\textsuperscript{57}*

Figure S3.4. Calculated and experimentally obtained SAXS profiles for pure TBP, the united-atom model was taken from the SET-5 model from Benay et al.\textsuperscript{15}

**Soft-core Potential**

Soft-core potential helps to avoid particles to get very close to each other during the simulations, especially at ξ close to 0 or 1. The soft-core potentials $E_{sc}$ are shifted versions of the regular potentials and take the form\textsuperscript{63}

$$E_{sc}(r) = (1 - \xi)E^A(r_A) + \xi E^B(r_B),$$ (3.7)

$$r_A = (\alpha \sigma^6_A \xi^p + r^6)^{1/6},$$ (3.8)

$$r_B = (\alpha \sigma^6_B (1 - \xi)^p + r^6)^{1/6},$$ (3.9)

where $E^A$ and $E^B$ are the normal ‘hard core’ Van der Waals or electrostatic potentials in state A ($\xi = 0$) and state B ($\xi = 1$) respectively, $\alpha$ is the soft-core parameter, $p$ is the soft-core $\xi$ power, $\sigma$ is the radius of the interaction. In this study, $\alpha$, $p$ and $\sigma$ were set to be 1.0, 1 and 0.3 nm, respectively.
Acknowledgments

The authors would like to thank Professor Shengting Cui for helpful email contact and discussions. We also thank the University of Manchester for use of the Computational Shared Facility (CSF). This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant-in-Aid for Scientific Research B, 2014-2018, No. 26289368).

3.7 References


4 A novel micro-emulsion phase transition: towards the elucidation of third phase formation in spent nuclear fuel reprocessing

4.1 Preface

This chapter presents part of some collaborative research with Dr. Ryuhei Motokawa, on the investigation of light-organic/third phase co-existence and their corresponding microscopic structure in the TBP/n-dodecane/HNO\textsubscript{3}/H\textsubscript{2}O systems.

J. Mu carried out all the molecular dynamics simulations and analysis while Dr. Motokawa carried out the experiments.

The Chapter was written as a manuscript and submitted to The Journal of Physical Chemistry B, and is reproduced here with a few minor modifications.
A Novel Micro-Emulsion Phase Transition: Towards the Elucidation of Third Phase Formation in Spent Nuclear Fuel Reprocessing

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Abstract

We present evidence that the organic/third phase transition, as may be observed in the Plutonium Uranium Reduction EXtraction process (PUREX) at high metal loading, is an unusual transition between two isotropic, bi-continuous micro-emulsion phases. As this system contains so many components, however, we seek first to investigate the properties of a simpler system, viz. the related metal-free, quaternary system of water/n-dodecane/nitric acid/tri-butyl phosphate (TBP). Under appropriate conditions, this system exhibits three co-existing phases, namely the light organic phase, the third phase and the aqueous phase. In this paper, we focus on the two phase co-existence between the light organic and the third phase. Using Gibbs Ensemble Monte Carlo (GEMC) simulations, we find phase co-existence between a phase rich in nitric acid and dilute in n-dodecane (the third phase) with a phase more dilute in nitric acid and rich in n-dodecane (the light organic phase). The compositions and densities of these two co-existing phases are in good agreement with experiment. Because the systems are dense and the molecules involved are not simple, the particle exchange rate in the GEMC simulation can be rather low. To show that the system, at a composition intermediate between that of the observed third and organic phases, is indeed unstable with respect to phase separation, we use the Bennett acceptance ratio method to calculate the Gibbs energies of the homogeneous phase and the weighted average of the two co-existing phases, where the compositions of these phases were taken both from GEMC and from experiment. Both demixed states have a statistically significant lower Gibbs energy than the uniform, mixed phase, providing confirmation that GEMC correctly predicts phase separation. Snapshots from the simulations as well as the cluster analysis of the organic and third phases reveal structures akin to bi-continuous micro-emulsion phases, where the polar species reside within a mesh whose surface consists of amphiphilic TBP molecules. The non-polar n-dodecane molecules are outside this mesh. The large-scale structural differences between the two phases lie solely in the dimensions of the mesh. Evidence for the correctness of these structures comes from small-angle X-ray scattering (SAXS), where the profiles obtained for both the organic and third phases agree well with those calculated from simulation. Finally we look at the microscopic structures of the two phases. In the organic phase, the basic motif is that of one nitric acid molecule hydrogen bonded to a TBP. In the third phase, the most common structure was that of the hydrogen bonded chain TBP–HNO$_3$–HNO$_3$. A cluster analysis provides evidence that the TBP forms an extended, connected network in both phases. Studies of the effects of metal ions on these systems will be presented elsewhere, but
suffice it to say here that these ions do not change the basic bi-continuous structure of the phases. The metal ions reside inside the mesh along with the other polar molecules.
4.2 Introduction

The Plutonium Uranium Reduction EXtraction (PUREX) process is a well-established liquid-liquid extraction process for extracting plutonium and unused uranium from the other fission products formed in a nuclear reactor. The metals are dissolved in concentrated nitric acid whereupon an organic diluent (typically odourless kerosene) and a ligand, tributyl phosphate (TBP) are added. The TBP selectively complexes with the uranyl and plutonium nitrates and the complexes end up in the organic phase. From there, the uranium and plutonium are recovered. At high metal loading, however, the organic phase may itself separate into two phases. The heavy lower layer, which is commonly named the third phase, contains high concentrations of the metal-ion/TBP complexes and mineral acids. The light upper layer, which is commonly named the light organic phase, contains a lower concentration of metal ions, TBP and mineral acids but is rich in the organic diluent. Third phase formation is highly undesirable as firstly it spoils the extraction process and secondly, the concentrations of uranium and plutonium in the third phase may be high enough to risk nuclear criticality.

In the past few decades, extensive experiments have been carried out to delineate under what conditions the third phase forms and to investigate the microscopic structures of the two, co-existing phases. Nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), and infra-red spectroscopy gave information about the molecular structures into atomic-length scale, while small-angle X-ray and neutron scattering (SAXS and SANS) measurements aimed to characterise larger structures at the nano-length scale. A popular hypothesis was that the metal/TBP complexes formed reverse micelles, as was first proposed by Chiarizia and co-workers on the basis of SANS profiles. A problem, however, is that a SANS, or indeed a SAXS profile can be reproduced by several, different structural models. Considerable care is required to arrive at a correct, unique structure.

It should be noted that third phase formation is not restricted to just the PUREX process. Other extraction processes also show organic/third phase co-existence and it has been suggested that reverse micelles play a key role here also.

To cast further light on the nature of the light organic and third phases in the solvent extraction of plutonium and/or uranium ions, molecular simulation studies have been performed. The results are sensitive to the quality of the force-field used. In particular, one requires a good model of TBP which can describe the interaction of TBP both with an
alkane and with water. In a recent paper\textsuperscript{39} we proposed a TBP model that provided a satisfactory account of TBP with both polar and non-polar molecules, both in terms of thermodynamic and structural properties. It is known, however, that some mineral acids, such as nitric acid, give rise to third phase formation even in the absence of metal ions.\textsuperscript{15} It is therefore sensible to consider such simpler systems before moving on to investigate the effects of metal nitrates. We thus study the phase behaviour of the TBP/\textit{n}-dodecane/HNO_3/H_2O system and investigate the nature of any structures formed. To do this, we perform both Gibbs Ensemble Monte Carlo (GEMC)\textsuperscript{40} and molecular dynamics (MD) simulations in conjunction with SAXS experiments. The findings obtained here should contribute to the evolving understanding of the mechanism of third phase formation involving the metal ions.

4.3 Methodology

4.3.1 Experimental section

4.3.1.1 Materials.

TBP was purchased from Tokyo Chemical Industry (Tokyo, Japan) and dried overnight under molecular sieves (Wako Pure Chemical Industries, Osaka, Japan) before use. Fuming nitric acid and \textit{n}-dodecane were purchased from Wako and used as received. The water used in this study was deionized by a Millipore Milli-Q purification system.

<table>
<thead>
<tr>
<th>Molecular species</th>
<th>Mole fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light organic phase</td>
</tr>
<tr>
<td>TBP</td>
<td>15.2</td>
</tr>
<tr>
<td>\textit{n}-dodecane</td>
<td>69.2</td>
</tr>
<tr>
<td>HNO_3</td>
<td>13.9</td>
</tr>
<tr>
<td>H_2O</td>
<td>1.6</td>
</tr>
</tbody>
</table>

4.3.1.2 Sample preparation.

Samples of both the third phase (heavy organic phase) and the light organic phase were prepared as follows. A given volume of 15.8 M nitric acid was mixed with the same
volume of a 1.1 M TBP solution in \( n \)-dodecane. The mixture was shaken for 1 h at 298 K in a glass tube, and then centrifuged. This led to the formation of three co-existing phases, i.e. an aqueous phase, the third phase and the light organic phase (see Section 4.6). Each aliquot of third and light organic phases was loaded into glass capillary cells with 0.01-mm-thick walls and a 2.0 mm sample thickness. All of the SAXS profiles were acquired at 298 K. The compositions of the third and light organic phases are given by Ivanov and co-workers\(^{41}\) and are reproduced in Table 4.1.

4.3.1.3 SAXS experiments.

SAXS measurements were performed using X-ray diffraction apparatus (NANO-Viewer, Rigaku). The wavelength of the incident X-ray beam generated from a Cu-K\(\alpha\) line, \( \lambda \), was 0.154 nm, where the incident beam was focused to a spot 450 \( \mu \)m in diameter at the sample position with a confocal optic (Max-Flux, Rigaku) equipped with a pinhole slit collimator. The scattered X-rays from the sample were detected by a two dimensional position-sensitive detector (PILATAS 100K/R, RIGAKU), with 195 \times 487 pixels (33.5 \times 83.8 mm) and a spatial resolution of 0.172 mm, covering a \( q \) range from 0.2 to 34 \( \text{nm}^{-1} \) at three sample-to-detector distances of 64, 115, and 671 mm. \( q = \frac{(4\pi/\lambda)\sin\theta}{\text{r}} \) is the magnitude of the scattering vector, where \( 2\theta \) is the scattering angle. The scattering data recorded by the detector were corrected for counting efficiency, instrumental background and air scattering on a pixel-to-pixel basis. The X-ray scattering intensity distribution, \( I(q) \), was circularly averaged, and converted to absolute unit of the scattering intensity of reciprocal centimetre (cm\(^{-1}\)) by calibration with water scattering.\(^{42}\) Cell scattering was subtracted from \( I(q) \) by considering the transmission, where the \( I(q) \) can be reproduced on the basis of atom pair radial distribution functions from simulations as employed in our previous literature.\(^{39}\)

4.3.2 Simulation approaches

In this study, the force field potentials and the all-atom TBP model used are as described in our previous publication.\(^{39}\) The \( n \)-dodecane model was taken from the OPLS-2005 force field\(^{43}\) and the TIP3P model was used for \( \text{H}_2\text{O} \) as it was optimised for use with OPLS force fields.\(^{44}\) The models used here were able to describe both TBP/alkane and TBP/water systems with reasonable accuracy both in terms of thermodynamic properties and in terms of reproducing experimental SAXS data.\(^{39}\) The HNO\(_3\) in our system was treated as an
undissociated molecule, based on the assumption that the dissociation constant of HNO_3 is small in an organic environment. The force field parameters for HNO_3 were taken from Price et al.\textsuperscript{45} and was parameterised for the conformational energetics and pure liquid properties. Following OPLS procedures, geometric combining rules were used to obtain the unlike pair interactions.

Both MD and GEMC simulations were carried out to calculate the properties of the light organic and third phases. The GEMC simulations were used to investigate the phase separation of the TBP/n-dodecane/H_2O/HNO_3 systems where the detailed simulation protocol is provided in Section 4.4.1. The MD simulations were performed to calculate the excess Gibbs energy of certain systems as well as to investigate the microscopic structures of the light organic and third phases. For all the MD simulations, cubic periodic boundary conditions were employed and the equations of motion were integrated using the Leapfrog algorithm\textsuperscript{46} with a time step of 1 fs. The OPLS-AA force-field\textsuperscript{47} was used with the specific parameters as given in our previous work.\textsuperscript{39} For both the Lennard-Jones and short range Coulomb interactions a 1.2 nm cut-off was used and potential switch functions\textsuperscript{48,49} were applied from 0.9 nm to 1.2 nm to conserve the energies at the cut-off. For the long-range electrostatic potential the particle-mesh Ewald (PME) method was applied.\textsuperscript{50} The NpT ensemble was used in all MD simulations where the pressure and temperature were set as 1 bar and 298.15 K respectively. For each system considered, an equilibrated structure was obtained from the starting configuration using the velocity-rescaling thermostat\textsuperscript{51} and the Berendsen barostat\textsuperscript{52}. The Nosé-Hoover thermostat\textsuperscript{53,54} and Parrinello-Rahman barostat\textsuperscript{55,56} were applied in the subsequent production runs, during which the simulation results were generated. The number of time steps performed varies with different MD simulations and are provided in detail in Sections 4.4.2 and 4.4.3.

4.4 Results and discussion

4.4.1 Phase co-existence via GEMC simulations

GEMC simulation is a powerful method to investigate the phase behaviour of multiple phases. Unlike conventional Monte Carlo simulations which usually have only one simulation box, GEMC involves the simultaneous use of several simulation boxes. In a GEMC simulation, there are not only particle movements within a simulation box but also different simulations boxes may exchange particles. As the GEMC method simulates different phases in different boxes, it can simulate phase equilibrium using relatively small
systems without suffering from problems associated with phase interfaces, which can be a problem for other methodologies.

GEMC simulations were performed at constant pressure and temperature to discover if our force-field predicted a phase separation of the TBP/$n$-dodecane/H$_2$O/HNO$_3$ system at a high concentration of HNO$_3$. The Towhee 7.1 simulation package was used for these simulations. To investigate two phase co-existence, a GEMC simulation simultaneously does two $NpT$ Monte-Carlo simulations on the system, where the compositions of the two simulation boxes are, in general, different. In addition to the normal $NpT$ Monte Carlo moves on each box, however, there are additional moves that allow particles to transfer from one box to another. When there is no net flux of any species from one box to another, the two boxes are at equilibrium with each another and the average compositions of the two boxes correspond to the compositions of the two co-existing phases. For our particular system, we began with two boxes which initially were of the same volume and which contained mixtures of identical composition and density. This composition was taken as the average of that of the organic and third phases given in Table 4.1. A total number of 520 molecules were simulated in the GEMC simulations. The pressure and temperature were set as 0.1 MPa and 298.15 K respectively. Each GEMC simulation was run for 100,000 cycles, where a cycle consists of $n$ Monte Carlo moves, where $n$ is the total number of the molecules in the two boxes combined. A total of eight types of Monte Carlo moves, which are summarised in Table S4.1 in Section 4.6, were allowed where each molecule species and each box had the same chance to perform a Monte Carlo move. Ten GEMC simulations were performed and the results were calculated as the averages over these ten runs.

The results of the GEMC simulations are shown in Figure 4.1, where the average concentrations of all the molecule species in box 1 and box 2 are shown in Figures 4.1a and b, respectively. In each of the simulation, the box which has fewer $n$-dodecane molecules in the final configuration is always regarded as box 1 due to the fact that each box has equal possibility of becoming either the diluent-dominant phase or the HNO$_3$-dominant phase. Note that the box 1 and 2 correspond to light organic and third phases, respectively, at the late stage of the simulation.
In Figures 4.1a and b, the molar fractions of all molecule species in both boxes vary quickly at the beginning of the GEMC simulations and level off after approximately $0.4 \times 10^5$ Monte Carlo cycles. As noted above, box 1 becomes rich in $n$-dodecane while box 2 becomes rich in HNO$_3$ and H$_2$O at the end of the simulations. The final molar fraction of $n$-dodecane in box 1 is almost twice as much as that in box 2 while the final molar fractions of HNO$_3$ and H$_2$O in box 2 are almost twice and four times as much as that in box 1, respectively. We thus find that the two boxes, even though starting with identical compositions, transform into two different phases. In addition, the final compositions of each molecular species in box 1 and box 2 are similar to the experimentally determined compositions of the organic and third phases as shown in Table 4.1.

While this is extremely encouraging, it must be noted that the system of interest is a dense and viscous system where the swap rate of TBP at the end of the simulations can be as low as $3 \times 10^{-4}$. Hence one may question whether the system is fully equilibrated. In order to provide further evidence that the two-phase co-existence, predicted by the GEMC
simulations, is thermodynamically stable compared to the homogeneous mixture, the Gibbs energies of both mixed and demixed states were calculated and analysed. This is described in Section 4.4.2.

4.4.2 Gibbs energy calculations

Under conditions of constant temperature and pressure, the Gibbs energy of a system is a minimum at equilibrium. To verify that a homogeneous fluid, of composition intermediate between that of the light organic and third phases, is unstable with respect to demixing, we compare the Gibbs energy of a homogeneous state with that of a phase-separated state.

<table>
<thead>
<tr>
<th>System</th>
<th>Species</th>
<th>Molar fraction of each species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Set I (^a)</td>
</tr>
<tr>
<td>Box 1</td>
<td>TBP</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>(n)-dodecane</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>HNO(_3)</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>7.0</td>
</tr>
<tr>
<td>Box 2</td>
<td>TBP</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(n)-dodecane</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>HNO(_3)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)Only one simulation was performed for Set I as it has only one composition.

In this study, the Gibbs energies of three compositions were calculated through MD simulations. These were the homogeneous mixture (set I), the two co-existing phases predicted by GEMC simulations (set II) and the two co-existing phases whose compositions were measured by Ivanov et al. (Table 4.1), denoted by set III. Sets II and III each consist of two boxes, corresponding to the compositions of two demixed systems. This way one may compare the Gibbs energy of the homogeneous system with the weighted average of two sets of demixed systems. The compositions studied are given in Table 4.2. The compositions of the two boxes in configuration set II are the same as the final results of GEMC simulations shown in Figure 4.1. The compositions of the two boxes in set III are as close as possible to the measured compositions of the light organic and third phases shown in Table 4.1, given that a simulation must deal with an integer number
of molecules. The composition of the homogeneous mixture, set I, is a 1 to 1 v/v mixture of the organic and third phases, with compositions corresponding to set II. In all cases the simulations were run at 298 K and 1 bar.

The MD simulations were performed using the GROMACS 4.6.7 simulation package,\textsuperscript{59-61} where the equilibration and production runs were performed for 5 ns and 1 ns, respectively. The short simulation time not only guarantees the convergence of the temperature and pressure but also prevents the homogeneous systems from demixing. The Gibbs energy of each box of a configuration set was calculated as using Eq. 4.1.

$$G_{\text{total}} = G_{\text{ideal}} + G_{\text{ex}} = \frac{1}{N} \sum_i -k_B T N_i \cdot \ln \left( \frac{\langle V \rangle}{A_i^3} \right) + \frac{1}{N} \sum_i \mu_{i}^{\text{ex}} \cdot N_i. \quad (4.1)$$

Here $G_{\text{ideal}}$ and $G_{\text{ex}}$ are the ideal and excess Gibbs energy, respectively. $N$ and $N_i$ are the total number of molecules and the number of molecule of the species $i$ in the box, respectively. $T$ and $V$ are the temperature and volume of the box, respectively. $k_B$ is the Boltzmann constant and $\mu_{i}^{\text{ex}}$ is the excess chemical potential of molecule species $i$. This latter quantity was calculated using the Bennett acceptance ratio (BAR) method.\textsuperscript{62} $A_i$ is the thermal de Broglie wavelength of molecule species $i$, given by

$$A_i = \frac{h}{\sqrt{2\pi m_i k_B T}}, \quad (4.2)$$

where $h$ is Planck's constant and $m_i$ is the mass of molecule species $i$.

The BAR method was performed using the GROMACS 4.6.7 package. For each box, the excess chemical potential of a molecule species, $\mu_{i}^{\text{ex}}$, was estimated as the change of Gibbs energy during the process of slowly introducing a new molecule of that species into the box. The new molecule was firstly inserted in the centre of the box and the box was equilibrated by a short MD run. The BAR method was then performed using 28 intermediate states, $\xi$, between 0 and 1 ($\xi = 0, 0.01, 0.02, 0.05, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.92, 0.94, 0.96, 0.98, 0.99, and 1.00$). At $\xi = 0$ interactions between the new molecule and the surrounding molecules were switched off and at $\xi = 1$ the new molecule interacts fully with the other molecules. Both the Coulomb and van der Waals interactions were coupled simultaneously by $\xi$, and a soft-core potential\textsuperscript{63} was used for the new molecule to prevent discontinuities when $\xi$ approached either 0 or 1. The details of the soft-core potential are described in our previous
The $\xi$ points were chosen in order to get a smooth variation of the $dH/d\xi$ profile. For each value of $\xi$, the system was first equilibrated for 2 ns and the results were obtained from 2 ns production runs. A total of five individual BAR calculations were performed for each molecule species in each box, and the final results of $\mu_i^{ex}$ for each box were averaged over the five individual BAR calculations.

The calculated Gibbs energies of the three sets of configuration are shown in Figure 4.2, where set I has a significantly higher Gibbs energy than either set II or set III. This indicates that the homogeneous system is unstable with respect to demixing, supporting the results of the GEMC simulation. The demixed states, with the compositions of the co-existent phases predicted either by GEMC or as measured by experiment, are both more stable than the 1:1 v/v mixture of the two phases. In addition, the Gibbs energy of set II is identical to that of set III within statistical error.

![Figure 4.2. The Gibbs energy of the three configuration sets. The error bar is calculated by GROMACS package which follows the error estimation approach by Bennett.]

We now turn to the densities of the demixed phases. The MD simulations of Set III, corresponding to the experimental compositions of the two phases, gives densities of 0.841 and 0.987 g cm$^{-3}$ for the light organic and third phases respectively, as compared to the experimental values$^{41}$ of 0.85 and 1.0 g cm$^{-3}$. The agreement is good, providing further
validation of the quality of the force-field used. The densities of the two phases as predicted by GEMC are 0.885 and 0.952 g cm$^{-3}$ which are within 5% of the experimental values. The reason for these small discrepancies is that the GEMC compositions are slightly different from the experimental ones. This may be due to imperfections in the force-field used, but could also be due to the sluggish rate of equilibration in the GEMC simulations, so the compositions reported were close to but not quite the same as the fully equilibrated state.

In summary, both the results from GEMC simulations and the Gibbs energy calculations show that the models used in our simulations exhibit the light organic-third phase coexistence that occurs under experimental conditions and, furthermore, give good quantitative agreement with the observed compositions and densities.

4.4.3 SAXS profile calculation

The comparison of calculated SAXS profiles with experimental data is one of the best ways to verify the correctness of the microscopic structures predicted by molecular models.

In this study, MD simulations were performed using the compositions of both the third and light organic phases that are measured in Ivanov’s experiments, as shown in Table 4.1. Cubic periodic boundary conditions were used for these MD simulations. For each composition, 4 different system sizes, ranging from about 0.1 million to 1.0 million total number of atoms, were used in order to check the effect of system size on the calculated SAXS profiles. These system sizes correspond to 12.3 nm, 15.1 nm, 18.0 and 21.1 nm cubic boxes, respectively. All the systems were simulated for 50 ns where the equilibration and production runs were 30 ns and 20 ns, respectively.

SAXS profiles were calculated based on the trajectories of the production runs. The calculated $I(q)$ covered a $q$ range from 0.3 to 25 nm$^{-1}$, where the relation between $q$ and the corresponding distance $d$ is defined by $d = 2\pi/q$. The minimum $q$ values depend upon the size of the simulation boxes. The corresponding distance of the maximum $q$ is 0.25 nm, which is smaller than the majority of the intermolecular distance in our system. Distances that are smaller than 0.25 nm, which correspond to $q$ range that are larger than 25 nm$^{-1}$, may correspond to the bond lengths of covalent bonds of the molecules and therefore are meaningless to calculate. This is because that in our atomistic models the covalent bonds
are represented with harmonic strings instead of electron clouds, which can cause inaccuracy in the calculated SAXS profiles.

The calculated and experimentally obtained SAXS profiles of the third and light organic phases are shown in Figures 4.3 and 4.4, respectively. In Figure 4.3, the black circles shows the experimentally measured SAXS profile while the red, yellow, blue and green curves show the calculated SAXS profiles from simulations that used 12.3 nm, 15.1 nm, 18.0 nm and 21.1 nm boxes, respectively. Two scattering peaks are observed at around $q = 6.7$ and 14.5 nm$^{-1}$. Our previous research indicated that these two peak positions corresponded to the length of a TBP dimer and an alkane chain respectively. The calculated SAXS profiles reproduce well the major scattering peaks of the experimental SAXS profiles and reproduce the overall shape, especially in the higher $q$ region where $q > 2$ nm$^{-1}$. This corresponds to a distance $d$ that is shorter than 3.1 nm. The calculated SAXS profiles show good agreement with experiment in the higher $q$ region but there are differences in the low $q$ region for $q < 3$ nm$^{-1}$. We note, though, that the differences get smaller with larger box sizes.

**Figure 4.3.** Calculated and experimentally obtained SAXS profiles of the third phase systems.
In order to further investigate the effect of the box size on the calculated profile in the lower \( q \) region, we extrapolate the calculated profiles to infinite box size. The extrapolation was made, for each value of \( q \), by plotting \( I(q) \) against the inverse box length and using a linear extrapolation to estimate the infinite box length limit. The quality of the fit is good and examples of the extrapolation are provided in Table S4.2 and Figure S4.2 in Section 4.6.

The extrapolated SAXS profile at infinite box size is shown as a purple solid curve in Figure 4.3. It is seen that the extrapolated curve agrees well with the experimental SAXS profile in the low \( q \) region. Again this provides validation of the quality of the force-field and gives us confidence that the simulations are correctly capturing nano-scale structures in the third phase. The observed system size effects indicate the presence of structures that are larger than the size of even our biggest simulation box. The larger the box, of course, the larger the structures that can be observed, but the computational effort in significantly increasing the size of the simulations still further would be enormous.

We now turn to the light organic phase. In Figure 4.4, again the black circles show the experimentally measured SAXS profile while the red, yellow, blue and green curves show the calculated SAXS profiles from simulations that used 12.3 nm, 15.1 nm, 18.0 nm and 21.1 nm boxes, respectively. Two scattering peaks at around \( q = 6.1 \) and 13.9 nm\(^{-1}\) respectively are observed and, again, the calculated SAXS profiles reproduce the major scattering peaks of the experimental SAXS profiles. The calculated SAXS profiles show little dependence on box size and they all agree well with the experimental SAXS profile over the whole \( q \) range. This indicates that the microscopic structure of the light organic phase can be well predicted through MD simulations.

No extrapolation was made in Figure 4.4 due to the fact that the calculated SAXS profiles converge reasonably well in the lower \( q \) region and there is no clear trend of variation in the calculated SAXS profiles. This provides evidence that the characteristic dimensions of aggregates in the light organic phase system are smaller than the smallest box size we used and that the sizes of aggregates in the light organic phase system are smaller than those found in the third phase.
**Figure 4.4.** Calculated and experimentally obtained SAXS profiles of light organic phase systems.

In addition to the comparison between the calculated and experimentally obtained SAXS profiles, one can observe two major differences between the experimentally measured SAXS profiles of the light organic and third phases, namely, the height of the peak at $q \sim 6.5\ \text{nm}^{-1}$ and the trend of the profile in the region of $q < 2\ \text{nm}^{-1}$. The differences between the SAXS profiles of the light organic and third phases primarily arise from the HNO$_3$, H$_2$O and the phosphate groups of TBP, due to the fact that the X-ray scattering length densities between the hydrophobic butyl groups in TBP and n-dodecane are roughly equal to each other. Hence, the SAXS profiles directly reflect the hydrogen bonding networks that consist of HNO$_3$, H$_2$O and the phosphate groups of TBP. As mentioned above, the peak at $q \sim 6.5\ \text{nm}^{-1}$ probably corresponds to the length of a TBP dimer. However, the difference between the two profiles in the region of $q < 2\ \text{nm}^{-1}$ may shed light on the characteristic length of the hydrogen bonded unit clusters. In particular, one can estimate the average radius of gyration, $R_g$, of the unit clusters using the Guinier region of the SAXS profile, which corresponds to the region of $q < 0.5\ \text{nm}^{-1}$. The equation used for the estimation of $R_g$ is given in Eq. 4.3.
\ln I(q) = \ln I_0 - \frac{1}{3} R_g^2 q^2, \quad (4.3)

where $I_0$ is the scattering intensity at $q = 0$ and the condition $q R_g < 1$ should be satisfied. By performing the calculation using Eq. 4.3, one can obtain the results that $R_g = 1.04 \text{ nm}$ in the light organic phases and $R_g = 1.26 \text{ nm}$ in the third phase. The details of the calculation are shown in Figure S4.3 in Section 4.6. The results show that the average size of the hydrogen bonded unit clusters in the third phase is about 21% larger than that in the light organic phases, indicating that the third phase is likely to have a more extensive hydrogen bonding network between the polar molecules.

In addition, the average $R_g$ values of molecule species in the simulations were calculated by

$$R_g = \left( \frac{\sum_i \| \mathbf{r}_i \|^2 m_i}{\sum_i m_i} \right)^{\frac{1}{2}}, \quad (4.4)$$

where $m_i$ is the mass of atom $i$ and $\mathbf{r}_i$ the position of atom $i$ with respect to the centre of mass of the molecule. Our results show that $R_g$ as calculated from simulation for an isolated TBP and H$_2$O molecule are 0.96 nm and 0.14 nm, respectively. Thus both the extrapolated $R_g$ values from the SAXS profiles are relatively small through comparison. This indicates that the unit clusters in both phases consist of only a few polar molecules.

In summary, the calculated SAXS profiles exhibit good agreement with the experimental SAXS profiles, indicating that the molecular models used in the MD simulations are capable of predicting the microscopic structure of the third and light organic phase at nanometre scale with good accuracy. Given the validations in this section, we now turn to an analysis of structures of the third and light organic phases, as revealed by simulation.

### 4.4.4 Unusual phase transition

One of the quickest ways to get an impression of the structure of a simulated system is to look at snapshots. We do this first for the 21.1 nm box systems, looking at both the third and light organic phases. Representative snapshots are shown in Figures 4.5a and 4.6a, where, for clarity, each system is shown as a 2 nm thin slice. Our observations are that while these structures are mobile and flexible, the basic motifs do not change over time. In Figures 4.5b and 4.6b, the hydrogen bonds between the molecules are shown as green dashed bonds, where the criterion for determining the presence of a hydrogen bond is that
the donor-acceptor distance is no more than 0.35 nm and that the acceptor-donor-hydrogen angle is no more than 30°. This criterion was based on the typical hydrogen bonds formed by SPC/E H₂O molecule pairs.⁶⁴ The oxygen atoms that have covalent bonds with the hydrogen atoms in the H₂O and HNO₃ molecules were regarded as potential donors and the electronegative atoms that possess a lone electron pair were regarded as potential acceptors.

We first consider the snapshot of the light organic phase, shown in Figure 4.5a. For clarity the n-dodecane molecules are hidden from view, TBP molecules are in yellow, HNO₃ is in red and H₂O is in blue. We observe that the TBP, HNO₃ and H₂O molecules aggregate into an extended mesh where TBP molecules provide the surface film while the HNO₃ and H₂O molecules are inside the mesh. This mesh-like aggregation extends homogeneously over the whole box and there is no evidence of finite aggregates, such as micelles. We observe an extended network of TBP molecules. Within this network there are rather small, isolated molecular-sized clusters of the polar HNO₃ and H₂O molecules. These are the unit structures that are discussed above. The whole network is surrounded by the non-polar n-dodecane molecules. Our hypothesis is that this is a bi-continuous micro-emulsion.

Figure 4.5b shows one of the typical local clusters in the light organic phase. This is primarily composed of hydrogen bonded dimers, including three TBP–HNO₃ dimers and a TBP–H₂O dimer. A short hydrogen bonding chain is also observed which is in the form of TBP–HNO₃–H₂O–HNO₃. However, TBP–HNO₃ dimers are observed to be the predominant form of individual clusters in the light organic phase.

In Figure 4.6a we show a representative snapshot of the third phase, where again we hide the n-dodecane and show the TBP in yellow, HNO₃ in red and H₂O in blue. Again we observe that the TBP, HNO₃ and H₂O molecules form an extended mesh-like structure. This is similar to the structure of the light organic phase shown in Figure 4.5. The main difference is that the mesh is thicker than that of the light organic phase and the clusters of HNO₃ and H₂O within the mesh are much larger. This again in is accord with the SAXS data as discussed in the previous section.
Figure 4.5. (a) A 2 nm thin slice of the final trajectory of the 21.1 nm light organic phase system. TBP, HNO\textsubscript{3} and H\textsubscript{2}O molecules are represented in yellow, red and blue, respectively; n-dodecane molecules are not shown for clarity. (b) Atomic scale of the purple-colour selected area in Figure 4.5a, where the hydrogen bonds are represented in green dashed bonds, the double bond oxygen and phosphorous from TBP are highlighted in cyan and purple respectively. Molecules that are not hydrogen bonded are hidden from view for clarity.
Figure 4.6. (a) A 2 nm thin slice of the final trajectory of the 21.1 nm third phase system. TBP, HNO$_3$ and H$_2$O molecules are represented in yellow, red and blue, respectively; n-dodecane molecules are not shown for clarity. (b) Atomic scale of the purple-colour selected area in Figure 4.6a, where the hydrogen bonds are represented in green dashed bonds, the double bond oxygen and phosphorous from TBP are highlighted in cyan and purple respectively. Molecules that are not hydrogen bonded are hidden from view for clarity.
Figure 4.6b shows one of the typical local clusters in the third phase and more complex hydrogen bonding chains are observed. There are one TBP–HNO$_3$ dimer, one HNO$_3$–H$_2$O dimer, two HNO$_3$–HNO$_3$ dimers, one TBP–HNO$_3$–HNO$_3$ trimer and two complex hydrogen bonding chains that involve multiple HNO$_3$ and H$_2$O. It is impossible to analyse the detailed structure of the hydrogen bonding networks through visual observation, but it is clear from Figures 4.5b and 4.6b that the third phase contains more hydrogen bonding chains than the light organic phase. Quantitative analysis, including hydrogen bonding analysis and cluster analysis were performed to further investigate the structures and the methods and the results are presented in Sections 4.4.6 and 4.4.7, respectively.

However, despite the difference between the thickness of the mesh, the sizes of individual clusters and the complexity of the hydrogen bonding chains of the two boxes, we see no difference in symmetry between the two phases.

Iso-surface analysis$^{65,66}$, using a revised code from the DL_MESO package$^{67}$, shows that the clusters in both phases show no order, indicating that both the phases are isotropic. In other words, both the boxes are isotropic phases that consist of extended mesh-like aggregates. Our hypothesis is that both phases are isotropic micro-emulsions and that the transition is an unusual isotropic-isotropic micro-emulsion phase transition. One must, of course, be wary of drawing conclusions based on snapshots alone, so we now turn to a more quantitative analysis of the structures of these phases.

### 4.4.5 Coordination number analysis

To aid the analysis, we first consider coordination numbers, which tell us how many atoms of type $j$ are, on average, close neighbours of an atom of type $i$. The coordination number, $N_c$, is given by

$$N_c = \int_0^{r_m} \rho_j g_{ij}(r) 4\pi r^2 dr,$$

where $\rho_j$ is the number density of particle $j$ in the system, $g_{ij}(r)$ is the pair correlation function between particles $i$ and $j$ and $r_m$ is the position of the first minimum in $g_{ij}(r)$. An illustration of a pair correlation function, which corresponds to the nitrogen atom pair from HNO$_3$, and its corresponding coordination numbers is shown in Figure S4.4 in Section 4.6.
Table 4.3. Coordination numbers of atom species around a reference atom species, where the results were calculated as the block average among ten blocks of data. Errors were estimated as the standard deviation of the results from all blocks.

<table>
<thead>
<tr>
<th>Atomic pair</th>
<th>Coordination number; ( N_c )</th>
<th>( r_{\text{m}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P (TBP)} \rightarrow \text{P (TBP)} )</td>
<td>0.97 ± 0.03</td>
<td>0.95 ± 0.04</td>
</tr>
<tr>
<td>( \text{O=} \rightarrow \text{H (HNO}_3) )</td>
<td>0.84 ± 0.03</td>
<td>1.00 ± 0.02</td>
</tr>
<tr>
<td>( \text{O=} \rightarrow \text{H (H}_2\text{O)} )</td>
<td>0.11 ± 0.03</td>
<td>0.04 ± 0.02</td>
</tr>
<tr>
<td>( \text{N (HNO}_3) \rightarrow \text{N (HNO}_3) )</td>
<td>0.29 ± 0.02</td>
<td>2.65 ± 0.05</td>
</tr>
<tr>
<td>( \text{O (H}_2\text{O)} \rightarrow \text{O (H}_2\text{O)} )</td>
<td>0.04 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>

\( a \) The reference atom is written before the dash, while the atom that closely surround the reference atom is written behind the dash; the molecule species written in the brackets is what the atom in the front belongs to; \( \text{O=} \) is short for the double bond oxygen in the TBP molecules.

In this study, the trajectories from the 21.1 nm box systems were used to calculate the coordination numbers. These are shown for a selection of atom pairs in Table 4.3. It is seen that the average coordination number of P atoms around P atoms is close to 1 in both phases, which indicates that on a molecular scale, TBP molecules tend to form dimers. This is consistent with our previous findings in the TBP/alkane systems.\(^{68}\) The coordination number of H, from HNO\(_3\), around the double bond oxygen (O=) from TBP is 1.00 in the third phase and 0.84 in the light organic phase. The coordination numbers of H from H\(_2\)O around O= in both phases is small (0.04 in the third phase and 0.11 in the light organic). This indicates, especially in the third phase, that TBP is much more strongly associated with HNO\(_3\) than H\(_2\)O. On average, in both phases each TBP molecule is attached to one HNO\(_3\).

Turning now to the coordination number of N around N, this is 2.65 in the third phase and 0.29 in the light organic phase. This indicates that the HNO\(_3\) molecules are locally associated in the third phase but, on average, these molecules are isolated in the light organic phase. The snapshots shown in Figures 4.5 and 4.6 show molecular scale structuring that accords with this analysis.

4.4.6 Hydrogen bonding analysis

A hydrogen bond is the strong, primarily electrostatic attraction between an electronegative atom and a hydrogen atom bonded to a highly electronegative atom. In our case, these
electronegative atoms may be oxygen or nitrogen. A hydrogen bond analysis can cast much light on the driving forces for aggregation.

In this study, the average numbers of hydrogen bonds formed between molecule pairs in the 21.1 nm box systems were analysed. The criterion for determining the presence of a hydrogen bond is the same as that defined in Section 4.4.4.

The average numbers of hydrogen bonds between pairs of TBP, HNO₃ or H₂O molecules are shown in Table 4.4. Note that in the simulations, the number of TBP, n-dodecane, HNO₃ and H₂O molecules were 4288, 19456, 3904 and 448 respectively in the light organic phase and, were 9176, 10928, 18400 and 4504 respectively for the third phase.

Table 4.4 shows that in the light organic phase, there are 0.825 TBP-HNO₃ hydrogen bonds per TBP molecule and 0.906 TBP-HNO₃ hydrogen bonds per HNO₃ molecule. In the third phase these numbers change to 1.034 TBP–HNO₃ hydrogen bonds per TBP and 0.516 TBP–HNO₃ hydrogen bonds per HNO₃. Thus in both phases each TBP molecules is hydrogen bonded to approximately one HNO₃ in a mono-dentate structure. There may, however, be a small amount of bidentate coordination in the third phase, as the number of TBP–HNO₃ hydrogen bonds per TBP exceeds 1.

For the TBP–H₂O hydrogen bonds, the number is 1.089 per H₂O in the light organic phase, which shows that all H₂O molecules tend to hydrogen bond with TBP in a mono-dentate structure. This is not surprising as H₂O is a strong polar molecule and it naturally seeks to form hydrogen bonds when there are enough TBP molecules available. However, in the third phase, the number of TBP–H₂O hydrogen bonds per H₂O drops to 0.314. This indicates that at high concentrations of HNO₃ and H₂O, the H₂O molecules have much lower degree of association with the TBP. It is probably the case that the HNO₃ molecules are preferentially hydrogen bonding to the vast majority of TBP molecules, leaving no opportunity for the H₂O molecules for such association.

The numbers of HNO₃–HNO₃ hydrogen bonds per HNO₃ molecule are 0.016 and 0.238 in the light organic and third phases, respectively. Note that a HNO₃–HNO₃ hydrogen bond is shared by two HNO₃ thus almost half of the HNO₃ molecules are connected by hydrogen bonds in the third phase. In the light organic phase, however, HNO₃ molecules tend not to associate. The numbers of HNO₃–H₂O hydrogen bonds are 0.973 and 1.991 per H₂O molecule in the light organic and third phases, respectively. This shows that H₂O and HNO₃ molecules form a mono-dentate associated structure in the light organic phase but, in the third phase, a H₂O molecule is shared between two HNO₃ molecules. Last, but not
the least, the number of $\text{H}_2\text{O}–\text{H}_2\text{O}$ hydrogen bonds per $\text{H}_2\text{O}$ is 0.137 in the light organic phase and is only 0.064 per $\text{H}_2\text{O}$ in the third phase. This indicates that there is little association between water molecules in either phase.

### Table 4.4. Normalised numbers of hydrogen bonds that are formed between molecule species (avg.).

<table>
<thead>
<tr>
<th>Molecule pair</th>
<th>Reference molecule</th>
<th>Light organic phase</th>
<th>Third phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP – $\text{HNO}_3$</td>
<td>$\text{TBP}$</td>
<td>0.825 ± 0.006</td>
<td>1.034 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>$\text{HNO}_3$</td>
<td>0.906 ± 0.006</td>
<td>0.516 ± 0.002</td>
</tr>
<tr>
<td>TBP – $\text{H}_2\text{O}$</td>
<td>$\text{TBP}$</td>
<td>0.114 ± 0.002</td>
<td>0.154 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{O}$</td>
<td>1.089 ± 0.015</td>
<td>0.314 ± 0.004</td>
</tr>
<tr>
<td>$\text{HNO}_3$ – $\text{H}_2\text{O}$</td>
<td>$\text{HNO}_3$</td>
<td>0.112 ± 0.002</td>
<td>0.487 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{O}$</td>
<td>0.973 ± 0.018</td>
<td>1.991 ± 0.011</td>
</tr>
<tr>
<td>$\text{HNO}_3$ – $\text{HNO}_3$</td>
<td>$\text{HNO}_3$</td>
<td>0.016 ± 0.000</td>
<td>0.238 ± 0.002</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ – $\text{H}_2\text{O}$</td>
<td>$\text{H}_2\text{O}$</td>
<td>0.137 ± 0.005</td>
<td>0.064 ± 0.002</td>
</tr>
</tbody>
</table>

*The normalised numbers are calculated as the number of hydrogen bonds between molecule pairs divided by the total number of the reference molecule in that system.

To sum up, the results of the hydrogen bonding analysis is in agreement with the coordination number analysis as well as our visual observation. As polar molecules, both $\text{H}_2\text{O}$ and $\text{HNO}_3$ tend to form strong electrostatic associations with the phosphate group of TBP. Rather than bidentate connections, TBP molecules prefer a mono-dentate hydrogen bond with either an $\text{HNO}_3$ or an $\text{H}_2\text{O}$. The major difference between the third and light organic phases is that the third phase consists of much more complex hydrogen bonding networks formed by $\text{HNO}_3$, $\text{H}_2\text{O}$ and TBP. Each TBP molecule is closely connected to an $\text{HNO}_3$. In the light organic phase one finds primarily TBP–$\text{HNO}_3$ dimers but in the third phase there are complex strings such as TBP–$\text{HNO}_3$–$\text{HNO}_3$ and TBP–$\text{H}_2\text{O}$–2$\text{HNO}_3$. These results are similar to those previously been reported by Servis *et al.* and Ivanov *et al.* These different hydrogen bonding structures no doubt play a crucial role in driving the light organic/third phase transition.

#### 4.4.7 Cluster analysis

Cluster analysis is generally used as a tool to estimate the connections between particles or molecules in a molecular system based on certain criteria. In this study, cluster analyses
were performed to estimate the number and size of the hydrogen bonded clusters that are formed by TBP, HNO₃ and H₂O molecules in our systems. In addition, cluster analyses were also performed to verify if all the TBP molecules in the light organic or third phase are connected, which gives an indication of whether the light organic or third phase is indeed akin to bi-continuous micro-emulsion phases. The results presented are time averages over the molecular dynamics production runs.

In the cluster analyses, all the atoms were treated as mass points. The distance between each atom was calculated as the distance between the mass points and, the angle between three atoms was also calculated as the angle between three mass points. For the cluster analysis which calculated the hydrogen bonded clusters, we chose the same criteria that were used in hydrogen bonding analysis in Section 4.4.4.

The molecule pairs are regarded as directly hydrogen bonded if they meet these criteria. When determining the connectivity between the indirect hydrogen bonded molecules we use the connectivity matrix method proposed by Sevick et al., where the detailed illustration is in the appendix of Sevick’s paper. The cluster size is calculated as the number of hydrogen bonded molecules in a cluster, which is determined by the connectivity matrix method.

From the cluster analysis we are able to calculate the average number of hydrogen bonded clusters and the sizes of the clusters in both the light organic and third phases. In this study, we performed cluster analysis using the trajectories from the 21.1 nm box systems. The results are shown in Figure 4.7.

Figure 4.7 shows that the cluster sizes are within the range of 1 to 10 in the light organic phase while in the range of 1 to 13 in the third phase. Most interestingly, the predominant cluster sizes in the light organic and third phases are 2 and 3, respectively, indicating that the predominant clusters are dimers in the light organic phase and trimers in the third phase. Compared with the light organic phase, the third phase has a higher concentration of larger hydrogen bonded clusters and a significant lower concentration of monomers. This indicates that the TBP, HNO₃ and H₂O molecules in the third phase tend to form more extensive hydrogen bonding networks and thus slightly larger clusters, which is consistent with our hydrogen bonding analysis in Section 4.4.4. Interestingly, there are still a large number of hydrogen bonded dimers in the third phase, indicating that the polar molecules in the third phase are sufficiently mobile that they can break and form hydrogen bonds, rather than always remaining in a rigid structure.
Figure 4.7. Average number of hydrogen bonded clusters against cluster size in both the light organic and third phases in a semi-log plot, where cluster size measures the number of molecules in a cluster. The dashed lines show the trend of change between each point.

In addition to the cluster analysis that estimates the distribution of hydrogen bonded clusters, we also performed a cluster analysis in both phases that calculates the connectivity between all the TBP molecules. In this calculation, a 0.74 nm distance cut-off, which corresponds to the $r_m$ value in the carbon-carbon pair correlation function of TBP molecules, was used as the criterion for determining the connectivity between the butyl groups from TBP molecules. In addition, a 0.75 nm distance cut-off, which corresponds to the $r_m$ value in the phosphorous-phosphorous pair correlation function of TBP molecules, was used as the criterion for determining the connectivity between the phosphate groups from TBP molecules. In the cluster analysis calculations, only the P and C atoms from TBP molecules were taken into account while the H and O atoms were discarded, as this is consistent with the cut-off criteria and can improve the efficiency of the calculation. Our results show that there are on average 93.2% TBP molecules in the organic phase are connected, based on our criteria, which indicates that the polar molecules in the organic
phase indeed form a mesh-like structure that contains the vast majority of TBP molecules. This mesh-like structure is similar to the structure of a bi-continuous micro-emulsion. What is more, our results show that the percentage of connected TBP increase to 98.6% in the third phase, which again indicates a mesh-like structure that is similar to a bi-continuous micro-emulsion. These results are consistent with our observations in Section 4.4.4. It is difficult, though, to give a clear account of the driving forces for the formation of this structure. The inter-molecular forces that hold this mesh together are not simply strong short range Coulombic attractions between the phosphate groups or the effect of polar bridging molecules. The butyl groups are sometimes seen to be in contact, so their interactions may play a role. Similarly long-range Coulomb interactions between the phosphate groups are also likely to provide an important contribution. This warrants further study.

4.5 Concluding remarks

We have shown that our TBP model, combined with the \( n \)-dodecane, H\(_2\)O and HNO\(_3\) models taken from literature, is capable of predicting light organic/third phase co-existence and can also predict the microscopic structure of both phases, with our simulation results comparing well with experiment. The simulation approaches were GEMC and MD, and the analysis included the calculations of Gibbs energies and SAXS profiles, supplemented by hydrogen bonding and cluster analysis. GEMC reveals a demixing transition, where the compositions and densities of the co-existing phases are in good agreement with recent experiments.\(^{41}\) Also the predicted SAXS profiles are in good agreement with our experimental data, providing evidence that our simulations are predicting correct structures. We find that both the organic and third phases exhibit a bi-continuous, micro-emulsion structure and there is no evidence of reverse micelles. Instead there are relatively small molecular clusters of polar molecules embedded in a mesh of TBP. We believe that the organic/third phase transition is therefore an unusual transition between two, isotropic bi-continuous phases. Finally we use our MD simulations to look at the hydrogen bonding networks in both phases, obtaining results that are consistent with previous NMR and IR experiments and which are also consistent with the predictions of a very recent simulation study conducted by Servis \textit{et al.} on this system.\(^{38}\)

The broad structures of both the organic and third phases at nanometre scale were explored. Both the light organic and third phases consisted of extended mesh-like aggregates. Within
this mesh were unit clusters of HNO₃, H₂O and TBP molecules, connected by hydrogen bonds. The only macroscopic difference between the two phases was the thickness of the mesh and thus the volume fraction of the aggregates. In other words, both phases are similar to the Winsor-III classification of surfactant micro-emulsion systems that consist of water/oil/surfactant species, where bi-continuous micro-emulsion phases are found. However, the difference between our system and most water/oil/surfactant systems is that we believe the co-existing phases studied here are both bi-continuous micro-emulsion phases with isotropic symmetry. In other words, the formation of the third phase is an unusual isotropic-isotropic micro-emulsion phase transition. Typically, in the Winsor-III phase diagrams, a bi-continuous micro-emulsion co-exists with micellar phases containing small, discrete aggregates or with cubic phases which are anisotropic. A review of the phase behavior of water/oil/surfactant systems is given by Chevalier and Zemb and Erlinger also described a phase transition from reverse micelles to a bi-continuous phases. Interestingly, the microscopic structure of the bi-continuous phases, which were represented by the two level-cut Gaussian random wave model by Duvail et al., shows remarkable similarity to the simulation snapshots in Figures 4.5 and 4.6. In addition, their results indicate that micro-emulsion systems with small volume fractions of water prefer bi-continuous structures rather than reverse micelles, which is in agreement with our results presented here.

The microstructures of the third and organic phases were analysed by calculating the coordination numbers and hydrogen bonds between atom pairs using MD simulations. The TBP molecules were primarily coordinated with HNO₃ molecules that possess strong hydrogen bonding potentials. It was concluded that most of the TBP was in the form of TBP–HNO₃ dimers in the organic phase but formed TBP–HNO₃–HNO₃ strings in the third phase. In addition, H₂O molecules played an important role of joining the TBP/HNO₃ clusters together, especially in the third phase system. The complex and extensive hydrogen bonding network formed by HNO₃, H₂O and TBP molecules is likely to be a major driving force for the third phase formation in the TBP/n-dodecane/HNO₃/H₂O systems.

While the results obtained greatly further one’s understanding of the properties of the light organic and third phases, it is still not clear why, in molecular terms, a homogeneous system, of composition intermediate between that of the light organic and third phases, should demix. That is a topic for future research.
It is also of interest to investigate the role of metal nitrates on the structures and properties of these phases. Preliminary results indicate that the metal complexes form unit structures within the extended mesh observed in the TBP/n-dodecane/HNO₃/H₂O systems and again the light organic/third phase transition is of similar nature to that observed here. We hope to present simulation results pertaining to this in the near future.

### 4.6 Supporting information

**Table S4.1. Types and probabilities of the Monte Carlo moves**

<table>
<thead>
<tr>
<th>Type of Monte Carlo move</th>
<th>Probability to perform the move *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume exchange between the two boxes</td>
<td>0.5%</td>
</tr>
<tr>
<td>Volume adjustment due to barostat</td>
<td>0.5%</td>
</tr>
<tr>
<td>Inter-box rotational-bias molecule transfer</td>
<td>10%</td>
</tr>
<tr>
<td>Inter-box configurational-bias molecule transfer&lt;sup&gt;76,77&lt;/sup&gt;</td>
<td>10%</td>
</tr>
<tr>
<td>Intra-box configurational-bias molecule transfer</td>
<td>10%</td>
</tr>
<tr>
<td>Aggregation volume bias move</td>
<td>9%</td>
</tr>
<tr>
<td>Intra-box centre-of-mass molecule translation</td>
<td>30%</td>
</tr>
<tr>
<td>Intra-box molecule rotation</td>
<td>30%</td>
</tr>
</tbody>
</table>

*The chance to perform a certain type of move in a Monte Carlo move.

**Figure S4.1.** Experimental illustration of the three phase coexistence, where from bottom to top the three phases are the aqueous phase, the third phase and the light organic phase, respectively.
Table S4.2. Data points used in the extrapolation of SAXS profile

<table>
<thead>
<tr>
<th>Box length L (nm)</th>
<th>1/L (nm⁻¹)</th>
<th>q (nm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.51</td>
<td>0.6</td>
</tr>
<tr>
<td>12.3</td>
<td>0.0813</td>
<td>0.3563</td>
</tr>
<tr>
<td>15.1</td>
<td>0.0662</td>
<td>0.3361</td>
</tr>
<tr>
<td>18.0</td>
<td>0.0556</td>
<td>0.3146</td>
</tr>
<tr>
<td>21.1</td>
<td>0.0474</td>
<td>0.2904</td>
</tr>
<tr>
<td>infinity</td>
<td>0.0000</td>
<td>0.2265</td>
</tr>
</tbody>
</table>

Figure S4.2. Extrapolation of SAXS profile to infinite box length using the data points provided in Table S4.2.
Figure S4.3. Calculation of $R_g$ values for the hydrogen bonded unit clusters in both the third and light organic phases.

Figure S4.4. The pair correlation function of the nitrogen atom pair from HNO$_3$ and its corresponding coordination number.
Acknowledgments

The authors would like to thank Dr. Peter Ivanov for his experimental results, Dr. Michael Seaton for his help in the iso-surface calculation code and, Prof. Daan Frenkel and Prof. Gordon Tiddy for their helpful discussion. We also thank the University of Manchester for use of the Computational Shared Facility (CSF). This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant-in-Aid for Scientific Research B, 2014-2018, No. 26289368).

4.7 References


(8) Kolarik, Z. In The formation of a third phase in the extraction of Pu (IV), U (IV) and Th (IV) nitrates with tributyl phosphate in alkane diluents, ISEC 1979 Conference, 1979; pp 178-182.


5 The microscopic structure of the Zr(IV)/TBP/n-octane/HNO₃/H₂O system as related to the nuclear extraction process

5.1 Preface

This chapter presents part of some collaborative research with Dr. Ryuhei Motokawa, on the microscopic structure of the TBP/n-octane/HNO₃/H₂O system containing low concentrations of Zr⁴⁺ ions.

J. Mu carried out all the simulations and analysis while Dr. Motokawa carried out the experiments.

Due to the fact that the experimental results by Dr. R. Motokawa are still being prepared and analysed, this chapter contains only the simulation results so far.
The Microscopic Structure of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O System as related to the Nuclear Extraction Process

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Abstract

We report simulation studies on the structure of the light organic phase of Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems, which are related to third phase formation in the Plutonium Uranium Reduction EXtraction process (PUREX). Co-ordination number, hydrogen bonding and cluster analysis were performed and the results show that the Zr$^{4+}$, nitrate, TBP and H$_2$O form an extended aggregated network with embedded local clusters centred on Zr$^{4+}$. The extended aggregated network is similar to the bi-continuous structure in the TBP/n-dodecane/HNO$_3$/H$_2$O system in our previous study. The local clusters are primarily in the form of Zr(NO$_3$)$_4$·3TBP which is in agreement with the extrapolated structure from extended X-ray absorption fine-structure (EXAFS) experiments. These embedded local zirconium-centred clusters are usually connected into dimers by polar bridging molecules such as H$_2$O, HNO$_3$ or NO$_3^-$ as they can form strong hydrogen bonds with each other. The formation of the extended aggregated network is due to three kinds of driving forces, namely the strong short-range hydrogen bonds between polar molecules and the phosphate groups from TBP, the attraction between the hydrophobic butyl groups from TBP, and the long-range electrostatic interactions between Zr$^{4+}$ and the phosphate groups. This findings in this paper provide a new view of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems which differ from the common hypothesis that the structure of the Zr(IV) containing systems are large reverse micelles.
5.2 Introduction

The Plutonium Uranium Reduction EXtraction (PUREX) process is the predominant approach for reprocessing spent nuclear fuel, which recovers the U(VI) and Pu(IV) for recycling and reuse. In the PUREX process the radioactive ions are extracted from an aqueous mineral acid solution by tri-butyl phosphate (TBP) dissolved in an aliphatic hydrocarbon diluent. This liquid-liquid extraction process, however, is sensitive to the concentration of the metal ions and mineral acid in the aqueous solution, as when the concentration of the metal ions exceeds the limiting organic concentration (LOC) in the organic phase of the extraction process, the organic extraction solution tends to separate into two organic phases\(^1\text{-}^8\). The light upper phase, which is commonly named the light organic phase, contains a lower concentration of metal ions, TBP and mineral acids but is rich in aliphatic hydrocarbons. The heavy lower phase, which is commonly named the third phase, contains high concentrations of the metal-ion/TBP complexes and mineral acids. This separation of the organic phase is usually called third phase formation and it is highly undesirable. This is because that it has the potential to wreck the extraction process where the metal ions are prevented from being extracted into the organic phase by the third phase.\(^9\text{-}^{10}\) Additionally, the accumulation of the metal ions in the third phase could potentially lead to criticality issues.\(^7\text{-}^{10}\)

In the last few decades, third phase formation has been extensively investigated through experimental approaches, where the U(VI) and ions including Zr(IV), Th(IV), Pu(IV) are widely involved. This experimental work studied not only the variables that affect the LOC, such as temperature and the concentration of mineral acid, but also, more interestingly, the microscopic structures of the light organic and third phases. One of the most popular hypotheses on the microscopic structures is that the Zr(IV), mineral acids, water and TBP aggregate into reverse micelles in both phases. A typical reverse micelle is an aggregate of water and surfactant, where the hydrophobic “tail” regions of the surfactant are in contact with surrounding solvent while the hydrophilic “head” regions and water molecules are in the centre. In the systems relevant to PUREX, however, reverse micelles are usually regarded as being the large aggregates formed by metal ions, nitrates, water and TBP, where the hydrophobic tails of TBP form spherical or ellipsoidal shells that shelter all the polar molecules (HNO\textsubscript{3}, H\textsubscript{2}O, NO\textsubscript{3}\textsuperscript{-}) and ions in the centre.

Osseo-Asare\(^11\text{-}^{12}\) first proposed the reverse micelle structure to describe the metal complexes in the light organic phases based on an extensive analysis of existing
experimental data such as nuclear magnetic resonance (NMR) and vapour pressure osmometry. Osseo-Asare maintained that the light organic and third phases are both microemulsions with reverse micelles, each consisting of dozens of molecules. Through small angle neutron scattering (SANS) experiments, Chiarizia et al.\textsuperscript{13} proposed that U(IV) is extracted as UO$_2$(NO$_3$)$_2$·2TBP in the U(VI)/HNO$_3$/TBP/n-dodecane systems, where the U(IV) is in the form of ellipsoidal reverse micelles that contain four to six TBPs. For metals in the +4 oxidation state, such as Th(IV), Borkowski et al.\textsuperscript{14} carried out SANS measurements and proposed an ellipsoidal reverse micellar structure in the Th(IV)/HNO$_3$/TBP/n-octane systems. According to Borkowski most of the Th(IV) ions are in the form of Th(NO$_3$)$_4$·3TBP and, the size of the reverse micelles could reach 230 and 24 Å in the major and minor axes respectively. The speciation of Th(NO$_3$)$_4$·3TBP is supported by Kumar and Koganti\textsuperscript{15} who carried out stoichiometric studies. Kumar and Koganti also pointed out the possibility of having Th(NO$_3$)$_4$·3TBP·HNO$_3$ in the Th(IV)/HNO$_3$/TBP/n-octane systems. In addition, Srinivasan et al.\textsuperscript{16} who performed infra-red spectrometry and Suresh et al.\textsuperscript{17} who performed stoichiometric studies also confirmed the speciation of both UO$_2$(NO$_3$)$_2$·2TBP and Th(NO$_3$)$_4$·3TBP. Hence, it seems that experimentalists have reached a consensus that, in the PUREX systems, the U(VI) is coordinated with two TBPs and Th(IV) is coordinated with three TBPs.

However, such agreement is not the case for Zr(IV), as there is dissent about the number of coordinated TBPs around a Zr$^{4+}$ ion. Chiarizia et al.\textsuperscript{18} carried out SANS experiments on the Zr(IV)/TBP/n-octane/HNO$_3$ systems and proposed that both the Zr(NO$_3$)$_4$·2TBP and Zr(NO$_3$)$_4$·3TBP structures fit the SANS profiles well. The problem here, however, is that a SANS profile can be reproduced by several, different structural models. Considerable care is required to arrive at a correct, unique structure.\textsuperscript{19} Recently, Chang et al.\textsuperscript{20} carried out extended X-ray absorption fine-structure (EXAFS) study on the light organic and third phases of the Zr(IV)/TBP/n-dodecane/HNO$_3$ system and they concluded from their results that it is highly likely that each Zr$^{4+}$ coordinates with three TBP molecules to form Zr(NO$_3$)$_4$·3TBP in both phases.

In recent years, molecular simulation studies on the PUREX process, especially on third phase formation and the speciation of the clusters, are getting increasingly popular. Some simple systems related to PUREX process, such as TBP/n-alkane and TBP/n-alkane/HNO$_3$ solutions, have been widely investigated.\textsuperscript{21-30} Apart from these, simulation studies have also focused on the behaviour of metal ions such as U(VI), Pu(IV) and Zr(IV) in the PUREX-related systems. For the behaviour of U(VI), Baaden et al.\textsuperscript{31} first studied the
speciation by U(VI) in the U(VI)/TBP/n-alkane/HNO\textsubscript{3} systems through molecular dynamics (MD) simulations and their results show the formation of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP which is in agreement with Chiarizia et al.\textsuperscript{13} Bühl et al.\textsuperscript{32,33} performed Car-Parrinello MD\textsuperscript{34} to study the coordination forms of some typical uranyl complexes such as [UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}]\textsuperscript{−}, [UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{4}]\textsuperscript{2−} and, they drew the conclusion that the mono-dentate nitrate is more stable than bi-dentate nitrate. Later, Ye et al.\textsuperscript{35} carried out MD simulations using updated molecular models and found that, in the organic environment, U(VI) is more likely to form UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP·H\textsubscript{2}O or UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·3TBP than UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP. However, recent simulation studies reported the lack of accuracy of the TBP models used in all the simulation work mentioned above.\textsuperscript{28,29,36} What is more, in all these simulations, metal ions have large charges which these will exert a considerable electric field on neighbouring molecules and will polarise them. The commonly used non-polarisable models neglect this effect. Polarisable models, in theory, should be able to catch these effects more accurately.

An MD study by Benay and Wipff,\textsuperscript{37} which used united-atom polarisable models, predicted the formation of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP complexes. However, the united-atom models they used treated methyl and methylene groups on TBP as single particles and omitted the hydrogen atoms which resulted in, comparing to experimental data\textsuperscript{38}, 6 % higher in density of TBP liquid at ambient condition. Thus it is still difficult to draw solid conclusions on the speciation by U(VI) in PUREX process. For the behaviour of metal ions in the +4 oxidation state in the PUREX-related systems, Gopakumar et al.\textsuperscript{39} recently performed quantum mechanical calculations using Density Functional Theory (DFT) to investigate the conformations of both Pu(IV)/HNO\textsubscript{3}/TBP and Zr(IV)/HNO\textsubscript{3}/TBP complexes. However, as they believed that the complexes of Pu(IV) and Zr(IV) should be in the form of Pu(NO\textsubscript{3})\textsubscript{4}·2TBP and Zr(NO\textsubscript{3})\textsubscript{4}·2TBP respectively, their investigation was confined to those stoichiometries and competitor structures were not considered.

It is known that Zr-93 is one of the longest lived fission products as it has a half-life of 1.53 × 10\textsuperscript{6} years. In addition, the cumulative fission yield of Zr in the U-235 fission and Pu-239 fission are 6.502 % and 4.949 % respectively, which is high.\textsuperscript{40} What is more, zirconium alloys are commonly used for cladding of nuclear fuel in the nuclear industry as zirconium has high chemical resistance, low cross section for thermal neutrons and good mechanical properties, but dissolution of zirconium in nuclear fuel was reported\textsuperscript{41}. The LOC for zirconium is relatively high in the organic extraction\textsuperscript{42} For the PUREX process, it is important to have a better understanding of the speciation by Zr(IV) in the Zr(IV)/TBP/n-alkane/HNO\textsubscript{3} systems. This is because the process procedures, i.e. analytical monitoring and reaction kinetics control, are dependent on the assumption made about
molecular geometries and intermediates such as the complexes formed by Zr(IV).\textsuperscript{43,44} In addition, as zirconium alloys are usually used in nuclear fuel cladding it is also important for the long-term safety assessment of geological disposal facilities. A better understanding of Zr(IV) is also helpful to understand better the behaviour of chemically relate ions, such as Pu(IV) and Th(IV), in the PUREX process.

In this paper, we report evidence about the structure of Zr(IV)/TBP/n-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems, which have been widely investigated by SANS experiments,\textsuperscript{18,19} from MD simulations using all-atom molecular models using the Optimized Potentials for Liquid Simulations (OPLS) force field. The simulations were of the light organic phase of the Zr(IV)/TBP/n-octane/HNO\textsubscript{3}/H\textsubscript{2}O system with compositions corresponding to those studies in experiment.

5.3 Methodology

In this study, we performed MD simulations to investigate the microscopic structure of dilute Zr\textsuperscript{4+} in TBP/n-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems. Theoretically, polarisable models, where the partial charges on the atoms can vary according to the surrounding electrostatic environment, should be used in order to catch the electrostatics of the molecules more accurately. This is particularly important for species such as TBP and NO\textsubscript{3}\textsuperscript{−} that are near the Zr\textsuperscript{4+} as the induced dipole resulting from the electric field of Zr\textsuperscript{4+} should be strong. However, validated polarisable all-atom model for TBP have not yet been reported. Nevertheless, our previous study\textsuperscript{36} showed that the accuracy of the TBP model is vital for a correct description of TBP in contact with both \textit{n}-alkanes and polar molecules and these interactions lead to an extended aggregated network in TBP/\textit{n}-alkane/HNO\textsubscript{3}/H\textsubscript{2}O systems. Currently, it is thus better to use the non-polarisable models, especially TBP, that have been verified for other systems rather than using polarisable models that are of unknown quality. Hence, we followed our convention of our studies and used the non-polarisable models as the accuracy of all-atom model for TBP in TBP/\textit{n}-alkane/HNO\textsubscript{3}/H\textsubscript{2}O systems was validated.\textsuperscript{45}

In this study, the OPLS potential\textsuperscript{46} and all-atom molecular models were used for all the molecule species. The force field parameters for Zr\textsuperscript{4+} ion were taken from Li \textit{et al.}\textsuperscript{47} where the Zr\textsuperscript{4+} ion was parameterised for the metal-oxygen distance between Zr\textsuperscript{4+} and TIP3P water\textsuperscript{46} in Zr(IV)/H\textsubscript{2}O systems. According to Li \textit{et al.} the metal-oxygen distance predicted by Zr\textsuperscript{4+} model agreed well with experimental EXAFS data\textsuperscript{48}. The model for TBP were
taken from our previous publication\textsuperscript{36} which was optimised for nuclear extraction systems and has been shown to produce accurate structures in TBP/n-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems.\textsuperscript{45} The OPLS-2005 force field was used for the n-octane model and, as the OPLS force field was optimised for the TIP3P water model, this was used for H\textsubscript{2}O. Both the n-alkane and water models have been tested and validated in our previous studies.\textsuperscript{36,45} As all the systems in this study are organic phases and in an organic environment, we assume that all of the HNO\textsubscript{3} molecules are undissociated. Hence, there is only a small amount of NO\textsubscript{3}– in the system to coordinate with Zr\textsuperscript{4+} and keep the system charge neutral. The force field parameters for HNO\textsubscript{3} and NO\textsubscript{3}– were taken from Price \textit{et al.}\textsuperscript{49} and Sambasivarao \textit{et al.}\textsuperscript{50}, respectively. The HNO\textsubscript{3} model was parameterised for the conformational energetics and pure liquid properties and has also been proved to generate correct structures in TBP/n-alkane/HNO\textsubscript{3}/H\textsubscript{2}O systems as compared to SANS data.\textsuperscript{45} The NO\textsubscript{3}– model, however, has not yet been well tested by us but, according to Sambasivarao \textit{et al.}, it was optimised using a quantum mechanical DFT method and fits to the densities and heats of vaporisation of corresponding ionic liquids. The NO\textsubscript{3}– model has a planar structure and the partial charges on each of the oxygen atoms are equal.

In the simulations, cubic periodic boundary conditions were employed and the Leapfrog algorithm\textsuperscript{51} was used to integrate the equations of motion. Following our previous study\textsuperscript{36} the time step was set as 1 fs. The total potential energy of interaction follows the convention of the OPLS-AA force-field\textsuperscript{52} and is the same as our previous work,\textsuperscript{36} which consists of bonded potentials, non-bonded Lennard-Jones potentials and non-bonded Coulomb potentials. For both the Lennard-Jones and short range Coulomb interactions a 1.2 nm cut-off was used and potential switch functions\textsuperscript{53,54} were applied from 0.9 nm to 1.2 nm to conserve the energies at the cut-off. For the long-range electrostatic potential the particle-mesh Ewald (PME) method was applied.\textsuperscript{55} The \textit{NpT} ensemble was applied to all MD simulations where the pressure and temperature were set as 1 bar and 298.15 K, respectively. To converge the temperature, pressure and density of each MD system the velocity-rescaling thermostat\textsuperscript{56} and the Berendsen barostat\textsuperscript{57} were applied. This procedure is regarded as pre-equilibration run and it was run for 150 ns for each system. These pre-equilibration runs are much longer than common MD simulations because a long simulation time is needed to allow all of the NO\textsubscript{3}– ions, which are randomly distributed in the box at the beginning of the simulations, to coordinate with Zr\textsuperscript{4+} and form Zr(NO\textsubscript{3})\textsubscript{4} complexes. Usually, according to our observation, these individual Zr(IV) complexes do not exchange NO\textsubscript{3}– with each other due to the strong electrostatics between Zr\textsuperscript{4+} and NO\textsubscript{3}– that result from large positive and negative partial charges. The Nosé-Hoover
thermostat 58,59 and Parrinello-Rahman barostat 60,61 were applied in the 50 ns production runs, during which the simulation results were generated.

To investigate the behaviour of Zr$^{4+}$ in the light organic phases, four different systems with a variety of Zr$^{4+}$ concentrations were selected and these are summarised in Table 5.1. These compositions follow the experimentally measured compositions from Motokawa et al., 19 who investigated the Zr$^{4+}$/TBP/n-octane/HNO$_3$/H$_2$O systems using SANS measurements. The concentration of Zr$^{4+}$ varies from zero to 32 mM. System I consists of 30 v/v % TBP in n-octane and is regarded as a blank controller, while systems II, III and IV contain extracted Zr$^{4+}$, nitrates and water with ascending concentrations of Zr$^{4+}$, which are 7 mM, 17 mM and 32 mM, respectively. The major difference between Systems II, II and IV is the concentration of Zr(NO$_3$)$_4$. In this study, four simulations were performed to mimic the compositions of the four systems in Table 5.1, where each simulations box contains around 0.1 million atoms. These correspond to system sizes that are approximately 10.1 nm cubic simulation boxes. It is noted that, in order to keep electrical neutrality, the number of NO$_3^-$ is four times the number of Zr$^{4+}$ in each of the simulation system.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar fraction of each species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>System I</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>-</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-</td>
</tr>
<tr>
<td>TBP</td>
<td>8.54</td>
</tr>
<tr>
<td>n-octane</td>
<td>91.46</td>
</tr>
</tbody>
</table>

*a* We assume that all HNO$_3$ is in an undissociated form.

### 5.4 Results and discussion

#### 5.4.1 The broad structure

To get a first impression of the structure of the four simulated systems, snapshots are shown in Figure 5.1. We first consider the snapshot of System I in Figure 5.1a, which is the metal-free control system. In Figure 5.1a, the TBP molecules are represented by yellow
bonds while, for clarity, the $n$-octane molecules are hidden from view. It is seen that the TBP molecules self-aggregate to form small clusters and the clusters are distributed among the whole box. Typically, the small clusters are dimers or trimers of TBP and it is quite rare to observe a cluster that consists of more than five TBP molecules. This observation agrees with the simulation results of Cui et al.\textsuperscript{62}, Vo et al.\textsuperscript{63}, Servis et al.\textsuperscript{29} and our previous study\textsuperscript{36} as well as with the experimental work of Motokawa et al.\textsuperscript{64}, where the TBP molecules are reported to aggregate into primarily dimers and trimers in $n$-alkane diluents.

![Figure 5.1. Snapshots of (a) System I, (b) System II, (c) System III and (d) System IV, where TBP is represented in yellow, HNO$_3$ and NO$_3^-$ are in red, H$_2$O is in blue and, Zr$^{4+}$ ions are represented by black spheres. For clarity the $n$-octane molecules are hidden from view.](image)

Systems II, III and IV, which are shown in Figures 5.1b, c and d respectively, exhibit a more extended aggregation of TBP molecules as compared with System I shown in Figure
5.1a. In Systems II, four Zr\(^{4+}\) ions, together with nitrates, H\(_2\)O and TBP, form a large cluster at the centre of the box. This cluster, however, is not restricted to the volume immediately around the four Zr\(^{4+}\) ions as it also connects with surrounding smaller clusters that are formed by TBP and HNO\(_3\). As a result, this large cluster stretches from the box centre to the edges and eventually presents itself as an extended aggregated network inside the simulation box. One should note that there is still a certain amount of isolated TBP or polar molecules distributed within the box. In System III there are ten Zr\(^{4+}\) ions inside the box and again these Zr\(^{4+}\) ions form a large aggregated network together with nitrates, H\(_2\)O and TBP. It is worth noting that this aggregated network connects across the periodic boundary at the front and back of the box, thus one should regard the two clusters located at the top and bottom of the box as being connected. Similarly, in System IV, twenty Zr\(^{4+}\) and other polar molecules forms a large worm-like cluster with smaller branches that spans the box. More importantly, visual inspections suggest far fewer isolated TBP and nitric acid molecules in System IV as compared to System II.

It is obvious that the electrostatic interactions between Zr\(^{4+}\), nitrates, H\(_2\)O and the phosphate groups from TBP provide strong attractions that bond them together. The role of water and nitrates in TBP/\(n\)-alkane has been discussed by Servis et al.\(^\text{30}\) and also in our previous work\(^\text{45}\). However, with the presence of highly-charge cations, the small polar molecules seem able to form more complex and extensive connections, such as the local zirconium-centred clusters shown in Figure 5.2., which were not observed in TBP/\(n\)-alkane/HNO\(_3\)/H\(_2\)O systems

![Figure 5.2. The typical structure of two zirconium-centred clusters that are connected by hydrogen bonds.](image-url)
Figure 5.2 shows a typical structure of two connected zirconium-centred clusters that are formed in System IV. Each $\text{Zr}^{4+}$ is closely surrounded by four $\text{NO}_3^-$ and three TBP and is also associated with one or two other polar molecules, such as $\text{H}_2\text{O}$ or $\text{HNO}_3$, at slightly further distances. The motif of a $\text{Zr}^{4+}$ ion surrounded by three TBP molecules is interesting, as there has been debate as to whether the heavy metal ions are coordinated with two TBPs or three.\textsuperscript{18,20,39} The TBP molecules, with their phosphate group pointing towards the $\text{Zr}^{4+}$, stretch their alkane tail to cover the outer space of the $\text{Zr}^{4+}$ ions and form small zirconium-centred cluster. Apart from this, the connection between the two $\text{Zr}^{4+}$ ions is also interesting, as one can see that two $\text{H}_2\text{O}$ molecules penetrate the hydrophobic shells and bridge the $\text{Zr}^{4+}$ ions together. It is obvious that the two $\text{H}_2\text{O}$ molecules form strong hydrogen bonds that overcome the repulsive electrostatics between the two $\text{Zr}^{4+}$ ions. This bridging structure, however, is not always seen as $\text{HNO}_3$ and $\text{NO}_3^-$ are also observed to bridge the zirconium-centred clusters, although with a much lower frequency. In addition, the number of polar molecules that bridge the zirconium-centred clusters is not always confined to 2. Up to four polar molecules have been observed to form hydrogen bonding bridges between zirconium-centred clusters. Based on the snapshots, the systems containing $\text{Zr}^{4+}$ ions can form a much larger and extensive aggregated network as opposed to metal free system. With the strong electrostatics between the ions, polar molecules and TBP, the $\text{Zr}^{4+}$ ions form zirconium-centred clusters locally with polar molecules and TBP and, these zirconium-centred clusters are jointed together globally through two ways. One way is the hydrogen bonds, which are formed by polar molecules and the phosphate head groups from TBP. These hydrogen bonds mainly help the local zirconium-centred clusters to form dimers or, in rear cases, trimers and tetramers. In addition, these hydrogen bonds can connect $\text{HNO}_3$, $\text{H}_2\text{O}$ and TBP molecules and form small clusters even without $\text{Zr}^{4+}$. The other way that joint the zirconium-centred clusters globally is the interactions between TBP molecules. It is seen that many zirconium-centred clusters are solely connect by the butyl groups from TBP molecules, without the contribution from any polar molecules. This indicates that the interactions between the butyl groups may play a role in the formation of aggregation network. What is more, the long-range electrostatic interactions between the phosphate groups may also contribute to this network. A quantitative analysis of the connections between TBP molecules will is shown in Section 5.4.4. Overall, the whole motifs of System II, III and IV can be described as extended networks with embedded zirconium-centred clusters.
Although the snapshots of the simulations can reveal quite a lot of information directly, one must be wary of drawing conclusions based solely on the snapshots. Hence we now turn to some more quantitative analysis of the structures of the four systems.

5.4.2 The structure of local clusters

As mentioned in Section 5.4.1, the snapshots suggest that Zr\(^{4+}\) ions, polar molecules and amphiphiles assemble into small zirconium-centred clusters locally and form extended aggregated network globally. We now present quantitative evidence, based on coordination number analysis, to help establish a typical structure of the local zirconium-centred clusters. The co-ordination number, \(N_c\), is the number of atoms of type \(j\) that are close neighbours of an atom of type \(i\). It is given by

\[
N_c = \int_0^{r_m} \rho_j g_{ij}(r) 4\pi r^2 dr ,
\]

where \(\rho_j\) is the number density of particle \(j\) in the system, \(g_{ij}(r)\) is the pair correlation function between particles \(i\) and \(j\) and \(r_m\) is the position of the first minimum in \(g_{ij}(r)\). An illustration is the Zr\(^{4+}\)–O= pair correlation function of System IV, in which O= is the double bonded oxygen in a TBP molecule. The corresponding coordination numbers are shown in Figure S5.1 in Section 5.6. According to the calculated Zr\(^{4+}\)–O= pair correlation function the corresponding \(r_m\) is approximately 0.21 nm for all of the three systems, indicating that the average Zr\(^{4+}\)–O= distance is near 0.21 nm. This is in agreement with the EXAFS results from Chang et al.\(^20\) as their extrapolated Zr\(^{4+}\)–O= distance was 0.214 nm.

In this study, the coordination numbers of a few types of particles that lie close to Zr\(^{4+}\) are calculated in Systems II, III and IV. The trajectories of the production runs were used to perform the coordination number analysis. The results of the analysis are shown in Table 5.2.

In Table 5.2, the coordination numbers of six particle pairs are presented. These particle pairs were carefully chosen to represent the close neighbours of different molecular species around Zr\(^{4+}\). More specifically, the double bond oxygen (O=) from TBP was chosen because O= is the nearest to Zr\(^{4+}\) ion when a TBP is coordinated with Zr\(^{4+}\). Both the nitrogen and oxygen atoms from NO\(_3^-\) were chosen because, by comparing the two
coordination numbers, one can not only find the co-ordination number of NO$_3^-$ around Zr$^{4+}$ but also get an idea of whether each NO$_3^-$ is, on average, bonded to Zr$^{4+}$ in a mono-dentate or bi-dentate form. The nitrogen in HNO$_3$ and the oxygen in H$_2$O were chosen as these atoms conveniently represent the centres of HNO$_3$ and H$_2$O respectively. Finally, the coordination number of Zr$^{4+}$ around Zr$^{4+}$ was calculated to assess the degree of association between the local zirconium-centred clusters.

Table 5.2. Coordination numbers of one type of particle around Zr$^{4+}$, where the results were calculated as the block average over ten blocks of data. Errors were estimated as the standard deviation of the results from all blocks.

<table>
<thead>
<tr>
<th>Particle pair $^a$</th>
<th>Coordination number</th>
<th>$r_m$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>System II</td>
<td>System III</td>
</tr>
<tr>
<td>Zr$^{4+}$ – O= (TBP)</td>
<td>2.96 ± 0.02</td>
<td>2.89 ± 0.03</td>
</tr>
<tr>
<td>Zr$^{4+}$ – N (NO$_3^-$)</td>
<td>3.98 ± 0.01</td>
<td>3.97 ± 0.01</td>
</tr>
<tr>
<td>Zr$^{4+}$ – O (NO$_3^-$)</td>
<td>7.37 ± 0.05</td>
<td>7.34 ± 0.04</td>
</tr>
<tr>
<td>Zr$^{4+}$ – N (HNO$_3$)</td>
<td>0.11 ± 0.09</td>
<td>0.13 ± 0.10</td>
</tr>
<tr>
<td>Zr$^{4+}$ – O (H$_2$O)</td>
<td>0.32 ± 0.04</td>
<td>0.33 ± 0.04</td>
</tr>
<tr>
<td>Zr$^{4+}$ – Zr$^{4+}$</td>
<td>0.97 ± 0.08</td>
<td>0.99 ± 0.06</td>
</tr>
</tbody>
</table>

$^a$ The Zr$^{4+}$ before the dash is the reference particle, while the particle that closely surround the reference particle is written behind the dash; the molecule species written in the brackets is what the particle in the front belongs to; O= is short for the double bond oxygen from TBP molecules.

From Table 5.2 one can see that the co-ordination numbers of all the tabulated atom pairs do not vary greatly over the three systems. Although, as one goes from System II to System IV, there is an increasing trend in the coordination number of Zr$^{4+}$ around Zr$^{4+}$ and a decreasing trend in that of O= around Zr$^{4+}$, the rate of this increase or decrease is dramatically lower than the increase of the concentration of Zr$^{4+}$. Hence, one may draw the conclusion that the concentrations of Zr$^{4+}$ and nitrates do not have a large impact on the local structure of the zirconium-centred clusters.

For all the three systems, the average coordination number of O= around Zr$^{4+}$ is close to 3, which indicate that on average there are three TBPs around a Zr$^{4+}$ in all of the three systems. This agrees with the visual observation in Section 5.4.1 as well as with the conclusion of Ye et al.$^{35}$ who carried out simulation studies on TBP/n-alkane systems that involved uranyl nitrate. The relation between the NO$_3^-$ and Zr$^{4+}$ pair is also interesting, as the average coordination number of N from NO$_3^-$ around Zr$^{4+}$ is close to 4 while the average number of O from NO$_3^-$ around Zr$^{4+}$ is around 7.3. These facts indicate that each
Zr\(^{4+}\) is surrounded by four NO\(_3^-\) and, the majority of the NO\(_3^-\) should bind with Zr\(^{4+}\) in the bidentate form. This also agrees with Ye et al.\(^{35}\) who proposed that the nitrates prefer bidentate coordination with uranyl under organic environment. As for the cases where NO\(_3^-\) binds with Zr\(^{4+}\) in the mono-dentate form, this may be well explained by the coordination number of O from H\(_2\)O around Zr\(^{4+}\), which is on average around 0.33. The \(r_m\) values for the Zr\(^{4+}\)–O (NO\(_3^-\)) and Zr\(^{4+}\)–O (H\(_2\)O) pairs are close to each other and thus any H\(_2\)O that binds with Zr\(^{4+}\) forces out an oxygen atom from NO\(_3^-\). Based on the average coordination number of the Zr\(^{4+}\)–N (NO\(_3^-\)), Zr\(^{4+}\)–O (NO\(_3^-\)) and Zr\(^{4+}\)–O (H\(_2\)O) pairs, the number of mono-dentate NO\(_3^-\) bound to Zr\(^{4+}\) is about twice the number of coordinated H\(_2\)O. Hence our hypothesis is that, for a Zr\(^{4+}\) ion in any of the three systems, two of the coordinated NO\(_3^-\) will be transformed from bidentate to mono-dentate form when a H\(_2\)O coordinates with that Zr\(^{4+}\). Our simulations thus show that the most common form of the local zirconium-centred clusters are Zr(NO\(_3^-\))\(_4\)·3TBP with small fraction of Zr(NO\(_3^-\))\(_4\)·3TBP·H\(_2\)O and a tiny proportion of Zr(NO\(_3^-\))\(_4\)·3TBP·HNO\(_3\). This agrees with Chang et al.\(^{20}\) as they found Zr(NO\(_3^-\))\(_4\)·3TBP to be the most commonly occurring Zr(IV) complex in both the light organic and third phase, through model fitting to EXAFS data.

In addition, due to the fact that the average coordination number of N from HNO\(_3\) around Zr\(^{4+}\) is as low as around 0.1, it is obvious that the HNO\(_3\) molecules are less competitive in binding as compared to NO\(_3^-\) and H\(_2\)O and nitric acid does not play an important role in the formation of local zirconium-centred clusters. However, HNO\(_3\) is indeed an important agent in binding with most of the TBP molecules so as to create an extensive aggregated network. This will be discussed in detail in Sections 5.4.3 and 5.4.4. Last, but not the least, the average coordination number of Zr\(^{4+}\) around Zr\(^{4+}\) is close to 1, which indicates that these zirconium-centred local clusters are most likely to form dimers with a separation of around 1.5 nm. Based on this, along with the results mentioned above, one may draw the conclusion that these zirconium-centred cluster dimers are primarily connected by H\(_2\)O molecules that form hydrogen bonding bridges between the Zr\(^{4+}\) ions.

5.4.3 Hydrogen bonding network

In this section, we turn to the analysis of the hydrogen bonding networks, which support the structure of the extended aggregated networks we described in Section 5.4.1. By doing so, we carried out hydrogen bonding analysis to calculate and count the strong, primarily
electrostatic attraction between an electronegative atom and a hydrogen atom bonded to a highly electronegative atom.

In this study, the average numbers of hydrogen bonds formed between molecule pairs in Systems II and IV were calculated so as to analysis not only the hydrogen bonding between the polar molecules but also the effect of the concentration of nitrates. The criterion for determining the presence of a hydrogen bond was based on the typical hydrogen bonds formed by SPC/E H₂O molecule pairs, which is that the donor-acceptor distance should be no more than 0.35 nm and the acceptor-donor-hydrogen angle should be no more than 30°. The oxygen atoms that have covalent bonds with the hydrogen atoms in the H₂O and HNO₃ molecules were regarded as potential donors and the electronegative atoms that possess a lone electron pair were regarded as potential acceptors.

Table 5.3 shows that in System II, there are 0.271 TBP–HNO₃ hydrogen bonds per TBP molecule and 0.799 TBP–HNO₃ hydrogen bonds per HNO₃ molecule. In Systems IV these numbers change to 0.480 TBP–HNO₃ hydrogen bonds per TBP and 0.766 TBP–HNO₃ hydrogen bonds per HNO₃. Clearly the concentration of nitrate plays an important role here as the number of TBP–HNO₃ hydrogen bonds per TBP molecule almost doubled when doubling the molar ratio of nitrate. It is also the case with respect to the number of some other hydrogen bonds, for example, the number of nitrate–H₂O hydrogen bonds per H₂O and the number of nitrate–nitrate hydrogen bonds per nitrate. However, the relation between the number of TBP–HNO₃ hydrogen bonds per TBP and the concentration of nitrate is not always linear, as we have shown in our previous study that each TBP preferably hydrogen bonded with only one HNO₃.

<table>
<thead>
<tr>
<th>Molecule pair</th>
<th>Reference molecule</th>
<th>System II b</th>
<th>System IV b</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP – HNO₃</td>
<td>TBP</td>
<td>0.271 ± 0.002</td>
<td>0.480 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>0.799 ± 0.006</td>
<td>0.766 ± 0.005</td>
</tr>
<tr>
<td>TBP – H₂O</td>
<td>TBP</td>
<td>0.149 ± 0.003</td>
<td>0.115 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>1.331 ± 0.021</td>
<td>1.031 ± 0.018</td>
</tr>
<tr>
<td>nitrate – H₂O</td>
<td>nitrate *</td>
<td>0.240 ± 0.002</td>
<td>0.274 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>0.835 ± 0.005</td>
<td>2.012 ± 0.005</td>
</tr>
<tr>
<td>nitrate – nitrate</td>
<td>nitrate *</td>
<td>0.163 ± 0.001</td>
<td>0.236 ± 0.001</td>
</tr>
<tr>
<td>H₂O – H₂O</td>
<td>H₂O</td>
<td>0.083 ± 0.004</td>
<td>0.271 ± 0.007</td>
</tr>
</tbody>
</table>

* In this work, nitrate stands for both the NO₃⁻ and HNO₃ in the system. b The normalised numbers are calculated as the number of hydrogen bonds between molecule pairs divided by the total number of the reference molecules in that system.
More interestingly, the total number of TBP–HNO$_3$ and TBP–H$_2$O hydrogen bonds per TBP molecule in System IV is 0.595. This number is, according to our previous study, approximately 40 % lower than that of the light organic phase without metal ions. However, one should be aware that the TBP molecules that coordinate with Zr$^{4+}$ ions cannot form hydrogen bonds with HNO$_3$ and H$_2$O as their phosphate groups are occupied by Zr$^{4+}$. Hence, this number increases to 0.736 if we discard the TBP molecules that coordinate with Zr$^{4+}$ and, this number is close to 0.739, which is the molar ratio of (HNO$_3$ + H$_2$O) to TBP in System IV. This indicates that HNO$_3$ and H$_2$O still favour the hydrogen bonds between themselves and TBP and, almost all of the HNO$_3$ and H$_2$O are hydrogen bonded with TBP. This agrees with the results in our previous study$^{45}$ which focused on metal-free PRUEX systems. Although this number is still about 24 % lower than that of the metal-free systems, it is noted that the molar ratios between HNO$_3$ and TBP in both System IV and the light organic phase in the metal-free systems are close to 1. It is thus believed that more TBP molecules should be hydrogen bonded if one increases the total concentration of HNO$_3$ and H$_2$O to a value that is approximately equals to the concentration of TBP.

Moreover, in System IV, there are 0.274 nitrate–H$_2$O hydrogen bonds per nitrate and 2.012 nitrate–H$_2$O hydrogen bonds per H$_2$O. This indicates that that, in System IV, each H$_2$O is shared by two nitrate particles on average. It seems that H$_2$O molecules serve as the joint of the hydrogen bonding branches that are formed by HNO$_3$ and TBP. Hence, H$_2$O, HNO$_3$ and NO$_3^-$ are still the key components to form hydrogen bonds in the systems. This, once more, agrees with the conclusions in our previous study.$^{45}$

In Section 5.4.2, the HNO$_3$ molecules are found to be less competitive as compared to NO$_3^-$ and H$_2$O, in terms of close contact with Zr$^{4+}$ ions. This may be explained by their strong ability to form hydrogen bonds, as their hydrogen atoms seem to have very strong electrostatic interactions with the double bond oxygens from TBP. According to our previous study, the hydrogen bond formed between HNO$_3$ and TBP is stronger than that between H$_2$O and TBP. In addition, the partial charges on the oxygens from our HNO$_3$ model are less negative than that on the oxygen from H$_2$O model. This results in that the oxygen from H$_2$O has a higher attraction to the Zr$^{4+}$ ions than the oxygens from HNO$_3$. Hence, the HNO$_3$ molecules in our simulated systems primarily act as the key component that provides hydrogen bonds to TBP rather than the bridge between Zr$^{4+}$ ions.
One of the most interesting results is that there are 0.083 $\text{H}_2\text{O}–\text{H}_2\text{O}$ hydrogen bonds per $\text{H}_2\text{O}$ in System II while this number increases to 0.271 in System IV. This number increases about two times from System II to System IV though the concentration of $\text{H}_2\text{O}$ slightly decreases. What is more, this result is different from that in our previous study, where the metal-free systems were investigated.\textsuperscript{45} Hence, Zr$^{4+}$ must play a vital role in introducing more $\text{H}_2\text{O}–\text{H}_2\text{O}$ hydrogen bonds. Based on the result here and the discussions in Sections 5.4.1 and 5.4.2, one may draw the conclusion that Zr$^{4+}$ provide strong electrostatic attraction to $\text{H}_2\text{O}$ and thus $\text{H}_2\text{O}$ molecules prefer to concentrate near the Zr$^{4+}$. As a result, $\text{H}_2\text{O}$ are more likely to connect with each other through hydrogen bonds and form hydrogen bonding bridges between Zr$^{4+}$ ions. HNO$_3$ molecules are more competitive than $\text{H}_2\text{O}$ when bonding with the phosphate groups from TBP but are less competitive than $\text{H}_2\text{O}$ when they coordinate with Zr$^{4+}$. Thus the major role of HNO$_3$ is to provide hydrogen bonds to TBP and form small hydrogen bonded clusters.

### 5.4.4 Cluster analysis

To estimate the average number and size of the clusters that are formed by strong electrostatic interactions, we performed a cluster analysis on all the four systems. In the cluster analysis, all the particle species expect $n$-octane are considered to have the potential to form clusters and all the atoms and ions were treated as mass points. The distance between each atom was calculated as the distance between the mass points and, the angle between three atoms was calculated as the angle between the three mass points.

The criteria for determining whether two molecule species or ions are within the same cluster are as follows. Firstly, if the two molecules or ions are able to form hydrogen bond then the criterion for hydrogen bond, which is described in Section 5.4.3, is used. The two molecules or ions are regarded as directly connected within the same cluster if they meet the criterion for hydrogen bonding. Secondly, if the two molecules or ions are attracted by strong electrostatics but are not able to form hydrogen bonds, simple distance cut-off criterion is used to check if certain atoms in the two molecules are within the cut-off. For example, a TBP and a Zr$^{4+}$ are regarded as directly connected within the same cluster if the distance between Zr$^{4+}$ and the O= atoms from TBP is smaller than 0.21 nm, where 0.21 nm is the position of the first minimum in the pair correlation function of Zr$^{4+}$ and O=. In this study, the simple distance cut-off criterion is applied to the six types of particle pairs that are tabulated in Table 5.2, where the tabulated $r_m$ values were used for the cut-off distance.
used for each particle pair. Apart of the particle pairs in Table 5.2, the distance cut-off criterion is also applied to P–P pair with a cut-off of 0.82 nm so as to represent the aggregation between TBP molecules through strong electrostatics. These criteria follow Servis et al.\textsuperscript{30} who proposed the use of $r_m$ values as the cut-off radius for cluster analysis.

By performing calculations using the criteria mentioned above, the direct connections between particles that are within the same clusters can be found. Afterwards, the connectivity between the indirectly connected molecules, which are within the same clusters, was calculated using the connectivity matrix method proposed by Sevick et al.\textsuperscript{67} A detailed illustration is provided in the appendix of Sevick’s paper. The results of cluster analysis, which are the time averages over the MD production runs, are shown in Figure 5.3.

![Figure 5.3](image)

**Figure 5.3.** Average number of clusters against cluster size in a semi-log plot. Only n-octane molecules are excluded from cluster analysis. The dashed lines show the trend of change between each point. The point is not shown if the value of number of cluster at that point is smaller than 0.01.

In Figure 5.3, the point is not shown if the value of number of cluster at that point is smaller than 0.01, as the probability of having the corresponding cluster size is remarkably low. It is obvious that, in System I, the most common cluster sizes are 2 to 3. However, the numbers of clusters with these sizes decrease quickly from System II to System IV. In addition, there is quite a fraction of isolated particles in System I but this number also
drops dramatically from System II to System IV. More obviously, the cluster sizes in Systems II, III and IV can reach up to 44, 53 and 68 respectively, while the probability of finding a cluster size that larger than 7 is extremely low in System I. These facts indicate that, with the addition of Zr$^{4+}$, nitrates and H$_2$O, the system tends to form more connections between the TBP through electrostatics and form much larger clusters. What is more, the higher concentrations of the Zr$^{4+}$ and nitrates generate the largest cluster sizes possible. This is in agreement with the visual observation in Section 5.4.1 as well as the results in Section 5.4.3.

From the profiles in Systems II, II and IV, a few peaks, which shared by all the three systems, can be found around the cluster size of 11, 21, 30 and 40 respectively. Obviously the peaks indicate that the probability of finding a cluster with the corresponding sizes at the peaks is higher than other cluster sizes. As proposed in Section 5.4.2 that the most common form of the local zirconium-centred clusters is Zr(NO$_3$)$_4$·3TBP, there should commonly be around 8 molecules in a zirconium-centred cluster in Systems II, III and IV. However, one should note that the zirconium-centred clusters may be hydrogen bonded with a few polar molecules. What is more, in our previous work we found that the TBP/n-dodecane/HNO$_3$/H$_2$O systems do not have large probability of forming cluster sizes that are larger than 13.$^{45}$ Hence, the cluster sizes at the peaks of the profiles, namely, the sizes of around 11, 21, 30 and 40, should related to a single, double, triple or quadruple of the local zirconium-centred clusters, respectively. In other words, oligomers of the zirconium-centred clusters should exist in our simulated systems. The massive clusters that are formed in Systems II, III and IV should be resulted from the addition of Zr$^{4+}$ ions. What is more, in Figure 5.3, the peak around cluster size of 21 is higher than that of around 11 and, much higher than the peaks around 30 and 40. This indicates that the zirconium-centred clusters form dimers, but that these dimers are loosely associated within polar clusters, the concentration of Zr$^{4+}$ does not have much effect on this. This is, again, in agreement with the results in Section 5.4.2. It is worth noting that Chang et al.$^{20}$ also proposed, according to their EXAFS fitting results, the existence of Zr(IV) oligomers in both the light organic and third phases of the Zr(IV)/TBP/n-dodecane/HNO$_3$/H$_2$O system. They think that both the light organic and third phases of the Zr(IV)/TBP/n-dodecane/HNO$_3$/H$_2$O system are dominated by oligomers of Zr(IV)/HNO$_3$/TBP complexes, although they cannot tell whether the oligomers are primarily dimers. Hence, their results and our findings are in good agreement in terms of the existence of oligomers of Zr(IV)/HNO$_3$/TBP complexes in Zr(IV)/TBP/n-alkane/ HNO$_3$/H$_2$O systems.
Apart from the cluster analysis mentioned above, we have also analysed the clustering behaviour of TBP molecules through the contact of functional groups. As mentioned in Section 5.4.1, according to our observation, the vast majority of the TBP molecules in Systems II, III and IV are connected with each other through contact of butyl groups. But conclusions should not be drawn based on solely the observation of snapshots. Hence, cluster analysis was performed to provide a quantitative view of the connections between TBP through functional group.

Similar to our previous work\textsuperscript{45}, a 0.74 nm distance cut-off, which corresponds to the \( r_m \) value in the carbon-carbon pair correlation function of TBP molecules, was used as the criterion for determining the connectivity between the butyl groups from TBP molecules. In addition, a 0.75 nm distance cut-off, which corresponds to the \( r_m \) value in the phosphorous-phosphorous pair correlation function of TBP molecules, was used as the criterion for determining the connectivity between the phosphate groups from TBP molecules. In the cluster analysis calculations, only the P and C atoms from TBP molecules were taken into account while the H and O atoms were discarded, as this is consistent with the cut-off criteria and can improve the efficiency of the calculation. Our results show that there are, on average, at most 31.2 \%, 69.4 \%, 78.1 \% and 86.8 \% of total TBP molecules are regarded as being in one cluster in Systems I, II, III and IV. In other words, on average, the largest cluster of TBP in System I, based on our criteria, contains approximately 31.2 \% of total number of TBP. In a similar fashion, this number is 69.4 \%, 82.1 \% and 86.8 \% in System II, III and IV. Obviously, the TBP molecules, together with the polar molecules and the embedded zirconium-centred clusters, can be regarded as extended aggregated networks in Systems III and IV, although there are small portions isolated small TBP clusters or monomers. It addition, it is noteworthy that the molar ratio of TBP and H\(_2\)O in the four systems are similar but the average size of the largest TBP clusters increases from Systems I to IV. Thus the concentrations of HNO\(_3\) and Zr\(^{4+}\) should have strong impacts on the connections between TBP molecules. In our previous study, we concluded that, in the metal-free PUREX systems, the driving forces for the formation of the extended aggregated networks should include strong short-range electrostatic attractions between the phosphate groups, the effect of polar bridging molecules, the attraction between butyl groups and, probably, long-range electrostatic interactions between the phosphate groups. It seems that this is also the case in the Zr(IV)/TBP/n-octane/HNO\(_3\)/H\(_2\)O systems. In addition, apart from these possible driving forces mentioned above, the strong electrostatic interactions introduced by the large positive charges on Zr\(^{4+}\)
should also play an important role as they should have stronger impact on other charges as compared with the phosphate group.

5.5 Conclusions

The microscopic structures of three Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems have been explored through an MD simulation approach, where the force field parameters for the atomic models had been proved to give accurate predictions of the microscopic structures of TBP/n-dodecane/HNO$_3$/H$_2$O systems.$^{45}$ All the compositions of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems investigated, which are classified as the light organic phase, were taken from experiments and were similar to the experimental conditions.$^{19}$ The broad structures of the simulated systems at a nanometre scale were extensively investigated through visual observation and coordination number, hydrogen bonding and cluster analysis.

According to our results, Zr$^{4+}$ ions have a strong impact on the microscopic structure of the systems. The large positive charges on the Zr$^{4+}$ ions give rise to strong electrostatic attractions with the electronegative atoms in the polar molecules and amphiphiles in the system. As a result, the amphiphiles and polar molecules coordinate with Zr$^{4+}$ ions and form local zirconium-centred clusters such as Zr(NO$_3$)$_4$·3TBP, Zr(NO$_3$)$_4$·3TBP·H$_2$O and Zr(NO$_3$)$_4$·3TBP·HNO$_3$, but the primary species is Zr(NO$_3$)$_4$·3TBP. These local zirconium-centred clusters, however, are not isolated from each other, as the polar molecules such as H$_2$O and nitrate can form hydrogen bonding bridges that penetrate the hydrophobic shells of the local clusters and connect the adjacent Zr$^{4+}$ ions at a distance of around 1.5 nm. These hydrogen bonding bridges do not connect all the local zirconium-centred clusters together, as evidence from coordination number analysis and cluster analysis show that the zirconium-centred clusters tend to form primarily dimers and this is invariant to the concentration of Zr$^{4+}$ ions. However, all the zirconium-centred clusters may be regarded as connected if one takes into account the contact between the butyl groups from TBP. Thus the extended aggregated networks comes about not only from the strong short-range electrostatic interactions between Zr$^{4+}$, polar molecules and the phosphate groups from TBP, but also from the attractions between the hydrophobic butyl groups from TBP. What is more, long-range interactions may also play an important role in stabilising these polar networks.
In our previous study where the TBP/n-dodecane/HNO$_3$/H$_2$O systems were investigated, TBP, HNO$_3$ and H$_2$O formed extended aggregated network akin to bi-continuous micro-emulsion, but the maximum size of the hydrogen bonded clusters was around 13 molecules.$^{45}$ However, in the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems, the cluster sizes can reach around 80 particles due to the formation of local zirconium-centred clusters and the hydrogen bonding connections between them. The broad structures of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems, especially for the one with higher concentration of Zr$^{4+}$, are akin to extended aggregated networks with embedded zirconium-centred clusters. This structure not only is different from that of the metal-free TBP/n-alkane/HNO$_3$/H$_2$O systems but also differs from the hypothesis of Chiarizia et al.$^{18}$ who proposed that the systems are dominated by large reverse micelles. This interesting finding may shed some new light on the investigations of the microscopic structure of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems that related to the PUREX process.

However, one should be wary that the simulation results presented in this chapter may be limited to the pre-formation of larger aggregates, which may require more than ten times longer simulation time to evolve. In the future, further simulations should be carried out to analyse the evolution of the cluster size distribution with time so as to check if the system has reached equilibrium or the system is still slowly evolving.

Despite the interesting findings in this work, one should be wary that the classical, non-polarisable atomic models used in this work, especially the Zr$^{4+}$ model, may have limitations. Theoretically the high positive charge on Zr$^{4+}$ should result in strong induced dipoles in neighbouring particles. Furthermore it is likely that there will be a degree of covalent interaction between a Zr$^{4+}$ ion and a nitrate ligand. However, this effects were missing in our simulations as the force field potential we used did not take polarisability or charge transfer into account. To verify that our simulations indeed catch the major characteristic structures of the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems at a nanometer scale, we will compare the calculated SANS profiles from our simulations to the results of our SANS experiments. The SANS experiments on these systems have been performed and the results are currently being prepared. The calculated SANS profiles form our simulations are shown in Section 5.6.
5.6 Supporting information

5.6.1 Atomic pair correction function and coordination number

![Image](image.png)

**Figure S5.1.** The Zr$^{4+}$ – O= pair correlation function and its corresponding coordination numbers from System IV in a log-log scale.

5.6.2 Calculated SANS profiles

In this study, the trajectories of the production runs were used to calculated the SANS profile. The coherent scattering cross section per unit volume, $I(q)$, where the magnitude of scattering vector $q$ is defined as $q = (4\pi/\lambda) \cdot \sin(\theta/2)$ with $\theta$ being the scattering angle and $\lambda$ being the neutron wavelength, is given by

$$I(q) = \frac{1}{V} \left\langle \sum_j \sum_k b_j b_k \exp\left[-i q \cdot (r_j - r_k)\right] \right\rangle,$$  \hspace{1cm} (5.2)

in which $r_j$ and $r_k$ are the position of atom $j$ and $k$, $V$ is the volume of the system, $b_j$ and $b_k$ are the coherent atomic scattering length of the $j^{th}$ and $k^{th}$ atoms, $i$ is the imaginary unit and the angle brackets stand for ensemble average of the inner part. The calculated SANS profiles of the four simulated systems are shown in Figure S5.2.
In Figure S5.2, the calculated SANS profile for System 1 is obviously different from those of Systems 2, 3 and 4. The calculated SANS profiles for Systems 2, 3 and 4 show an increasingly negative slope in $q < 3 \text{ nm}^{-1}$ region with increased concentration of Zirconium nitrate. This phenomenon may result from an increase of average cluster sizes. In addition to this, one should also be wary of the system size dependence of the calculated SANS profiles as the simulated systems are only around 10.1 nm in size and may not be big enough to capture the whole motif of the extended aggregated network. In our previous study,$^{45}$ even a 21.3 nm cubic box proved to be too small to capture the whole microscopic structure of the third phase in TBP/$n$-dodecane/HNO$_3$/H$_2$O, let alone the 10.1 nm boxes for more complicated Zr(IV)TBP/$n$-octane/HNO$_3$/H$_2$O systems. However, due to the fact that the equilibrium runs for the Zr(IV)TBP/$n$-octane/HNO$_3$/H$_2$O requires much longer times than the metal free system, it is currently not feasible to simulate such systems using systems sizes as large as 20 nm. Still, we still intend to study system-size dependence in the future, albeit making do with a smaller range of box-lengths.
Acknowledgments

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5.7 References


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6 Conclusions and future work

6.1 Conclusions

The research presented in this thesis concerns the mechanism of third phase formation in the PUREX process. This entailed investigations into the microscopic structure of the light organic and third phases as well as the molecular speciation of the aggregates. A large number of simulation results have been generated, many of which were validated by experiments. We now summarise the main contributions made by this work towards an understanding of third phase formation in the PUREX process.

6.1.1 Development of a new molecular model of TBP

As reviewed in Section 1.2.2, accurate molecular models are essential to molecular simulations, as the microscopic structure, speciation of molecular complexes, and the thermodynamic and kinetic properties of molecules in a simulated system are all highly dependent on the molecular models used. Different models have shown different strengths and weaknesses in predicting thermodynamic, kinetic, and structural properties as the models were optimised based on different criteria. Many molecular models for TBP have been developed in recent years\(^1\)\(^8\), most of which were optimised for the thermodynamic properties of pure TBP liquid, i.e. density, enthalpy of vaporisation and dielectric dipole moment. These models were proved to show good accuracy in organic environments. However, they fail in describing the behaviour of TBP in water, showing demixing for compositions that are known to be homogeneous solutions under experimental conditions. Apart from these TBP models, some TBP models were optimised to yield a good solvation free energy for water in TBP, aiming to give good predictions for TBP–H\(_2\)O interactions. However, these TBP models perform badly in predicting TBP–n-alkane interactions.

In this study, a new all-atom model for TBP was developed to give good predictions for both TBP–n-alkane and TBP–H\(_2\)O interactions. This model is a good candidate for use in situations where the TBP interacts simultaneously with both polar and non-polar molecules. In addition, this model is particularly important in the modelling of the PUREX process where TBP acts as a ligand to certain actinide ions and transports them from an acidic aqueous phase to an n-alkane-rich organic phase. To our knowledge, it is the only TBP model that has been validated to show good prediction of the microscopic structure of systems that consist of both hydrophobic and hydrophilic species.
Another aspect of the uniqueness of our TBP model is that it was developed to fit not only thermodynamic properties but also SAXS data, which is a measurement of the microscopic structure of the systems. The advantage of this optimisation strategy is that the model can give a good prediction of the microscopic structure of the systems that are relevant to the PUREX process, which is essential to the investigation of molecular speciation and nanometre-scale structure of the systems. To our knowledge, it is the only TBP model available to use SAXS data as one of the parameterisation criteria.

6.1.2 Observation of the co-existing light organic and third phases through simulations

As is reviewed in Section 1.2.2, no simulation studies have been conducted to determine co-existence between the light organic and third phases of PUREX-related systems. This may be because, according to our simulations, in order to convincingly show phase coexistence between the light organic and third phases of a PUREX-related system in a single MD simulation box, the system size required would be far too large to be feasible. In addition, the accuracy of the force field is also a crucial factor in determining phase co-existence.

In this study, instead of using MD simulations, we performed GEMC simulations on a TBP/n-dodecane/HNO₃/H₂O system and revealed a demixing transition, where the compositions and densities of the co-existing phases were in good agreement with experiments. The simulation results of GEMC were validated using Gibbs free energy calculations. To our knowledge, this study is the first to report the observation of coexisting light organic and third phases of a system relevant to the PUREX process through computational simulations.

6.1.3 Revealing a novel micro-emulsion phase transition

The broad structures of both the light organic and third phases, which correspond to the TBP/n-dodecane/HNO₃/H₂O system under experimental condition, were explored at nanometre scale. Both the light organic and third phases consisted of extended mesh-like aggregates. Within this mesh were unit clusters of HNO₃, H₂O and TBP molecules, connected by hydrogen bonds. The only macroscopic difference between the two phases was the thickness of the mesh and thus the volume fraction of the aggregates. In other
words, both phases are similar to the Winsor-III classification of surfactant micro-emulsion systems that consist of water/oil/surfactant species,\textsuperscript{10} where bi-continuous micro-emulsion phases are found. However, the difference between our system and most water/oil/surfactant systems is that we believe the co-existing phases studies here are both bi-continuous micro-emulsion phases with isotropic symmetry. In other words, the formation of the third phase is an unusual isotropic-isotropic micro-emulsion phase transition. This phenomenon is different from the common phase behaviour of water/oil/surfactant micro-emulsion systems.\textsuperscript{11} However, it is still not clear why, in molecular terms, a homogeneous system, of composition intermediate between that of the light organic and third phases, should demix. To our knowledge, a phase transition of this nature has not previously been reported.

6.1.4 Providing a new view of the Zr(IV)/TBP/\textit{n}-alkane/HNO\textsubscript{3}/H\textsubscript{2}O systems

The microscopic structure of a few Zr(IV)/TBP/\textit{n}-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems have been explored through a MD simulation approach, where the compositions of the systems were similar to the light organic phase studied experimentally.\textsuperscript{12} In the past, the most popular hypothesis for the microscopic structure of metal/TBP/\textit{n}-alkane/HNO\textsubscript{3}/H\textsubscript{2}O systems, which are relevant to the PUREX process, is that the metal, polar molecules and amphiphiles form large ellipsoidal reverse micelles in both the light organic and third phases. For instance, Chiarizia \textit{et al.} suggested that the size of the ellipsoidal reverse micelles in the Zr(IV)/TBP/\textit{n}-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems could reach 230 and 15 Å in the major and minor axes respectively. However, based on the simulation results of this study and their agreement with EXAFS data, the light organic phases do not consist of large ellipsoidal reverse micelles. Instead, the Zr\textsuperscript{4+}, nitrate, TBP and H\textsubscript{2}O form an extended aggregating network with embedded local clusters centred on Zr\textsuperscript{4+}, where the local clusters are primarily of the form of Zr(NO\textsubscript{3})\textsubscript{4}·3TBP complexes. Hence, this finding provides a new view of the Zr(IV)/TBP/\textit{n}-octane/HNO\textsubscript{3}/H\textsubscript{2}O systems.

6.2 Future work

There are several possible directions for future studies and the major ones are discussed below.
6.2.1 The uncompleted work in Chapter 5

Although most of the simulation work related to Chapter 5 has been done, there are still objectives yet to be accomplished. These include the comparison between the calculated SANS profiles from simulation and the SANS data from experiments. A good match between the calculated and experimental SANS profiles would provide further validation of the results presented and would strengthen the conclusions in Chapter 5.

It is noteworthy, however, that the comparison between the calculated and experimental SANS profiles may be nontrivial, as the system size may have a strong impact on the calculated SANS profiles. Such an impact was presented and discussed in Chapter 4. In order to check the system size dependence of the calculated SANS profiles, it is recommended to perform MD simulations at the same conditions using at least three system sizes, i.e. 10 nm, 15 nm and 20 nm. However, as is introduced in Section 5.3, the Zr(IV)/TBP/n-octane/HNO$_3$/H$_2$O systems, which were around 10.1 nm in size, were simulated for 200 ns using MD. This corresponds to approximately 17 days of computer time using 48 computer cores. Doubling the number of molecules in the simulation box would at least double the computational cost. Hence many more computer cores would be needed to simulate a 20 nm system within a few weeks.

6.2.2 A theoretical model to explain the novel phase behaviour

As discussed in Chapter 4, third phase formation in the TBP/n-dodecane/HNO$_3$/H$_2$O systems may be regarded as an isotropic-isotropic micro-emulsion phase transition. However, the mechanism of such novel phase transition is yet to be explored. As both of the light organic and third phases are akin to the Winsor-III classification of bi-continuous micro-emulsion phase\textsuperscript{10}, one would firstly try explaining this phase behaviour using theories that are related to intermolecular and surface forces\textsuperscript{13}. For instance, the extensive aggregating network could be regarded as a large amount of connected cylinders, where the polar molecules (HNO$_3$ and H$_2$O) and the hydrophilic phosphate groups from TBP are inside the cylinders, leaving the hydrophobic butyl groups to form the surface of the cylinders. As the aggregating meshes in the third phase are thicker than that in the light organic phase, one may assume that the major difference between the cylinders in both phases is the thickness, namely, the light organic phase consists of thinner cylinders while the third phase consists of thicker cylinders. One may then consider, based on theories of intermolecular surface forces, how the thickness or bending of the cylinders affects the
structure of both phases and, if there are driving forces that separate the two different cylinders into two phases when they are mixed with each other.

There are, however, two problems in order to apply such theories. Firstly, according to our observation, not all of the polar molecules that form the aggregation network are covered by TBP. Instead, many HNO₃ molecules, which are hydrogen bonded with other polar molecules and TBP, were in contact with n-dodecane molecules that are around the unit clusters. In other words, there should be polar molecules at the surface of the cylinders. Hence, one may need to refine the theoretical model so that the correct structure of the aggregates can be represented. Secondly, assuming the compositions of the light organic and third phases are two points in a quaternary phases diagram where the molecule species are TBP, n-dodecane, HNO₃ and H₂O, one only knows one pair of co-existing points at the current stage. Hence, one may need to explore much more co-existing points in the phase diagram to gain knowledge of the overall phase behaviour of the TBP/n-dodecane/HNO₃/H₂O system. According to our results, GEMC is one of the best approaches to explore the coexisting points in the phase diagram through simulation. However, it is nontrivial to explore a large number of state points using GEMC due to its high computational cost.

6.2.3 Models using polarisable force field

As discussed in Chapters 1 and 5, molecular models using a polarisable force field should be more suitable than non-polarisable models when simulating systems that consist of highly charged metal ions. Polarisable models are particularly essential to the simulations which involves U(VI), Pu(IV), Th(IV) and Zr(IV).

However, as there are no validated polarisable models reported, efforts may be firstly put into the parameterisation of available polarisable models⁶,¹⁴ by fitting to particular experimental data. It is recommended that experimental data that describe microscopic structure, i.e. SAXS, SANS or EXAFS, should be considered as one of the most important criteria for the parametrisation of models.
6.3 References


Appendices

A  Pair correlation function

The pair correlation function, $g_{AB}(r)$, which is also called the radial distribution function, between particles of types A and B is given by

$$g_{AB}(r) = \frac{\langle \rho_B(r) \rangle}{\langle \rho_B \rangle_{local}} = \frac{\langle N_B(r) \rangle}{4\pi r^2 \Delta r \langle \rho_B \rangle_{local}}, \quad (A.1)$$

where the angle brackets denote the time average of the property, $\langle \rho_B(r) \rangle$ is the average number density of particle type B in a spherical shell with a thickness $\Delta r$ at a distance $r$ around particle A, $\langle \rho_B \rangle_{local}$ is the number density of particle type B averaged over all spherical slices around particle A within radius $r_{max}$, and $\langle N_B(r) \rangle$ is the average number of particles of type B in a spherical shell with a thickness $\Delta r$ at a distance $r$ around particle A. Usually $r_{max}$ is half of the side length of the simulation box.
Bennett Acceptance Ratio method

The Bennett Acceptance Ratio (BAR) method estimates the change of excess free energy as one slowly changes the Hamiltonian of a system from one state to another along a given pathway, where a series of intermediate states are defined. The pathway is usually chosen so that there is an overlap of micro-states in the phase space between adjacent intermediate states. A coupling parameter, \( \xi \), is used to describe the intermediate states of the system ranging from \( \xi = 0 \) to \( \xi = 1 \), where \( \xi = 0 \) corresponds to the initial state and \( \xi = 1 \) to the final state. Hence, for a NPT ensemble, the change of free energy, \( \Delta G \), can be calculated as the sum of all the small energy differences between adjacent states, \( \Delta G_\xi \), and is given by

\[
\Delta G = G_{\xi=1} - G_{\xi=0} = \sum_\xi \Delta G_\xi ,
\]

where \( G_{\xi=1} \) and \( G_{\xi=0} \) are the Gibbs free energies at \( \xi = 1 \) and 0, respectively.

In this study, the Bennett Acceptance Ratio method was performed by slowly inserting a molecule of particular type into a simulated system. Both the electrostatic and van der Waals potentials are coupled by \( \xi \), where the interactions between the inserted molecule and the rest of molecules are switched off at \( \xi = 0 \) while are fully turned on at \( \xi = 1 \). According to Bennett \(^2\), the Gibbs free energy difference, \( \Delta G(\xi_i \rightarrow \xi_j) \), for given trajectories generated at \( \xi_i \) and \( \xi_j \), which contain \( N_i \) and \( N_j \) frames of configurations respectively, is given by

\[
\Delta G(\xi_i \rightarrow \xi_j) = k_B T \ln \left\{ \frac{\langle f[U(\xi_i) - U(\xi_j) + C] \rangle_{\xi_j}}{\langle f[U(\xi_j) - U(\xi_i) + C] \rangle_{\xi_i}} \right\} + C ,
\]

where \( U(\xi_i) \) and \( U(\xi_j) \) are the potential energies of the configurations at states \( \xi_i \) and \( \xi_j \) respectively, \( f \) is the Fermi function

\[
f(x) = \frac{1}{1 + \exp\left(\frac{x}{k_B T}\right)} ,
\]

and \( C \) is the energy offset which is given by

\[
C = k_B T \ln \frac{Q_j N_j}{Q_i N_i} ,
\]

with \( Q_i \) and \( Q_j \) being the partition functions of states \( \xi_i \) and \( \xi_j \) respectively. Eq. B.2 is then iterated until the condition

\[
\langle f[U(\xi_i) - U(\xi_j) + C] \rangle_{\xi_j} = \langle f[U(\xi_j) - U(\xi_i) + C] \rangle_{\xi_i}
\]  

(B.5)

is satisfied. The value of \( C \) is obtained through iteration and the change of Gibbs free energy between adjacent states \( \xi_i \) and \( \xi_j \) is given by

\[
\Delta G(\xi_i \to \xi_j) = -k_B T \ln \frac{N_j}{N_i} + C.
\]  

(B.6)

The adjacent states \( \xi_i \) and \( \xi_j \) are treated equivalently in BAR method and, finally the change of Gibbs free energy between the final and initial states can be given by

\[
\Delta G = \sum_{k} \Delta G(\xi_{k-1} \to \xi_k),
\]  

(B.7)

where \( n \) is the total number of states in the BAR calculation, \( k = 1, \ldots, n, \xi_i = 0 \) and \( \xi_j = 1 \).
C Periodic shear flow method for viscosity calculation

As is introduced in Section 3.4.1.2, in the periodic shear flow method, an external force is applied only in the $x$ direction to the simulated system. This gives rise to an acceleration $\mathbf{a}$, where the magnitude of $\mathbf{a}$ in the $x$ direction, $a_x$, is a function of $z$ only. According to the Navier-Stokes equation given in Eq. 3.2, the relation between $a_x(z)$, and the resulting velocity field in the $x$ direction, $u_x(z)$, is given by\(^3\,^4\)

$$\rho \frac{\partial u_x(z)}{\partial t} = \rho a_x(z) + \eta \frac{\partial^2 u_x(z)}{\partial z^2}, \quad (C.1)$$

where $\rho$ is the density of the simulated system, $t$ is the time and $\eta$ is the shear viscosity of the simulated system. At steady state, Eq. C.1 simplifies to

$$a_x(z) + \frac{\eta}{\rho} \frac{\partial^2 u_x(z)}{\partial z^2} = 0. \quad (C.2)$$

The acceleration, $a_x(z)$, and velocity profile, $u_x(z)$, must be periodic as periodic boundary conditions are used in our simulations. In addition, $a_x(z)$ should be smooth in order to obtain a smooth velocity profile. A cosine function which satisfies both conditions is given by

$$a_x(z) = A \cos(kz), \quad (C.3)$$

$$k = \frac{2\pi}{l_z}, \quad (C.4)$$

where $l_z$ is the side length of the simulation box in the $z$ direction and $A$ is amplitude of $a_x(z)$. If we assume that $a_x(z) = 0$ at $t = 0$, solving Eq. C.1 gives

$$u_x(z) = v \left[1 - \exp\left(-\frac{t\eta k^2}{\rho}\right)\right] \cos(kz), \quad (C.5)$$

$$v = A \frac{\rho}{\eta k^2}, \quad (C.6)$$


where \( \nu \) is related to the velocity profile \( u_s(z) \). In the NEMD simulations the instantaneous \( \nu(t) \) is given by

\[
\nu(t) = \frac{2 \sum_{j=1}^{N} m_j v_{j,x}(t) \cos(k r_{j,z}(t))}{\sum_{j=1}^{N} m_j},
\]

(C.7)

where \( v_{j,x} \) is the velocity of atom \( j \) in the \( x \) direction, \( r_{j,z} \) is the position of atom \( j \) in the \( z \) direction and \( m_j \) is the mass of atom \( j \). The \( A \)-dependent shear viscosity can finally be calculated and is given by

\[
\eta(A) = \frac{A \rho}{\langle \nu \rangle k^2},
\]

(C.8)

where the angle brackets denote the time averaged \( \nu \) over the trajectory of the simulation.
D Connectivity matrix method for cluster analysis

In this section, the connectivity matrix method proposed by Sevick et al.\(^5\) is introduced, which takes the connectivity information for directly connected particles and use this to obtain full connections. A full connection means all molecules within the same cluster are connected, either directly or indirectly via a chain of connections. Figure D.1 shows a configuration of five atoms in a box, where atoms 1, 2, 4 and 5 form a cluster and atom 3 is regarded as a monomer.

![Figure D.1](image)

**Figure D.1.** A configuration of five atoms in a box to illustrate the simple application of the connectivity matrix method.

Firstly, we define a 5 by 5 matrix to describe the connectivity, \(C_{ij}\), between atoms \(i\) and \(j\) in the system, which is given by

\[
\begin{bmatrix}
C_{11} & C_{21} & C_{31} & C_{41} & C_{51} \\
C_{12} & C_{22} & C_{32} & C_{42} & C_{52} \\
C_{13} & C_{23} & C_{33} & C_{43} & C_{53} \\
C_{14} & C_{24} & C_{34} & C_{44} & C_{54} \\
C_{15} & C_{25} & C_{35} & C_{45} & C_{55}
\end{bmatrix},
\]

where \(C_{ij} = 1\) if particles \(i\) and \(j\) are directly connected while \(C_{ij} = 0\) if otherwise. Thus, in the example given, the connectivity matrix is given by

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 1 & 1 \\
1 & 0 & 0 & 1 & 1
\end{bmatrix}.
\]

Note that \(C_{ii}\) always equals 1.

Now we take column 1 and compare it with columns 2 through 5. Firstly, Column 1 has no element in common with Columns 2 or 3, so these columns are left unchanged. Then, since columns 1 and 4 have element 5 in common we replace columns 1 and 4 by the union of the two. The resulting intermediate matrix is

\[
\begin{bmatrix}
1 & 0 & 0 & 1 & 1 \\
1 & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 \\
1 & 1 & 0 & 1 & 1 \\
1 & 0 & 0 & 1 & 1 \\
\end{bmatrix}.
\]  
(D.3)

Next one finds that column 5 and the updated column 1 have elements 1, 4 and 5 in common. We then replace columns 1, 4 and 5 with the union of columns 1 and 5.

\[
\begin{bmatrix}
1 & 0 & 0 & 1 & 1 \\
1 & 1 & 0 & 1 & 1 \\
0 & 0 & 1 & 0 & 0 \\
1 & 1 & 0 & 1 & 1 \\
1 & 0 & 0 & 1 & 1 \\
\end{bmatrix}.
\]  
(D.4)

After the first loop, the second loop is started, where the updated column 1 is compared with columns 2 through 3 while columns 4 and 5 are discarded. This is because that we have already confirmed that the particles correspond to columns 1, 4 and 5 are within the same cluster. Since columns 1 and 2 have elements 2 and 4 in common we replace columns 1, 2, 4 and 5 by the union of columns 1 and 2. The resulting matrix is

\[
\begin{bmatrix}
1 & 1 & 0 & 1 & 1 \\
1 & 1 & 0 & 1 & 1 \\
0 & 0 & 1 & 0 & 0 \\
1 & 1 & 0 & 1 & 1 \\
1 & 1 & 0 & 1 & 1 \\
\end{bmatrix}.
\]  
(D.5)

Evidently, after we take the union of any two columns we may reduce the number of columns in the matrix by one since we only need to store the linearly independent columns. In this case we would end up with two columns corresponding to the two clusters in Figure D.1.