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Molecular-level Understanding of Metal Extraction via Simulation and Experiments for Sustainable Energy Application

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Publication Date
2018

Peer reviewed|Thesis/dissertation
Molecular-level Understanding of Metal Extraction via Simulation and Experiments for Sustainable Energy Application

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemical Engineering

by

Quynh Nhu Vo

Dissertation Committee:
Associate Professor Mikael Nilsson, Chair
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2018
DEDICATION

To

My mom, my Sun, friends, and everyone along the way.
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ACKNOWLEDGMENTS

I am thankful for my advisors, Professor Hung Nguyen and Professor Mikael Nilsson, for their continuous guidance, and encouragement throughout this journey. Thank you for seeing the potential in me and having the confidence in my ability to carry out this research. Thanks for knowing when to push me to overcome my own limitations and when to pull back and let me travel at my own pace. Thanks to my collaborator, Dr. Liem Dang, for being so patient and guiding me through the MD initial learning curve. Thanks to the member of my qualifying and dissertation committee, Professor Elizabeth Read, for generously giving her time and expertise to better my work.

Thanks to my labmates who made graduate school way more fun than it is supposed to be. Thanks Cade and Iris for being my very first mentors. Thanks Jackie for those spontaneous afternoons at the pub when life gets a little too stressful. Thanks Christian and Rose for always being parts of all of the Q’s episodes. Thanks Michael, Alex, Ko, Jeremy, Leila, Andy, Tro, Edward, Kara, Jisue, and Ted for all the help throughout the years and all the fun at conferences.

Thanks to all of my friends from the beginning to end, Lien, Ngan, Hung, Juile, Tuan, Dung, Diep, Adrienne, Kanch, Vivian, Phi, Maggie, Leo, Nhien, Thy, and Thao. You guys have touched my life and added your own marks to my journey.

Thanks Mom and Dad for your endless support and all the sacrifices you have made to provide me with the resources and opportunities I have today. Thank you for never forcing the path of a traditional Asian female on me. Thanks for instilling in me the senses of hard work and dedication for any purposes I aim for in life. I love you tremendously and hopefully, I’ve made you proud!

Finally, my Sun, thanks for always being there even through your darkest times.

This work would not have been possible without the financial support provided by the University of California, Irvine, the Nuclear Energy University Program, and the National Science Foundation Graduate Student Research Fellowship.
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PUBLICATIONS

1) Vo, Q. N., Dang, L. X., Nilsson, M., & Nguyen, H. D. Microscopic Behaviors of TBP, n-Dodecane and Their Mixtures at Air/Liquid and Liquid/Liquid Interfaces: A Polarizable Force Field Study (In Preparation)


ABSTRACT OF THE DISSERTATION

Molecular-level Understanding of Metal Extraction via Simulation and Experiments for Sustainable Energy Application

By
Quynh Nhu Vo

Doctor of Philosophy in Chemical Engineering
University of California, Irvine, 2018

Professor Mikael Nilsson, Chair

PUREX (Plutonium Uranium Reduction Extraction) is one of the most commonly used, and perhaps most studied solvent extraction (SX) process for the recycling of uranium and plutonium from spent nuclear fuel. This process employs tributyl phosphate (TBP) as its extracting agent which facilitates the transfer of metal ions from the aqueous phase into the organic solvent by forming complexes around the metal ions. However, the metal extraction mechanism and phase separation involve many molecular level events, including third phase formation, that are not well understood. This research utilizes atomistic molecular dynamics (MD) simulations in conjunction with experimental work to elucidate molecular-level processes involved in a SX system. A major part of this research project is dedicated to the optimization and validation of the force fields for the species that are present in the SX system. Utilizing the optimized force fields for each species for MD studies, in conjunction with experimental works, we gain new insights into the conformational behaviors of the TBP
molecule in its bulk liquid as well as in n-dodecane solution. We also report, for the first time, the dimerization and trimerization constants of TBP in several n-alkane diluents via both MD and FTIR studies.
INTRODUCTION

In the race for sustainable energy sources, nuclear energy is a strong candidate since nuclear reactors operate on abundant uranium. They also have the ability to provide massive amounts of energy with zero operating carbon emission and minimal air pollutants, both vital features in the struggle against the anthropogenic climate change and environmental impacts generated by energy production. Despite these high potentials, management of the spent nuclear fuel (SNF) is crucial due to its high radioactivity that lasts up to hundreds of thousands of years. One of the most effective strategies in dealing with the used fuel is to recycle certain elements in the material using advanced chemical separation, such as solvent extraction (SX), which can significantly reduce the high-level waste volume\(^1-^4\). PUREX (Plutonium Uranium Reduction Extraction) is one of the most commonly used, and perhaps most studied solvent extraction process for the recycling of U and Pu from SNF\(^5-^7\). This process employs tributyl phosphate (TBP) as its extracting agent that facilitates the transfer of metal ions from the aqueous phase into the organic solvent by forming complexes around metal ions. However, the metal extraction mechanism and phase separation involve many molecular level events that are not well understood. Specifically, TBP tends to self-assemble into reverse micelles, in which the polar hydrophilic head-groups and solutes (waters, acids, metal ions) are surrounded by a shell comprised of the nonpolar hydrophobic tail groups, interfering extraction kinetics and phase behavior. To intensify the problem, these reverse micelles can aggregate and form an undesired third phase, which interrupts the centrifugal contactor operation and can be potentially hazardous when metal ions are concentrated in a reduced volume. Up to now,
there are still debates concerning the mechanism of third phase formation and no solid conclusions with regards to the structural aspects of this undesired phase have been drawn8-11.

In recent years, there has been an upward trend in the utilization of molecular dynamics (MD) simulations techniques to gain insights and to visualize molecular level behaviors of extraction systems12-31. Wipff et. al reported the first theoretical model for the TBP molecule in 1998 and its structure was examined as a function of the environments: in the gas phase, in chloroform, and in pure water16. They also investigated interfacial behaviors and the coordination of the metal ion complexes17,18,32. Khomami group examined the extraction mechanism of the uranium complex25,26,33. However, minimal effort had been spent on reparameterizing/validating the accuracy of the force fields that were used for the species within the extraction system. Not until 2012, Khomami and co-workers performed a comparative study, which investigated four different atomistic force fields for TBP27. Their results showed that the default force fields, which were designed specifically for proteins and nucleic acids, failed to predict the basic mass density and dipole moment of TBP. Additionally, un-parametrized force fields showed the migration of charged species of $\text{UO}_2^{2+} \cdot 5\text{TBP}$ and $(\text{UO}_2\text{NO}_3)^- \cdot 4\text{TBP}$ to the organic phase, which is debatable due to the large resistant electric field that is, supposedly, produced by the charged species and will stop migration of the cationic complexes, in turn making the extraction process highly inefficient25.

There appears to be a disconnection between the experimental and computational fields regarding the elucidation of the extraction processes that involved in the spent
nuclear fuel treatment. This research aims to utilize atomistic molecular dynamics (MD) simulations in conjunction with experimental work to bridge the gap between the two fields so that they become complimentary to each other as well as pave the way for improving extraction efficiency and eliminating third phase formation in a typical solvent extraction system. To achieve this goal, this dissertation uses the “bottom-up” methodology in which force field reparametrization is performed for several species within the extraction system. The accuracy of these models is extensively validated using experimental values where available or additional experiments are carried out if required. At the end of this research, we report high quality force fields of several species such as TBP, n-dodecane, and uranyl ion. By utilizing these models in our study, we are able to gain direct visualization into the self-association of TBP in the organic phase as well as its microscopic behaviors at the air/liquid and liquid/liquid interfaces. For the first time, the dimerization and trimerization constants of TBP in several alkane diluents are reported both computationally and experimentally.
CHAPTER 1. Background

1.1. Purex Process & Solvent Extraction

Fresh nuclear fuel consists of uranium dioxide, UO₂, a ceramic material with a high melting point. The uranium in the fuel is usually enriched by 3-5% in Uranium-235 (²³⁵U) while the rest is consisted of Uranium-238 (²³⁸U). During the operation of nuclear reactors, energy is produced by the process of fission, where a heavy atom, typically ²³⁵U, is split into two lighter nuclei following the reaction:

\[
_{\text{235}}\text{U} + \text{neutron} \rightarrow \text{fission products} + 2.5 \text{ neutrons} + 194 \text{ MeV} \tag{Equation 1.1}
\]

Simultaneously, neutron capture reactions may also take place by ²³⁸U and produce other actinides, such as the useful fissile nuclide Plutonium-239 (²³⁹Pu):

\[
_{\text{238}}\text{U} + \text{neutron} \rightarrow _{\text{239}}\text{U} \xrightarrow{β^- 23.5 \text{ min}} _{\text{239}}\text{Np} \xrightarrow{β^- 2.3 \text{ day}} _{\text{239}}\text{Pu} \tag{Equation 1.2}
\]

Equation 1.1 shows one of many examples of neutron capture that can take place. The accumulation of fission products and other actinides in the fuel hinders the operation of the reactor because of buildup radiation and inefficient neutron economy. In this case, the fuel has reached its useful limit and needs to be removed and replaced with fresh fuel to continue the reactor’s operation. The spent nuclear fuel (SNF) removed from the reactors contains significant amounts of fertile and fissile nuclides, mainly the unutilized ²³⁸U (95%), ²³⁵U (1%) and the newly formed ²³⁹Pu (1%), which can be recycled and reused. The process of separating the re-usable materials (U and Pu) from the fission products in the fuel via the PUREX process is termed reprocessing.
PUREX is one of the most commonly used, and perhaps most studied, process for the recycling of U and Pu from SNF. This process makes use of the solvent extraction technique and employs TBP as its extractant for the separation and purification of U and Pu from other constituents in the SNF. The detailed reactions and chemistry of PUREX have been covered extensively elsewhere\textsuperscript{4-7}. Here an overview and important aspects of the PUREX process that are directly related to the objectives of this research are discussed.

The first step to treat used fuel, before the PUREX process, is decladding in which the fuel rod material is removed. Then, concentrated nitric acid (~5 – 6 M) is used to dissolve the uranium oxides fuels at elevated temperature (~ 70 – 110°C). This dissolution procedure involves these net reactions:

\[
\begin{align*}
UO_2 + 4H^+ + 4NO_3^- &\rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O \\
PuO_2 + 4H^+ + 4NO_3^- &\rightarrow Pu(NO_3)_4 + 2H_2O
\end{align*}
\]

Even though

At the end of dissolution, uranium is present in hexavalent state, U(VI), and plutonium is mostly in tetravalent state, Pu(IV). To ensure efficient extraction of Pu by TBP, tetravalent state of total Pu is secured by further addition of NaNO\textsubscript{2}.

1.2. TBP as an Extractant

TBP meets many conditions as an extractant for U and Pu. TBP is a neutral organophorous compound and is amphiphilic, which enables the formation of complexes around metal ions in an organic solvent. As a commercial product, it is cheaply available and can be easily purified. It has high boiling point and is non-volatile. Its solubility in water is only 0.4 g/l. It has high chemical, thermal and radiation stability. Its extracting
power is derived mainly from its phosphoryl oxygen atom coordinating to metal ions. Since TBP prefers to form complexes with metal ions in +4 and +6 oxidation states, it has very low extractability for most fission products resulting in excellent selectivity for U and Pu\textsuperscript{3+–36}. As can be seen in Figure 1.1, besides U, Pu, and Th (which normally is not present in SNF), other actinide elements are most stable when they are not in +4 or +6 oxidation state.

![Figure 1.1 Oxidations states of actinide elements](image)

TBP has a few unfavorable properties such as its high density and high viscosity. However, these drawbacks can be compensated by diluting it with an inert diluent such as kerosene or n-dodecane. A concentration of 30 volume percent of TBP in diluent has been prominent in most PUREX process work.

### 1.3. Solvent Extraction Technique

Solvent extraction (SX) is a technique that facilitates the separation of component(s) of a solution by using extracting agents (or extractants) and exploiting an unequal distribution of the component(s) between two immiscible phases. Frequently, this process is carried out by rigorously mixing the two immiscible phases, allowing for the solute(s) to be selectively transferred from one phase to the other. Typically, one phase is an acidic
aqueous solution containing the target solute(s), such as metal ions, while the other phase is the organic phase containing the extractant diluted in a suitable hydrocarbon diluent. Separation occurs due to the differences in affinities of the chosen extractant in the organic phase for certain solutes present in the aqueous phase. During vigorous mixing, the extractants bind to the solutes of interest and cause them to become more hydrophobic and therefore soluble in the organic phase while others are left behind in the aqueous phase. The transfer of solute from one phase into the other phase is referred to as extraction. The extraction process can be reversed by contacting the solvent loaded with solute(s) with another immiscible phase that has a higher affinity for the solute than the extractants in the organic phase. The transfer of the solute from the solvent back to the aqueous phase is known as back-extraction or stripping. The two immiscible phases must be able to separate rapidly after being mixed together, and this is primarily a function of the difference in densities between the two phases\textsuperscript{37-39}. A simplified example of a generic SX system is shown in Figure 1.2.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{simplified_sx_process.png}
\caption{A simplified solvent extraction process. The red dots represent the solute of interest. The red dots with orange boundaries are the solute-extractant complexes.}
\end{figure}
1.4. Extraction of U and Pu by TBP

In the PUREX process, the aqueous phase contains SNF dissolved in nitric acid while the organic phase usually contains 30 volume percent of TBP in kerosene. During vigorous mixing, U and Pu nitrates are solvated by TBP and then transported into the organic solvent during phase separation. The extraction mechanism of U(VI) and Pu(IV) by TBP has been proposed to follow the reactions as shown in Equation 1.5 and Equation 1.6 where the overhead bar indicates the species in the organic phase, otherwise aqueous phase:

\[
\text{Equation 1.5} \quad UO_2^{2+} + 2NO_3^- + 2\text{TBP} \rightleftharpoons \overline{UO_2(NO_3)_2 \cdot 2\text{TBP}}
\]

\[
\text{Equation 1.6} \quad Pu^{4+} + 4NO_3^- + 2\text{TBP} \rightleftharpoons \overline{Pu(NO_3)_4 \cdot 2\text{TBP}}
\]

Figure 1.3 shows the simplified extraction process of the metal ions \(UO_2^{2+}\) by TBP. Due to their amphiphilicity, the TBP molecules align themselves at the aqueous-organic interface with the polar heads and nonpolar tails pointing toward their preferred environments. The uranyl ions, while in the aqueous phase, possess a hydration shell of five to six waters. Upon vigorous mixing, TBP comes in contact with the metal ions, promotes the dehydration process to create metal ion complexes, which then move across the interface into the organic phase during phase separation. This extraction mechanism is still not well understood and can benefit from direct observation using MD simulations.
The partitioning of Pu from the organic phase is then performed by introducing either ferrous sulfamate or uranous nitrate to reduce Pu(IV) to Pu(III), which will not be complexed by TBP and will return to the aqueous phase. Finally, the stripping of U and Pu (after Pu solely being extracted one more time by TBP) can be accomplished through contacting the loaded organic phase with low nitric acid concentration solution (~ 0.01 M).

### 1.5. Third Phase Formation in the Solvent Extraction System of Uranium by TBP

Under certain conditions (e.g., high acidity or high metal concentration), a SX system may undergo an additional phase separation (or phase splitting) to create an additional phase between the aqueous phase and organic phase (Figure 1.4B)\textsuperscript{10,11,40-44}. The formation of this middle phase, termed “the third phase”, is usually an undesirable behavior that can disrupt the extraction process. Previous works have focused on the conditions under which phase splitting occurs and on the compositions of the species existing in this third phase.
Up to date, very little information is available on the structural arrangement of the third phase and the dynamic mechanism of third phase formation.

The traditional explanation of the organic phase splitting is based on insufficient solubility of the polar metal-extractant complexes in the nonpolar organic phase. Osseo-Asare proposed that third phase formation is due to reverse micelles (Figure 1.4A) in the organic phase that would grow into large aggregates until they coalesced into a heavy organic phase and segregate from the bulk organic phase. Later works carried out by Chiarizia et al. and Nave et al. confirmed that TBP indeed forms reverse micelles in the organic phase. Under visible spectrometry, the organic phase before phase splitting and the light organic phase after phase splitting display the same spectrum. However, the spectrum of the third phase is distinctly different indicating the unique coordination of U(VI) in third phase. EXAFS (extended x-ray absorption fine structure) data suggest that U(VI) is extracted as the $UO_2(NO_3)_2 \cdot 2TBP$ adduct into the organic phase while the third phase species have the average composition of $UO_2(NO_3)_2 \cdot 2TBP \cdot HNO_3$, neglecting...
water\textsuperscript{9,44}. Small angle x-ray scattering (SANS) data on TBP solutions loaded with $UO_2(NO_3)_2$ and $HNO_3$ reveal the presence of ellipsoidal aggregates with the major and minor axes up to 64 Å and 15 Å, respectively, right before phase splitting. Upon third phase formation, SANS data suggest the presence of smaller reverse micelles in the light organic phase while the third phase is described as a “continuous $UO_2(NO_3)_2 \cdot 2TBP \cdot HNO_3$ phase with pockets of n-dodecane”, each containing an average of two n-dodecane molecules\textsuperscript{11}. However, in a more recent study, contrary to Osseo-Asare’s and their own postulation early on, Chiarizia and co-workers, by using particle interaction model to interpret SANS data, concluded that third phase formation arises from interactions between small reverse micelles containing three to four TBP molecules\textsuperscript{5}. The particle growth model analysis suggested very large ellipsoidal “super-aggregates”, containing up to 40 TBP monomers, which they considered to be very improbable. They further explained that the stability of the organic phase is dependent on the balance between the thermal energy, $k_BT$, (where $k_B$ is the Boltzmann constant) which keeps the micelles dispersed in the solvent, and the intermicellar attraction that causes micellar adhesion. Organic phase splitting occurs when the attraction between particles in solution becomes about twice the average thermal energy\textsuperscript{6}.

Results from experiments that focus on third phase formation have, so far, not drawn solid conclusions with regards to the mechanism and structural aspects of the third phase. An understanding regarding this matter can benefit greatly from MD simulations where direct visualization into the molecular-level of the process can be achieved.
1.6. Molecular Dynamics Simulations

To our knowledge, the Wipff group in France is the first group that performed theoretical studies on TBP in vacuo, in water, in chloroform and at the water-chloroform interface using MD simulations. Their study in 1998 found that TBP dimerizes in water via hydrophobic interactions between the alkyl chains, yet such TBP dimers fail to exist in vacuo. Moreover, they also found that TBP is unstable in dry chloroform as dimers, which can be stabilized by two bridging water molecules. They treated a cluster of (TBP)$_{10}$ as a single molecule and observed that this cluster remains associated in water but not in chloroform$^{16}$. At the water-chloroform interface, TBP forms a monolayer where the phosphoryl oxygens point towards water while the alkyl chains point towards chloroform. In their other studies, they incorporated nitric acid into the system and compared two extreme models: neutral form of HNO$_3$ and ionic form of H$_3$O$^+$ and NO$_3^-$.

They saw that TBP extracts the neutral acid by hydrogen bonding while nitrate ions remain in the aqueous solution. The addition of nitric acid also disrupts the first shell TBPs at the interface and disorder gradually increased from the neat interface (no acid), to neutral acid and ionic acid interface. “Third phase” is observed at high TBP concentrations$^{18,32,45}$. They found a strong analogy when comparing supercritical CO$_2$ to chloroform as the organic phase. By performing quantum mechanics (QM) studies on trimethyl phosphate (TMP), they found that TMP forms stronger hydrogen bonds with neutral acid than with water and this interaction could be modeled for TBP by traditional force field calculations. High concentration of TBP promotes extraction of U and HNO$_3$ into the supercritical CO$_2$ phase. The complex UO$_2$(NO$_3$)$_2$·2TBP is only observed in dry system with neutral acid. In their
latest study on liquid-liquid extraction of uranyl by TBP in 2014, they modeled a system that more closely resembled the PUREX process in which hexane was employed to represent the organic phase. Departing from their previous studies, they modeled uranyl as the ionic form \(\text{UO}_2^{2+}\) instead of the neutral uranyl nitrate salt. They noticed that the extraction of \(\text{UO}_2(\text{NO}_3)_2\) by TBP is unfavorled when the uranyl ions were modeled with integer chargers as well as the cation-anion combination plays a key role in the extraction of \(\text{UO}_2(\text{NO}_3)_2\) as the extraction of the “naked” \(\text{UO}_2^{2+}\) resulted in very high free energy. They also concluded that polarization effects, while somewhat reduces the surface activity of TBP, have little influence on the interfacial behavior of its complexes.

In 2009, the Khomami group investigated the interfacial complex formation in uranyl extraction by TBP in n-dodecane diluent. It should be noted that this is the same system that we are also interested in. In this study and two additional ones after this, the Khomami group utilized the TBP model from Wipff et al. but the methyl and methylene groups of TBP and n-dodecane were treated as united atoms. The uranyl and nitric acid were modeled in ionic forms, i.e. \(\text{UO}_2^{2+}, \text{H}_3\text{O}^+\) and \(\text{NO}_3^-\). They observed that uranyl exists mainly as the hydrated complex \(\text{UO}_2 \cdot 5\text{H}_2\text{O}^{2+}\) in the bulk aqueous phase; when near the aqueous-organic interface, \(\text{H}_2\text{O}\) of the complex is readily replaced by \(\text{NO}_3^-\); and an increase in the aqueous acidity promotes speciation of uranyl with nitrate ions. However, their simulations are not able to detect the complex \(\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}\). In 2012, the same group performed a comparative study, which investigated four different atomistic force fields for TBP bulk liquid behavior. Their results showed that these default force fields, including the one from Wipff group, fail to predict many of the physical properties of TBP.
such as the liquid mass density, the dipole moment and the self-diffusion coefficient. Additionally, the solvent n-dodecane, which is known to exist in the liquid form at room temperature, was observed to form crystal-like structure at 25°C in MD simulations (Figure 2.3). A few suggestions were attempted to better model TBP and n-dodecane including reducing the partial charges of TBP to 60% of the original ones or varying the scaling factor of the 1-4 intramolecular interaction. Later on, the Khomami group observed that the dipole moment of TBP has a significant effect on the predicted solubility of water into the TBP-n-dodecane solution. With the fixes mentioned above, they were able to predict accurately the mass density of a range of TBP in n-dodecane mixtures. However, the new models could only replicate the trend of variation of TBP dipole moments as a function of TBP concentration in n-dodecane, not the actual values.

While these previous studies are excellent starting points for a better understanding of the molecular mechanisms of the PUREX process, we recognize there still exist some serious issues that must be resolved. In 2014, we performed a systematic study on the bulk liquid behavior of TBP, n-dodecane and TBP in n-dodecane diluent. Our optimized force fields prove to be better at modeling these two molecules as several of their physical properties are accurately reproduced. Furthermore, we were able to gain insights into the self-association of TBP as a function of its concentration in n-dodecane diluent. The results from our MD and experiment studies agree well with each other. We strongly believe that in order to accurately study interface behavior, polarizable force fields should be employed for the studied systems. This belief is supported by several studies by the Dang group who developed the first rigid, four-site polarizable model for water. Only
with the polarizable models, one could observe the change in the total dipole moment of the species, which was confirmed to be important in interfacial studies, as a function of their distance from the interface. When investigating the liquid-liquid interface between water and chloroform (similar to Wipff’s system), Dang and coworkers concluded that the interfacial equilibrium properties change significantly by the omission of the polarization term in the potential models\textsuperscript{49}. Analogous to non-additive force fields, polarizable ones should also be systematically reparameterized and extensively validated.
CHAPTER 2. Force Fields Reparametrization of TBP and n-Dodecane Molecules

2.1. Abstract

In this chapter, atomistic parameterization was carried out using the AMBER force field to model TBP molecule and n-dodecane molecule, a commonly used organic solvent. Validation of the optimized force field was accomplished through various thermophysical properties of pure TBP and pure n-dodecane in the bulk liquid phase; mass density, dipole moment, heat of vaporization and self-diffusion coefficient were calculated from our simulations and compared favorably with experimental values.

2.2. Introduction

Molecular dynamics (MD) studies have been employed to gain insight and visualize molecular level behavior of extraction systems.\textsuperscript{16,22,23,25-27,32,33} However, to date, accurate force fields for modeling TBP and hydrocarbon molecules in the liquid phase are still lacking. For example, TBP has been examined as a function of its environments in the gas phase, in chloroform and in pure water previously by Wipff and co-workers who carried out MD studies.\textsuperscript{16} They employed the MNDO semi-empirical method to obtain the atomic charges for TBP and AMBER91 intramolecular parameter set for TBP force field. But this study did not focus on TBP bulk behavior in liquid phase or in organic solvent, which is the condition of thePUREX process. A recent comparative study from Khomami and co-workers who looked at four different atomistic force fields including the one from Wipff \textit{et al.}\textsuperscript{16} to study TBP bulk liquid behavior.\textsuperscript{27} Their results showed deviations of mass density and dipole moment of TBP from available experimental data unless charges are
significantly reduced by up to 40% of the original values. However, self-diffusion coefficient (SDC) was considerably under-predicted by all force fields even with scaled charges. Hence, there was not a definitive conclusion of an accurate force field to be employed for TBP molecule.

The PUREX process uses various kerosene-type solvents, which are most commonly emulated by n-dodecane, which has been parameterized for MD simulations using different force fields. As a pure diluent, n-dodecane is known as a liquid at room temperature; however, previous studies reported the liquid-to-gel-phase transition at room temperature for long chain hydrocarbons of more than 8 carbons (including n-dodecane) using the OPLS-AA force field. Khomami and coworkers attempted to correct this behavior by changing the scaling factor (SF) for the 1-4 intramolecular electrostatic and van der Waals interaction. The default SF for both interactions in OPLS-AA force field is 0.5 so they tested the SF of 0.4, 0.3, 0.2, 0.1 and 0. The simulated melting point of n-dodecane from their study did not match the experimental value except for a SF of 0 where 1-4 interaction was completely disregarded. The heat of vaporization and density of n-dodecane still deviated slightly while self-diffusion coefficient was remarkably smaller than experimental results for all values of SF. Nevertheless, they used a SF of 0.3 or 0.4 for their n-dodecane model in later papers. Moreover, Bockmann and co-workers extensively reparameterized the OPLS-AA force field for alkanes and alkenes by refining the depth of the Lennard-Jones potential, torsional parameters, and partial charges, which gave improved heats of vaporization values, densities, and phase transition temperatures.
In this work, we carried out a rigorous, self-consistent and systematic characterization study on bulk liquid behavior of TBP and n-dodecane separately by refining the Lennard-Jones (LJ) potential parameters of the general AMBER force field (GAFF)\(^5\) in order to achieve more accurate models for both TBP and n-dodecane molecules. We optimized the LJ potential parameters based on the experimental mass density and heat of vaporization of each molecule. Other properties such as self-diffusion coefficient of pure TBP and n-dodecane and dipole moment of TBP molecules were calculated and compared with literature values as means of validation for the optimized LJ potential parameters. Since there was only one value for the self-diffusion coefficient of TBP molecules reported in the literature back in 1953,\(^53\) we verified it by carrying out our own experiment adopting an NMR technique.

2.3. Computational Details

A schematic representation of the TBP and n-dodecane molecules is shown in Figure 2.1. The GAFF\(^5\) parameter set for bond length stretching, bond angle bending, dihedral angle torsion and non-bonded interactions was used for both TBP and n-dodecane. The partial electric charges of atoms of TBP and n-dodecane molecules were obtained from AM1-BCC model\(^54,55\) using antechamber\(^52,56\) package that is implemented in Amber12.\(^57\)
All simulations were performed using the GPU version of PMEMD of Amber12.\textsuperscript{58,59} The initial configurations of the studied systems were generated using Packmol software package,\textsuperscript{60} where all the molecules were randomly distributed. Equations of motion were integrated with the velocity Verlet algorithm with a time step of 1 femtosecond and a cut-off of 10 Å. Long range electrostatics (>10 Å) was treated by the particle-mesh Ewald (PME) method. The non-bonded interactions calculated for pairs of atoms in TBP and n-dodecane separated by three bonds (1-4 interaction) were applied with Amber default scaling factors 1/2 and 1/1.2 for van der Waals and electrostatics, respectively. Bonds involving hydrogen atoms were constrained using the SHAKE algorithm with tolerance of $10^{-7}$. Three-dimensional cubic periodic boundary conditions were applied. Both translational and rotational center of mass motions of the molecules were removed every 1000 steps (1ps). The initial systems were subjected to energy minimization using the steepest decent algorithm until the energies reach equilibration. Then each system underwent a heating process in which its temperature was increased gradually from 0K to 400K during 1ns. For the study of pure TBP at different temperatures, those systems with

---

*Figure 2.1 Schematic representations of (A) TBP and (B) n-dodecane molecules*
temperatures higher than 298 K were heated up to 600 K for 2 ns. All systems were then cooled slowly from 400K (or 600K) to the desired temperatures in 0.5ns (or 1ns), and stayed there for another 5 to 15 ns depending on the studied physical properties. The isothermal-isobaric (NPT) ensemble coupled with Langevin thermostat (ntt = 3) and Berendsen barostat were used to converge the system densities, followed by the canonical ensemble (NVT) where temperature was controlled by the weak-coupling algorithm (ntt = 1) for production runs or by microcanonical ensemble (NVE) with Ewald coefficient of 0.35 for PME method in the case of self-diffusion studies. The gas phase simulation was modeled by a single molecule of interest with no box information. The same constraints and simulation method were applied as in the liquid phase.

2.3.1. Force Fields Reparametrization of TBP and n-Dodecane Molecules

The total interaction potential energy of the Amber force field uses the following Hamiltonian:

\[ E_{\text{total}} = E_{\text{bonded}} + E_{\text{nonbonded}} \]  

\[ E_{\text{bonded}} = \sum_{\text{bonds}} K_r (r - r_o)^2 \]

\[ + \sum_{\text{angles}} K_\theta (\theta - \theta_o)^2 \]

\[ + \sum_{\text{dihedrals}} [\sum_n V_n (1 + \cos(n\varphi - \gamma_n))] \]  

\[ E_{\text{nonbonded}} = \sum_{i<j} \left[ \left( \varepsilon_{ij} \left( \frac{r_{ij}}{r_{ij}} \right)^{12} - 2\varepsilon_{ij} \left( \frac{r_{ij}}{r_{ij}} \right)^{6} \right) + \left( \frac{q_i q_j}{r_{ij}} \right) \right] \]  

The terms in order of appearance in \( E_{\text{bonded}} \) of Equation 2.2 account for bonds, angles, and dihedral angles formation; in \( E_{\text{nonbonded}} \) of Equation 2.3 for van der Waals and
electrostatic interactions. The specific parameters for each term can be taken from different Amber force fields. $R^*$ is related to $\sigma$ by the equation: $R^* = 2^{1/6}\sigma$.

Previously, various Amber force fields were primarily developed for proteins and nucleic acid. The general Amber force field (GAFF) was designed in 2004 to include most organic and pharmaceutical molecules\textsuperscript{52}. For the GAFF, while the force constants, the parameters of $E_{\text{bonded}}$, and the partial charges of $E_{\text{nonbonded}}$ received an overhaul, the LJ parameters were directly taken from older force fields of Amber parm94 and parm99. For this reason, our reparametrization process focuses on refining the LJ parameters and follows these steps:

1. Initialized MD simulations of bulk liquids using GAFF
2. Calculate density and enthalpy of vaporization of each molecule
3. Compare with experimental values
4. Modify the LJ parameter accordingly

Step 2 to 4 were repeated until the MD and experimental values match. Other properties such as electric dipole moment and self-diffusion coefficient were used as means to validate the refined force fields for TBP and n-dodecane.

2.3.2. Enthalpy of Vaporization Calculation

The enthalpy of vaporization of TBP was computed using the equation:\textsuperscript{48}

$$\Delta H_{\text{vap}}(T) = E_{\text{gas}}^{\text{potential}}(T) - E_{\text{liquid}}^{\text{potential}}(T) + R$$

Equation 2.4

where $E_{\text{gas}}^{\text{potential}}$ and $E_{\text{liquid}}^{\text{potential}}$ are the potential energies in the gas and liquid phases, respectively; $R$ is the gas constant; and $T$ is the simulation temperature.
Experimental value of enthalpy of vaporization of TBP is not directly available. Instead, the value was obtained by fitting the TBP vapor pressure over a range of temperatures using the Clausius-Clapeyron equation with the assumption that the enthalpy of vaporization remains constant over the investigated range of temperature (15°C to 30°C).

\[
\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + C
\]  

Equation 2.5

We chose to compare our simulated heat of vaporization of TBP to the data set provided by Skene et al.\textsuperscript{39} They reported six different sets of vapor pressure for TBP over the temperature range of 0-40°C from Hammer and Lyndersen\textsuperscript{62}, Perry and Weber\textsuperscript{63}, Small et al.\textsuperscript{64}, Dean et al.\textsuperscript{65}, Perry’s handbook\textsuperscript{66}, and Evans et al.\textsuperscript{67} They also performed their own experiments using two different methods: direct gas chromatography (DGC) and solid sorbent trapping/thermal desorption gas chromatography (STTD). It should be noted that the vapor pressure of TBP from Hammer and Lyndersen, Perry and Weber, Small et al., Dean, and Perry’s handbook were not directly measured using TBP. They utilized the DGC method to determine the retention times of TBP and dibutyl phthalate.\textsuperscript{46} The vapor pressures of TBP were then calculated using the retention times and previously reported vapor pressures of dibutyl phthalate at elevated temperature (170-200°C). Evans et al. measured the boiling points of TBP at three different pressures (50, 100 and 150 torr) and fitted the data to another equation to obtain the vapor pressure of TBP at high temperatures\textsuperscript{67}. These experimental points were then extrapolated to the lower temperature range (0-40°C) using linear regression. These kinds of analysis might lead to large errors due to few experimental points (three temperatures and three pressures), and the uncertainty of the extensive
extrapolation (from 170-200°C to 0-40°C). However, TBP vapor pressure determined using STTD method by Skene et al.\textsuperscript{47} was measured directly using pure TBP at the lower range of temperatures usually found in the work place (0-80°C), thus avoiding the uncertainties of extrapolation. The fitted value of enthalpy of vaporization of TBP from this set is 22.67 kJ/mol.

**2.3.3. Electric Dipole Moment Calculation**

The electric dipole moment (EDM) of TBP molecule, $p_D$, was calculated by averaging over the instantaneous EDM of all molecules in the system:

\[
p_i = \sum_a q_a (r_{ia} - r_{i\text{COM}})
\]

\[
p_D = \left\langle \left( \frac{1}{N} \sum_{i=1}^{N} p_i^2 \right)^{1/2} \right\rangle
\]

*Equation 2.6*

*Equation 2.7*

where $p_i$ is the instantaneous electric dipole moment of $i$th molecule; $q_a$ is the charge of atom $a$; $r_{i\text{COM}}$ is the center of mass of $i$ molecule; and $N$ is the total number of molecules in the system.

**2.3.4. Self-diffusion Coefficient Calculation**

The self-diffusion coefficient (SDC) was calculated from the slope of the mean-square displacement of the center of mass averaged over the trajectories of individual molecules using Einstein relation:

\[
D_s = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle \left( \sum_{i=1}^{N} |r(t) - r(0)|^2 \right) \right\rangle
\]

*Equation 2.8*

where $r(t)$ is the position vector of atom $i$ at time $t$; $N$ is the total number of atoms; and $\langle \rangle$ denotes the ensemble average.
A linear relation for the mean squared displacement (MSD) profile can only be achieved after extended simulation durations. Provided that long enough trajectories were used, the MSD method had been studied to be more advantageous over the velocity auto-correlation function following the Green-Kubo formula.\textsuperscript{68} Yeh and Hummer had shown that $D_s$ obtained from simulations under periodic boundary conditions suffered from system-size effect due to the simplification of long-range interactions calculations due to limited computer power.\textsuperscript{69} A corrected value $D_s^{\text{corr}}$ could be obtained from extrapolating the slope fitted to the $D_s$ as a function of inversed box lengths to the infinite system limit ($1/L \rightarrow 0$). Each MD trajectory was 100 ns long for TBP molecule and 55 ns long for n-dodecane molecule with the first 15 ns using NPT ensemble and followed by NVE ensemble for the rest of trajectory.

Simulation parameters used to calculate $D_s$ were compared to a previously reported value obtained by capillary experiments.\textsuperscript{53} Moreover, we conducted additional NMR experiments using $^1$H DOSY. $^1$H NMR measurements employed an ADVANCE600 Bruker NMR, equipped with a 5 mm triple resonance broad band probe with z-axis gradients and the temperature maintained at 298 K. 1D and pseudo-2D experiments were performed using a longitudinal encode-decode stimulated echo pulse sequence with bipolar gradient pulse pairs as developed by Wu \textit{et al.}\textsuperscript{70} The linear gradient ramp consisted of 16 steps from 2\% to 95\% attenuation and the gradient strength was externally calibrated using neat n-pentanol (≥99\% Sigma-Aldrich, St. Louis, MO, see Figure 2.2). Non-deuterated samples required manual shimming of the z-components without a solvent lock. To avoid resonance distortion due to signal saturation, neat samples of TBP ($\text{puriss.}$, ≥99.0\%, Fluka Analytical,
Germany) and n-pentanol were prepared in 2 mm thin wall tubes and housed in standard 5 mm thin wall tubes using glass spacers (Wilmad, Vineland, NJ). Diffusion coefficients were calculated automatically by the TopSpin software (Bruker Corp., v. 3.2) by fitting the peak intensity to the exponential:

$\frac{\text{Equation 2.9}}{}$

\[ I(g) = I_0 \exp \left\{ -D(\gamma \delta g)^2 \left( \Delta - \frac{1}{3} \delta - \frac{1}{2} \tau \right) \right\} \]

where $I(g)$ and $I_0$ represent integrated peak intensities in the presence and absence of gradient pulses of amplitude $g$. $\delta$ is the gradient duration, $\gamma$ the gyromagnetic ratio of the nucleus observed, $\Delta$ the separation between gradient pulse pairs, and $\tau$ the time allowed for gradient recovery before the next pulse. In the TBP experiments, $\tau$ was set to 200 $\mu$s, and values of $\Delta$ and $\delta$ were manually optimized to 75 ms and 3.2 ms respectively. On the basis of comparisons of repeated measurements as well as error in the estimation of the center of intensity of the signals in indirect dimension, we estimate the overall accuracy of the diffusion coefficient reported here to be $\pm$ 25%.
2.4. Parameterization Results

Similar to previous studies\textsuperscript{46,51}, which employed the OPLS-AA force field for \textit{n}-dodecane molecules, we observed the same liquid-to-gel phase transition behavior from using the NPT ensemble and the default General Amber Force Field (GAFF) at a temperature of 298 K and pressure of 1 bar. Liquid-to-gel phase transition occurs when \textit{n}-dodecane molecules initialized from a randomized liquid state (Figure 2.3A) interact with one another to form a much more ordered structure (Figure 2.3B). The density profile of the default GAFF showed pseudo equilibrium in density at 2 and 3 ns, then increasing for the next 12 ns (Figure 2.3D). Thus, if a simulation is performed for only a short period of...
time, one might not observe this crystallization behavior of \( n \)-dodecane leading to inaccurate results. Using our optimized parameter (OP) set without changing the default scaling factors, the liquid-to-gel phase transition of \( n \)-dodecane was completely eliminated as showed by Figure 2.3C-D. The \( n \)-dodecane density from this OP set remained around the experimental value of 0.74 g/cm\(^3\) over the whole simulation duration and the molecules were still distributed randomly representing the liquid phase (Figure 2.3C).

Figure 2.3 Snapshots of a \( n \)-dodecane system starting as (A) an initial randomized configuration and ending as (B) an ordered configuration using GAFF or (C) a disordered configuration using the Optimized Parameters. (D) The density profile of two simulations using GAFF and Optimized Parameters is shown as a function of time.

The OP set (Table 2.1) produced superior results when comparing to experimental data as opposed to the default GAFF for both molecules as seen in Table 2.2. It shows the results on enthalpies of vaporization and densities of TBP and \( n \)-dodecane plus electric dipole moment of TBP that were calculated using GAFF and our optimized parameters. The differences between the OP and literature values are well within experimental errors. To our knowledge, we are the first group to report the value of heat of vaporization of TBP via
computational methods. Moreover, the densities of TBP and n-dodecane, the heat of vaporization of n-dodecane, and the dipole moment of TBP agreed well with previous optimization studies.27,46,51

Table 2.1 Lennard Jones Parameters and partial electric charges for TBP and n-dodecane molecules used in this study

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Partial charge (q)</th>
<th>σ (Å)</th>
<th>ε (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.8033</td>
<td>3.4945*</td>
<td>0.050*</td>
</tr>
<tr>
<td>P</td>
<td>1.5955</td>
<td>3.7418</td>
<td>0.2000</td>
</tr>
<tr>
<td>O</td>
<td>-0.8033</td>
<td>3.0000</td>
<td>0.1700</td>
</tr>
<tr>
<td>C_a</td>
<td>0.1677</td>
<td>3.3997</td>
<td>0.1094</td>
</tr>
<tr>
<td>C_b</td>
<td>-0.0834</td>
<td>3.3997</td>
<td>0.1094</td>
</tr>
<tr>
<td>C_c</td>
<td>-0.0811</td>
<td>3.3997</td>
<td>0.1094</td>
</tr>
<tr>
<td>C_d</td>
<td>-0.0921</td>
<td>3.3997</td>
<td>0.1094</td>
</tr>
<tr>
<td>H_a</td>
<td>0.0454</td>
<td>2.4714</td>
<td>0.0157</td>
</tr>
<tr>
<td>H_b</td>
<td>0.0564</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
<tr>
<td>H_c</td>
<td>0.0417</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
<tr>
<td>H_d</td>
<td>0.0348</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
<tr>
<td>n-dodecane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_a</td>
<td>-0.0921</td>
<td>3.1324*</td>
<td>0.1444*</td>
</tr>
<tr>
<td>C_b</td>
<td>-0.0804</td>
<td>3.1324*</td>
<td>0.1444*</td>
</tr>
<tr>
<td>C_c</td>
<td>-0.0794</td>
<td>3.1324*</td>
<td>0.1444*</td>
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<tr>
<td>H_a</td>
<td>0.0317</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
<tr>
<td>H_b</td>
<td>0.0387</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
<tr>
<td>H_c</td>
<td>0.0397</td>
<td>2.6495</td>
<td>0.0157</td>
</tr>
</tbody>
</table>

Values marked by asterisk (*) were modified from the original GAFF. Partial charges were obtained using Antechamber package and AM1-BCC charge model.

The optimized parameter set also produced similar density of pure TBP as a function of temperatures. Vogel and Cowan measured the density of pure TBP at four different temperatures ranging from 16.6 to 121.6°C.71 Burgur recognized the linear relationship between the temperature and TBP’s density and reported an expansion
coefficient of 0.000933 g/cm$^3$/°C.$^{50}$ He also recommended the value of 0.9727±0.00004 g/cm$^3$ for TBP density at room temperature after weighting the data at different temperatures from many previous studies.$^{51}$ A comparison of simulated density of pure TBP at different temperatures with calculated value is summarized in Table 2.3. We simulated pure TBP at five different temperatures from 20 °C to 100 °C using NPT ensemble. The errors between the simulated and calculated values are less than 0.5%.

Table 2.2 Comparison of Densities, Enthalpies of vaporization, and Electric dipole moment of TBP and n-dodecane using the default GAFF, the Optimized Parameters (OP) derived from this study$^a$, and experimental data

<table>
<thead>
<tr>
<th></th>
<th>Δ$H_{\text{vap}}$ (kJ/mol)</th>
<th>Density (g/cm$^3$)</th>
<th>Dipole (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TBP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAFF</td>
<td>25.63 ± 0.12</td>
<td>0.995 ± 0.012</td>
<td>2.88 ± 0.32</td>
</tr>
<tr>
<td>OP</td>
<td>24.08 ± 0.04</td>
<td>0.971 ± 0.007</td>
<td>3.58 ± 0.34</td>
</tr>
<tr>
<td>expt.</td>
<td>22.67$^b$</td>
<td>0.973$^c$</td>
<td>3.51 ± 0.23$^c$</td>
</tr>
<tr>
<td><strong>n-dodecane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAFF</td>
<td>17.14 ± 0.08</td>
<td>0.763 ± 0.0070$^*$</td>
<td></td>
</tr>
<tr>
<td>OP</td>
<td>14.98 ± 0.04</td>
<td>0.744 ± 0.0005</td>
<td></td>
</tr>
<tr>
<td>expt.</td>
<td>14.70$^d$</td>
<td>0.745$^e$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Errors were estimated by block average (6 blocks of each 1 ns length for TBP molecule, 10 blocks of each 1 ns length for n-dodecane molecule). $^b$Experimental values are derived from Skene et al.$^{52}$ $^c$Experimental values are from Ref. 22. $^d$Experimental values are from Haynes.$^{72}$ $^e$Experimental values are from Yaws.$^{73}$ $^*$The starting density of the system was 0.742 g/cm$^3$ and gradually increased to 0.763 g/cm$^3$ at 10ns with a positive slope.

Table 2.3 Simulated Density of TBP at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Simulated Temperature (°C)</th>
<th>Simulated Pressure (bar)</th>
<th>Simulated Density (g/cm$^3$)</th>
<th>Experimental Value* (g/cm$^3$)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20.0 ± 0.03</td>
<td>0.98 ± 0.09</td>
<td>0.976 ± 0.0007</td>
<td>0.977 ± 0.0007</td>
<td>0.15</td>
</tr>
<tr>
<td>25</td>
<td>25.0 ± 0.03</td>
<td>0.98 ± 0.08</td>
<td>0.971 ± 0.0007</td>
<td>0.973 ± 0.0004</td>
<td>0.22</td>
</tr>
<tr>
<td>50</td>
<td>50.0 ± 0.03</td>
<td>0.98 ± 0.19</td>
<td>0.948 ± 0.0008</td>
<td>0.950 ± 0.0007</td>
<td>0.27</td>
</tr>
<tr>
<td>75</td>
<td>75.0 ± 0.05</td>
<td>0.96 ± 0.15</td>
<td>0.924 ± 0.0004</td>
<td>0.926 ± 0.0007</td>
<td>0.19</td>
</tr>
<tr>
<td>100</td>
<td>100 ± 0.03</td>
<td>0.98 ± 0.11</td>
<td>0.901 ± 0.0002</td>
<td>0.903 ± 0.0007</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*Experimental values were obtained from the density of pure TBP at 25°C of 0.9727±0.00004 g/cm$^3$ and the reported expansion coefficient of 0.000933 g/cm$^3$/°C.
The mean squared displacement (MSD) profiles of the system size of $N = 500$ molecules of pure TBP and n-dodecane systems show two regimes that correspond to different simulation ensembles as shown in Figure 2.4 MSD profiles of TBP and n-dodecane molecules ($N = 500$ molecules). The first 15 ns of both systems were simulated under the NPT ensemble to equilibrate the systems’ densities, temperatures and pressures, followed by 85 ns and 40 ns of the NVE ensemble for TBP and n-dodecane, respectively, to avoid introducing effects to the systems by employing the artificial thermostat and barostat. Indeed, the MSD slope under the NPT ensemble is remarkably different than that under the NVE ensemble. Such a difference between MSD slopes of the NPT part and the NVE part clearly demonstrate the effects of the thermostat and barostat. By relying on these regulators, the self-diffusion coefficient might be underestimated as in the case of n-dodecane$^{46}$ and overestimated as in the case of the TBP systems.$^{27}$ It should be noted that when we performed the NVE simulations, special care was given to conserve the systems energy. In this case, we used an Ewald coefficient of 0.35 and a SHAKE tolerance of $10^{-7}$, which are more stringent than the default Amber values (0.275 for Ewald coefficient and
$10^{-5}$ for SHAKE tolerance) to ensure system total energy drift is within the acceptable range for GPU version of PMEMD.$^{58}$ As a result, the temperatures deviate less than 2.5 K from 298 K over the 70 ns of simulation time for n-dodecane and over 100 ns of simulation time for TBP. This change in temperature should not have significant impact on the reported SDC. However, the average pressure under the NVE ensemble is $P = -6.9 \pm 9.2$ bar for TBP and $P = 20.1 \pm 11.4$ bar for n-dodecane. Even these pressures fluctuated over a wider range, they should not affect the SDC as demonstrated by Jorgensen and co-workers, who studied the effect of pressure and temperature on SDC of water and found that pressure plays such a minimal role on the SDC.$^{74}$

![Figure 2.5](image)

**Figure 2.5** A) Mean-square displacement of n-dodecane as a function of time of three systems: blue, $N = 200$ molecules and $L = 4.2$ nm; red, $N = 350$ molecules and $L = 5.1$ nm; green, $N = 500$ molecules and $L = 5.8$ nm. B) Self-diffusion coefficient of n-dodecane as a function of the inverse box length $1/L$ of the three systems.

The linearly system-size dependence of the SDC of n-dodecane molecules, as observed previously by Yeh and Hummer,$^{69}$ was confirmed as shown in Figure 2.5. Figure 2.5A shows the MSDs grow linearly with time after the equilibration period of 15ns NPT and more steeply with increasing system size. Figure 2.5B shows the apparent SDC of n-dodecane molecule as a function of inverse box length ($1/L$). By extrapolating the linear fit
to the apparent SDC profile, a corrected SDC of $D_{s}^{\text{corr}} = 7.24 \times 10^{-6}$ cm$^2$/s was obtained for an infinite system of n-dodecane molecules at room temperature and ambient pressure. This new corrected SDC of n-dodecane molecule, even though still deviates 17% from the experimental value of $8.71 \times 10^{-6}$ cm$^2$/s, is the best estimation compared to other studies by Khomami group and Bockmann group who reported the values of $4.64 \pm 0.234 \times 10^{-6}$ cm$^2$/s using SF = 0.4 and $5.29 \pm 0.13 \times 10^{-6}$ cm$^2$/s respectively.

Interestingly, the same correction study for system-size dependence did not work when applied to TBP molecules (Figure 2.6). We found the SDC of TBP was constant, independent of the system size, and significantly smaller than experimental value of $2.29 \times 10^{-6}$ cm$^2$/s, and the value we obtained using $^1$H DOSY ($2.8 \pm 0.7 \times 10^{-6}$ cm$^2$/s, see Figure 2.7). We suspect it is due to the complexity of the TBP molecule that possesses both polar and non-polar regions. We are in the process of parameterizing a polarizable force field in order to better represent this particular molecule. However, the uncorrected SDC of TBP $D_s$ = $2.1 \times 10^{-7}$ cm$^2$/s is comparable to a reported value from a previous study.$^{27}$

![Figure 2.6 A) Mean-square displacement of TBP as a function of time of four systems: blue, N = 200 molecules and L = 4.5 nm; red, N = 350 molecules and L = 5.4 nm; green, N = 500 molecules and L = 6.1 nm; purple, N = 1000 molecules and L = 7.7 nm. B) Self-diffusion coefficient of TBP as a function of the inverse box length 1/L of the four systems.](image)
2.5. Conclusion

In this work, we have successfully parameterized new sets of force fields for TBP and n-dodecane molecules using the AMBER force field. Parameterization was performed on the Lennard Jones potential parameters to match experimental heat of vaporization and densities that are dependent upon the temperature. Dipole moment and self-diffusion coefficient were used as means to validate the optimized parameter sets. The values resulting from our optimized parameters show better accuracy than the ones from the default GAFF when compared with experimental values. More importantly, the liquid-to-gel phase transition of n-dodecane observed with the default GAFF (or OPLS-AA\textsuperscript{46,51}) was completely eliminated. The result from our experiment, which utilized NMR technique to
determine the self-diffusion coefficient of pure TBP liquid, confirms the only one reported value.\textsuperscript{53} 

For the self-diffusion coefficient of n-dodecane molecule, we observed that it was necessary to perform the correction to remove the system-size dependency as recommended by the work of Yeh and Hummer.\textsuperscript{69} However this correction was not applicable for the self-diffusion coefficient of TBP molecule due to its complexity where the TBP molecule possesses both polar and non-polar regions. We are in the process of developing a polarizable force field for this particular molecule in order to better present TBP in the future.
CHAPTER 3. Structural Information of TBP Molecule in Pure Solution, in TBP/n-Dodecane Mixtures and its Self-Association Constants

3.1. Abstract

This chapter is an extended study in which MD simulations and FTIR experiments were carried out in tandem to look into the self-association of TBP in solutions. Microscopic pictures of TBP isomerism and its behavior in n-dodecane diluent were investigated utilizing MD simulations with previously optimized force field parameters for TBP and n-dodecane. Potential Mean Force (PMF) calculations on a single TBP molecule show seven probable TBP isomers. Radial Distribution Functions (RDF) of TBP suggests the existence of TBP trimers at high TBP concentrations in addition to dimers. 2D PMF calculations were performed to determine the angle and distance criteria for TBP dimers and trimers. The dimerization and trimerization constants of TBP in n-dodecane were obtained and match our own experimental values using FTIR technique. The self-association behavior of TBP in various alkane diluents of different chain lengths (8, 12 and 16 carbons) and a branched alkane (iso-octane) was investigated by Fourier Transform Infrared Spectroscopic (FTIR) measurements. By careful deconvolution of the spectra into multiple peaks, our results indicate that TBP does not only self-associate to form dimers, as previous studies showed, but also trimers in the practical concentration range. Using a mathematical fitting procedure, the dimerization and trimerization constants were determined. As expected, these equilibrium constants are dependent on the solvent used. As the alkane chain for linear hydrocarbon solvents becomes longer, dimerization decreases whereas
trimerization increases. For the more branched hydrocarbon, we observe a significantly higher dimerization constant. These effects are most likely due to the inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain as all solvents in this study are relatively non-polar.

3.2. Introduction

More than fifty years ago, a few studies had suggested that the P=O dipole-dipole interaction is responsible for the self-association of TBP in the organic phase\textsuperscript{76-79}. Different techniques such as vapor osmometry\textsuperscript{79} and FTIR spectroscopy\textsuperscript{77,78} had been utilized to determine the dimerization constant of TBP as a function of its environments. Petkovic, using FTIR, reported a value of $2.9 \pm 0.1 \text{ M}^{-1}$ for the dimerization of TBP in n-hexane with concentrations from 0.2 to 1.0 M\textsuperscript{77}. He also stated a value of $2.6 \pm 0.1 \text{ M}^{-1}$ and $2.5 \pm 0.1 \text{ M}^{-1}$ for TBP in n-dodecane and cyclohexane, respectively, without specifying the experimental concentration range\textsuperscript{78}. Haung and Bautista confirmed the value of $2.76 \pm 0.3 \text{ M}^{-1}$ for the dimerization constant of TBP in n-hexane in the concentration range of 0.02 M to 0.24 M using vapor osmometry\textsuperscript{79}. It should be noted that, to the best of our knowledge, there is not an experimental technique to directly measure the self-association constants. Most of the time, collected experimental data must be fit through different models and some assumptions must be made in order to arrive at the equilibrium constants\textsuperscript{80-82}. For those values listed above, right from the beginning, it was assumed that the largest aggregate that existed in TBP/alkane mixtures was a dimer regardless of the TBP concentration. Our computational effort, carried out in parallel to this experimental study, has shown otherwise\textsuperscript{57}. For a concentration as low as 0.2 M of TBP in n-dodecane, there are
indications that TBP trimers exist. In the same computational study, we were able to
determine a value of $1.54 \pm 0.07 \text{ M}^{-1}$ for the dimerization constant and of $0.56 \pm 0.09 \text{ M}^{-1}$ for
the trimerization constant of TBP in n-dodecane. The experimental study, employing FTIR
technique, was carried out in tandem to the computational effort to validate the
computational results\textsuperscript{58} as well as expand upon previous FTIR studies to see if it would be
possible to observe TBP trimers.

3.3. Isomerism of TBP Molecule

Various studies in the past have postulated the existence of more than one
rotational isomer by neutral organo-phosphoryl compounds using FTIR studies\textsuperscript{83-85}. In
1957, Mortimer examined the infrared spectra of both liquid and crystalline solid samples
of trimethyl phosphate, triethyl phosphate and triphenyl phosphate\textsuperscript{85}. They observed that
the double P=O bond stretching bands that existed in the liquid phase of these compounds
were missing from their solid phase spectra; hence, they concluded that the presence of
more than one rotational isomer was the probable explanation for the double P=O bond
stretching band in the liquid phase. Dyrssen \textit{et al.} and Katzin observed the splitting in the
P=O peak of tributyl phosphate (TBP) around the frequencies of $1270 \text{ cm}^{-1}$ and $1280 \text{ cm}^{-1}$ in
two separate studies\textsuperscript{84,86}. Dyrssen \textit{et al.} further explained that the TBP isomer with three
butyl tails pointing toward the P=O atoms would reduce the P=O bond vibration due to the
electrostatic interactions between the three hydrogen atoms with the oxygen atom of the
P=O group. The other TBP rotational isomer in which at least one butyl tail pointed away
from the P=O atoms would have a higher P=O bond stretching frequency. These studies
postulated that there are at least two TBP rotational isomers; however, they did not provide information on the exact structures of these isomers.

In our study, we utilized MD simulations to gain a more direct observation. We ran a series of gas phase simulations of three different conformations which are dictated by each of the three dihedral angles that made up of the P=O and the O-C bonds (O=P-O-C angle) was fixed while the rest of the molecule was free to rotate, as shown in Figure 3.1. The first conformation (Isomer A) involves one butyl tail pointing upward while two butyl tails pointing down; the second conformation (Isomer B) involves two butyl tails pointing upward while one butyl tail pointing down; and the third conformation (Isomer C) involves three butyl tails pointing up. The TBP monomer conformation in which all three butyl tails point down is not allowed due to steric hindrance between three butyl tails. The average potential energy of each isomer is reported in Table 3.1.

Figure 3.1 Three different initial conformations of TBP monomer: (A) one butyl tail pointing upward. (B) two butyl tails pointing upward. (C) three butyl tails pointing up; The dihedral angle made up by the P=O and the O-C of the butyl-tail is 0° (or 360°) and 180° for the upward and downward conformations, respectively. Only the first carbon of each butyl tail is shown for clarity.

Isomer B and isomer C had the lowest potential energies out of the three conformations as shown in Table 3.1. However, it was not conclusive whether B and C are really the only two rotational isomers of TBP with the lowest energetics since their O=P-O-
C angles were fixed, meaning they had no freedom to explore a lower energetic conformation if one existed. We expanded this study further by performing umbrella sampling of a single TBP monomer in n-dodecane solvent for the calculation of potential mean force (PMF) to seek the most energetically favorable conformation when each of the TBP butyl-tails was sequentially rotated by every degree in three separate PMF calculation cycles.

Table 3.1 Potential energy of each TBP isomer

<table>
<thead>
<tr>
<th>TBP isomer</th>
<th>Potential Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer A</td>
<td>-12.64 ± 4.53</td>
</tr>
<tr>
<td>Isomer B</td>
<td>-18.76 ± 4.47</td>
</tr>
<tr>
<td>Isomer C</td>
<td>-18.05 ± 4.50</td>
</tr>
</tbody>
</table>

Firstly, we fixed the O=P-O-C angles of two butyl tails at 0° for the upward orientation and varied the angle of the third butyl tail by a full rotation from 0° to 360°. There are three energy minima at around 60°, 180°, and 300° as shown by the black curve in Figure 3.2. The conformations at 60° and 300° are symmetric; therefore, those conformations have the same PMF value. The different PMF values associated with various conformations can be attributed to steric effect and the change in enthalpy and entropy when switching from one conformation to another. For example, the increase in free energy when switching from 60° to 120° conformation (or 300° to 240°) of the butyl tail is mainly caused by the decreasing number of attractive electrostatic interactions between positively charged hydrogen atoms on the first carbon of each butyl tail and the negatively charged oxygen atoms. When the tail is at 60°, the hydrogen atoms of the first carbon on the butyl tail could interact with both oxygen atoms of the P-O-C or the P=O head group.
When the tail is at 120° pointing down, that attractive electrostatic interaction is broken. Steric effect is responsible for the slight difference of the free energies between the 0° and 180° orientations, in which the butyl tails have more freedom to rotate around. Lastly, the free energy difference between 60° and 180° orientations is mainly due to the difference in entropy, since the 60° and 300° conformations are symmetric.

Figure 3.2 PMF results of TBP monomer. Black curve: first monomer PMF study: two O=P-O-C angles were fixed at 0°, one O=P-O-C angle was varied; Red curve: second monomer PMF study: one O=P-O-C angle was fixed at 0°, one O=P-O-C angle was fixed at 60°, and one O=P-O-C angle was varied; Blue curve: third monomer PMF study: two O=P-O-C angles were fixed at 60°, one O=P-O-C angle was varied.

Secondly, using the most energetically favorable conformation in which the O=P-O-C angle of one butyl tail is at 60° (sideway) from the first PMF calculation cycle (the black curve in Figure 3.2), we fixed the O=P-O-C angle of the second tail at 0° (upward) and varied the O=P-O-C angle of the third tail by a full rotation from 0° to 360°. The energy minimum of this second PMF calculation cycle is also at 60° as shown by the red curve in Figure 5, which is the same sideway orientation as the other tail by the black line from our first PMF calculation cycle. However, the symmetry between 60° and 300° conformations is
less balanced, which can be attributed to steric effect between the two butyl tails of the two
sideway angles.

Thirdly, the O=P-O-C angles of two butyl tails were fixed sideway at 60° while the
O=P-O-C angle of the third tail was varied by a full rotation from 0° to 360°. The most
prominent contrast between the free energy profile of the third PMF calculation cycle as
shown by the blue curve of Figure 3.2 and the other two cycles is the complete absence of
the local minimum at 300° angle and a significantly high peak at 240°. When two out of
three butyl tails are fixed sideways, the structure of the TBP molecule becomes more
restricted. This in turn decreases the entropy of the system, and, together with the increase
in steric hindrance, results in one less local energy minimum.

We quantified the amount of each conformation by tracking the O=P-O-C angles of
each butyl tail in three MD simulations that was conducted for 100 ns on a system
containing just one TBP molecule in n-dodecane solvent with no restraints. The angle
ranges for four different orientations were assigned based on our PMF study as shown in
Figure 3.2 and listed in Table 3.2. In addition to the upward orientation (denoted as U) and
downward orientation (D), there are two types of sideway orientations (Sideway up S1 and
Sideway down S2). Due to the S2 orientations being at the top of the energy barriers, the
number of monomers belonging to this conformation is modest with less than two percent
(not shown). We combined S1 and S2 as one orientation and referred to as S (sideway).
Figure 3.3 presents the average quantity of each isomer conformation in the solution
obtained from unconstrained MD simulations in which all tails of TBP are freely rotated. Of
ten possible conformational isomers, three conformational TBP isomers existed in significantly large populations of 37%, 26% and 20%, which correspond to the SUU, SSS and SSU conformations, respectively. The UUU, UUD, DSS and DSU conformational isomers are less dominant and existing in small populations due to steric effect which dictates that only one butyl tail of the TBP molecule can be pointing down at all time. Otherwise, when two or more tails are pointing down, the UDD, DDS and DDD conformational isomers are non-existent at a population of ~ 0%. When comparing this theoretical observation with the experimental one from previous studies where FTIR detects two different frequencies for TBP monomers\textsuperscript{78,84,86}, we can postulate that the lower FTIR frequency conformation corresponds to the UUU mode while the higher FTIR frequency conformation is the average of the SUU, SSS and SSU modes.

**Table 3.2 Assigned orientation of the O=P-O-C angle based on its range**

<table>
<thead>
<tr>
<th>Angle range</th>
<th>Orientation</th>
<th>Denotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>30° - 90° and 270° - 330°</td>
<td>Sideway up</td>
<td>S1</td>
</tr>
<tr>
<td>90° - 150° and 210° - 270°</td>
<td>Sideway down</td>
<td>S2</td>
</tr>
<tr>
<td>150° - 210°</td>
<td>Downward</td>
<td>D</td>
</tr>
<tr>
<td>330° - 360° and 0° - 30°</td>
<td>Upward</td>
<td>U</td>
</tr>
</tbody>
</table>
Figure 3.3 The percentage of various monomer conformations of one TBP molecule in n-dodecane solvent.

3.4. Quantifying Dimer and Trimer Formation of Tri-n-butyl Phosphates in n-Dodecane: Molecular Dynamics Simulations

3.4.1. Mass density of mixtures at different TBP concentrations

In order to investigate the self-association of TBP in n-dodecane, we simulated different concentrations of TBP in n-dodecane ranging from 0.05 M to 1.0 M using the optimized force fields developed in our previous work\textsuperscript{21}. For verification that the parameters of our optimized force fields are still valid for mixtures, we calculated the density of each mixture for comparison with the results of Tian and Liu, who determined the densities of binary mixtures over the entire composition range experimentally using a high-precision vibrating-tube digital density meter\textsuperscript{87}. Over a wide range of concentrations, our predicted densities agree well with the experimental results evidenced by the small error values of less than 1% as shown in Table 3.3.
### Table 3.3 Simulated vs. experimental densities of TBP/n-dodecane mixtures at 25°C

<table>
<thead>
<tr>
<th>TBP Concentration (M)</th>
<th>Simulated Temperature (°C)</th>
<th>Simulated Pressure (bar)</th>
<th>Simulated Density (g/cm³)</th>
<th>Experimental Value (g/cm³)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>24.9 ± 0.13</td>
<td>0.20 ± 14.39</td>
<td>0.748 ± 0.0002</td>
<td>0.753</td>
<td>0.67</td>
</tr>
<tr>
<td>0.10</td>
<td>25.1 ± 0.01</td>
<td>0.13 ± 2.27</td>
<td>0.751 ± 0.0020</td>
<td>0.756</td>
<td>0.60</td>
</tr>
<tr>
<td>0.20</td>
<td>25.0 ± 0.08</td>
<td>1.97 ± 6.16</td>
<td>0.756 ± 0.0002</td>
<td>0.761</td>
<td>0.65</td>
</tr>
<tr>
<td>0.37</td>
<td>25.1 ± 0.04</td>
<td>2.43 ± 0.38</td>
<td>0.766 ± 0.0001</td>
<td>0.770</td>
<td>0.53</td>
</tr>
<tr>
<td>0.60</td>
<td>25.0 ± 0.07</td>
<td>-0.13 ± 2.48</td>
<td>0.780 ± 0.0001</td>
<td>0.782</td>
<td>0.25</td>
</tr>
<tr>
<td>0.80</td>
<td>25.0 ± 0.06</td>
<td>0.70 ± 3.32</td>
<td>0.793 ± 0.0001</td>
<td>0.794</td>
<td>0.18</td>
</tr>
<tr>
<td>1.00</td>
<td>25.0 ± 0.12</td>
<td>2.40 ± 1.21</td>
<td>0.804 ± 0.0001</td>
<td>0.805</td>
<td>0.07</td>
</tr>
</tbody>
</table>

### 3.4.2. Radial Distribution Functions at Different TBP Concentrations

To gain insight into the structure of TBP in the liquid phase as well as the organization of TBP aggregates within the n-dodecane solvent, the radial distribution functions (RDFs) were computed for the O2-O2, O2-P and P-P atom pairs of each mixture concentration. We used a bin width of 0.25 Å and a cut-off distance of 32 Å (about half of the simulation box length). The RDFs were averaged over three 100-ns simulations and are shown in Figure 3.4. There are distinctive peaks at 4.9 Å for the O2-O2 pair (Figure 3.4A), at 5.1 Å for the O2-P pair (Figure 3.4B), and at 5.9 Å for the P-P pair (Figure 3.4C). These peaks are macroscopic averages from a large ensemble of many different conformations of dimers and larger oligomers in the mixture.
Figure 3.4 RDFs of (A) O2-O2 atoms; (B) O2-P atoms; (C) P-P atoms on two different TBP molecules. Concentration of TBP is displayed in legend. (D) Averaged TBP dimer conformation with anti-parallel orientation; the butyl tails are omitted for clarity.

Since the P=O double bond length is 1.48 Å, the O2–O2 distance of 4.9 Å and the O2–P distance of 5.1 Å create a sharp angle P–O2–O2 of 90°. Therefore, these three sides form a right triangle of which the O2–P distance of 5.1 Å is the hypotenuse as shown in Figure 3.4D. This suggests that two TBP molecules in a dimer at any concentration are positioned in the antiparallel orientation forming a dipole-dipole interaction. This dimer conformation is in agreement with the results from our PMF study in which two TBP molecules with a P–O2 distance around 5.25 Å and a P–O2-P–O2 pseudo-dihedral angle range of 0° to 60° and 300° to 360° have the lowest PMF values (section 3.4.3). Over this range, the distance between P and P atoms in a dimer ranges from 5.6Å to 6.3Å. In other words, the most energetically favorable conformation of a dimer allows polar groups of
two TBP molecules to form a dipole-dipole interaction. In this case, the bulky butyl tails point away from each another and are completely solvated in organic solvent of n-dodecane molecules.

The formation of larger TBP oligomers such as trimers is possible when there are more TBP molecules nearby in the system as shown by the first shell coordination numbers (CN) in Table 3.4. We computed the first shell CN of TBP at different concentrations by integrating the RDFs of P-P atom pair up to the minima of the first peaks. The CN value increases as the concentration of the mixtures increases. When the concentration of TBP in n-dodecane is higher than 0.4 M, the CN value is greater than 1.0, indicating that it is very likely to find more than just one TBP molecule within the first solvation shell of another TBP molecule. When the TBP concentration is higher than 0.8 M, the CN value is greater than 2.0, indicating that it is very likely to find more than two TBP molecules within the first solvation shell of another TBP molecule. Hence, it is necessary to account for these larger oligomers especially trimers in the calculation of the self-association constants. From this observation, we conducted a PMF study for TBP trimers as described in the later session of this paper using the same technique as in our previous work for TBP dimer\textsuperscript{21} in order to determine certain criteria on the distance and orientation of the participating TBP molecules.
Table 3.4 First shell coordination numbers calculated by integrating the areas under the first peaks of P-P RDFs.

<table>
<thead>
<tr>
<th>TBP concentration (M)</th>
<th>Coordination numbers (CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.45</td>
</tr>
<tr>
<td>0.2</td>
<td>0.86</td>
</tr>
<tr>
<td>0.4</td>
<td>1.25</td>
</tr>
<tr>
<td>0.6</td>
<td>1.77</td>
</tr>
<tr>
<td>0.8</td>
<td>2.19</td>
</tr>
<tr>
<td>1.0</td>
<td>2.42</td>
</tr>
</tbody>
</table>

3.4.3. PMF of TBP Dimer Conformations

In order to study the self-association of TBP in n-dodecane, we performed a Potential Mean Force (PMF) study using umbrella sampling technique to establish the criteria for identifying TBP dimer and larger aggregates. A 1D PMF study was first carried out along two separate reaction coordinates: distance and angle as depicted in Figure 3.5. Two TBP monomers were immersed in pure n-dodecane solvent. During equilibration, position constraints were put on the P and O2 atoms so that the monomers were 10.5 Å apart and adapted the antiparallel orientation. During production runs, position restraints were placed on the P and O2 atoms to impose the reaction coordinates. A harmonic force constant of 7 kcal/mol/Å^2 was used for distance restraint and 400 kcal/mol/rad^2 for angle restraint. The PMFs were then calculated using the weighted histogram analysis method (WHAM).88
1. The distance (D) between the Phosphorous (P) atom of one TBP molecule to the Oxygen (O2) atom of the other TBP molecule ranging from 3.0 Å to 11.0 Å with an 0.5 Å increment.

2. The pseudo dihedral angle (A) of the two P=O2 double bonds of two separate TBP molecules rotating from 0° to 360° with 5° increment in the curved arrow direction. An angle of 0° or 360° represents the perfect antiparallel orientation whereas 180° represents the perfect parallel orientation.

Figure 3.6A shows that it is energetically unfavorable for two TBP molecules, even with the anti-parallel orientation, to be too close to each other around 3 Å. A global free energy minimum is observed at 5.25 Å for TBP dimers in agreement with the peaks in the RDF study of previous section. In Figure 3.6B we fixed the distance between the two molecules to be at the optimal distance of 5.25 Å and let one of the TBP molecules rotate a full period (0° - 360°) to study the effect of orientation on the stability of TBP dimers. TBP dimers clearly favor the anti-parallel arrangement as can be seen by the low free energy of
the pseudo dihedral angles in the range of 0° - 60° or 300° - 360° (Figure 3.6B). However, these results did not provide a complete picture of the free energy map for TBP dimers over the wide range of distances and angles. Therefore, a 2D PMF study was carried out in which we sampled 1152 windows of different distances and angles for 2 ns each. The pseudo dihedral angle was rotated from the initial 0° to 360° for each distance ranging from 3.0 Å to 11.0 Å.

Figure 3.6 1D PMF of a TBP dimer as a function of (A) distance while the pseudo dihedral angle is fixed at 360° and (B) pseudo dihedral angle while the distance is fixed at 5.25 Å.

The contour map of the free energy along reaction coordinates of the pseudo dihedral angles and distances between two TBP molecules is presented in Figure 3.7A. There is the expected symmetry in the angle reaction coordinate as shown by the blue regions. When two TBP molecules are close to one another (D < 4.0 Å), it is difficult to sample structures in the regions of angles around 100° ~ 300° as demonstrated by the red regions that correspond to high free energy values. They can only assume the anti-parallel orientation due to steric effect, caused by the bulky butyl tails, and possibly the high
electrostatic interaction energy of like-sign charges. As they move further away, their free energies minimize but with a clear preference for the anti-parallel (Figure 3.7B) over the parallel orientation (Figure 3.7C). The free-energy minima are observed for distances above 4.0 Å with angles in the range of 0° to 60° and 300° to 360°. Specifically, at distances around 5.0 Å - 6.0 Å, the global free-energy minimum is observed over the angle range of 0° - 30°.

Figure 3.7 A) The 2D PMF profile along the reaction coordinates distance and angle obtained from umbrella sampling method and WHAM analysis of two TBP molecules; B) Two TBP molecules adopt the anti-parallel orientation and form a stable dimer with low free energy; C) Two TBP molecules assume parallel arrangement and possess high free energy due to steric effect. The arrows represent the direction of each TBP’s permanent dipole moment.

Recently Khomami and coworkers also studied the physical properties and molecular structure of TBP/n-dodecane mixtures using various AMBER and OPLS force fields for TBP and OPLS-AA for n-dodecane with different scaling factors for relatively
short MD simulations. They computed the angular distribution function over a range of fixed distances between 4.0 and 7.0 Å and found that this angular distribution peaks around 40 ° less than the perfect alignment in which the two dipoles of a TBP dimer in antiparallel orientation using the OPLS-DFT/RHF model for TBP. Moreover, when using the OPLS-MNDO model for TBP, they also found that the angular distribution peaks around 90 °, which belongs to a perpendicular orientation. These results disagree with our RDF and PMF results. We suspect that one of the reasons for this disagreement is related to the length of MD simulations that they conducted in comparison to our relatively long simulations of 180 ns and the exhaustively conformational search techniques of umbrella sampling and weighted histogram analysis method that we used to calculate PMFs.

### 3.4.4. PMF of TBP Trimer Conformations

As a continuation of our previous PMF study for TBP dimer, we added one more TBP molecule to the optimal TBP dimer to investigate the characteristic of TBP trimer. Three molecules forming a trimer can have different distances and orientation between every two neighbors. This creates a total of five independent variables (two for distance and three for orientation), which requires many sets of PMF calculations for ten two-dimensional contour plots and therefore becomes computationally expensive. Therefore, we assumed two molecules in the most energetically favorable dimer conformation first, then vary the distance between third molecule to the second molecule and the angle between those three molecules as shown in Figure 3.8. Based on these PMF results, we fixed the second and third molecules at the most energetically favorable conformation. Then we rotated the first
molecule and vary its orientation relative to the other two molecules as shown in Figure 3.10.

The first PMF study of TBP trimer was carried out along two different reaction coordinates, distance and angle, as depicted in Figure 3.8. The P=O’s of first TBP molecule (designated as TBP1 in Figure 3.8) and the second TBP molecule (TBP2) were held in the perfect anti-parallel orientation and 5.25 Å apart, representing the TBP dimer based on our previous study for dimers. The third TBP molecule (TBP3) was added so that the P=O’s of TBP2 and TBP3 are also anti-parallel. The distance between TBP2 and TBP3 was varied from 5.0 Å to 7.0 Å with a 0.25 Å increment while TBP3 moves around TBP2 from 60° to 180°. A harmonic force constant of 7 kcal/mol.Å² was used for distance restraint, and 400 kcal/mol.rad² was used for angle restraint. The contour map of the free energy extracted from this examination is presented in Figure 3.9A. Figure 3.9B shows one of the most energetically favorable conformations of TBP trimers while Figure 3.9C presents one of the most energetically unfavorable conformations.

![Figure 3.8](image.png)

**Figure 3.8** Reaction coordinates for PMF study of TBP trimer; (d) Distance in Å; (θ) angle in degree. The distance d between TBP2 and TBP3 is 5.25 Å and the angle θ is 160° in this figure. Color scheme: Red: oxygen molecule; Gold: phosphorus molecule; Cyan: (CH₂)₃CH₃. The butyl tails are shown using line representation for clarity.
The chief characteristic of this PMF contour plot in Figure 3.9A is the yellow to red regions, which correspond to high free energy, for angles lower than 90° for the full array of the distance reaction coordinate. This is expected since that particular angle range decreases the separation between TBP3 and TBP1 and also forces them to adopt the parallel orientation, which was proven to be highly energetically unfavorable. The angle range of 100° to 160°, in which there is sufficient distance between TBP3 and TBP1, possesses lower free energy indicating the more probable TBP trimer conformations. Another interesting feature obtained from this plot is TBP trimers tend to assume a more triangular conformation rather than a linear one. This feature is evidenced by the conformational global free energy minima are around 125°-135° angles and the regions above 160° where all three TBP align yield rather high free energy. The preference for the triangular form of TBP trimers can be rationalized by the fact that the polar head groups of TBP are hydrophilic and better shielded from the nonpolar environment of the n-dodecane solvent when they are in this form.
Our next step in this TBP trimer PMF study was to examine whether the addition of a third TBP would affect the existing TBP dimer. To do this, we separated the three TBP molecules by 5.25 Å. The TBP3 molecule was pivoted around TBP2 by an angle of $\theta_1$ from $60^\circ$ to $180^\circ$ while the antiparallel conformation was still maintained between them (Figure 3.10). The TBP1 molecule was rotated around its phosphorous atom to vary the pseudo dihedral angle, $\theta_2$, between TBP1 and TBP2 from $0^\circ$ to $60^\circ$. Again, a harmonic force constant of 7 kcal/mol.Å$^2$ was used for distance restraint, and 400 kcal/mol.rad$^2$ was used for angle restraint. The contour map of the free energy of this second step (Figure 3.11A) agreed well with our previous calculations. The global free energy minimum is in the TBP1
angle range of 0° to 30° (anti-parallel) and the TBP3 angle range of 125°-135° (triangular form) (Figure 3.11B).

Figure 3.10 Reaction coordinates for PMF study of TBP trimer. $\theta_1$, $\theta_2$ angles in degree. The butyl tails are shown using line representation for clarity.

The conformational results from this session agree well with our proposed trimer structure from the RDF calculation. The TBP conformation where its free energy is less than or equal to 3 kcal/mol is used as our criteria to identify TBP trimers. It should be noted that we also used the same free energy threshold for TBP dimers identification.
3.4.5. Determination of The Self-Association Constants of TBP in n-Dodecane via MD Simulations

The criteria extracted from previous PMF sessions for TBP dimers and trimers were used to identify these complexes in different mixtures whose TBP concentration ranges from 0.1 M to 1.0 M in n-dodecane as shown in Figure 3.12. As the concentration increases, the amounts of dimer and trimer increase. Whereas the amount of dimer exhibits an exponential growth with a sharp turn at 0.1 M and reaching a plateau at high concentrations, the amount of trimer keeps increasing linearly as the concentration increases.
As the mixture concentration increases, the amount of TBP monomers decreases as they form more TBP dimers and trimers. It should be noted that the criteria for both dimer and trimer are used to quantify the amount of TBP aggregates that are larger than trimers. For example, when a fourth TBP monomer (TBP4) is added to an existing TBP trimer (consisting of TBP1, TBP2, and TBP3) next to the third TBP monomer (TBP3), TBP3 and TBP4 have to satisfy our dimer criteria. Moreover, TBP2, TBP3, and TBP4 have to meet our trimer criteria. The results indicate that TBP aggregates that are larger than trimers are transient, evidenced by the modest average of 0.5 TBP (1.24 mol %) tetramer and 0.1 (0.27 mol %) TBP pentamer at the highest mixture concentration of 1.0 M and no TBP tetramer or pentamer is observed at the low concentrations of 0.1 M and 0.2 M at any time. This observation is in contrast with other studies that have reported detecting larger aggregates, up to heptamers, in MD simulations using a slightly different set of modified AMBER force fields.\(^{19}\)

![Figure 3.12 TBP species profile as a function of concentration. Solid lines: results from MD simulations; Circles: results from FTIR data.\(^{77}\)](image)
Several indications from our MD simulations of TBP/n-dodecane mixtures mentioned throughout this study have led us to believe that larger TBP aggregates, specifically TBP trimers, exist. However, experimental determination of the trimerization constant of TBP in n-dodecane has not been previously reported. As mentioned above, an experimental study using FTIR\textsuperscript{78} was carried out in parallel to this work in an attempt to determine the trimerization constant (Section 3.5). This work provided values of 1.68 ± 0.06 M\textsuperscript{-1} and 0.78 ± 0.12 M\textsuperscript{-1} for the dimerization and trimerization constants, respectively\textsuperscript{79}. Comparison of the mole percentage of each TBP species in the TBP/n-dodecane mixtures between MD simulations and FTIR experiments\textsuperscript{80} shows excellent agreement (Figure 3.12).

The TBP molecules at each concentration were then further categorized into different conformations as shown in Figure 3.13. Similar to the plot of a single TBP molecule in n-dodecane (Figure 3.3), we observe seven conformational isomers of TBP molecules of which the SSS, SSU, SUU conformations are predominant at almost 80 mole percent. The minor conformations, UUU, UUD, DSS and DSU, remain low around 20 mole percent of TBP population in the mixtures.
We next calculate the self-association constants of TBP from MD simulations for comparison with those obtained from FTIR experiments. In this case, we assume the formation of TBP complexes follow the step-wise association, depicted by the equation:

$$TBP_{q-1} + TBP \rightleftharpoons TBP_q$$  \hspace{1cm} \text{Equation 3.1}$$

where $q$ denotes the TBP complexes of different sizes.

The equilibrium (self-association) constant of the above equation can be written as:

$$K_q = \frac{\alpha_{TBP_q}}{\alpha_{TBP} \alpha_{TBP_{q-1}}} = \frac{[TBP_q]}{[TBP][TBP_{q-1}]} \times \frac{\gamma_{TBP_q}}{\gamma_{TBP_{q-1}}}$$  \hspace{1cm} \text{Equation 3.2}$$

where $\alpha$ is the chemical activity, and the square brackets denote the concentration of each species. In the case where information regarding the activity coefficients ($\gamma$) of the components at equilibrium are unknown, one can employ the stoichiometric constant $K'$ that can be obtained by knowing the concentrations of each species. Table 3.5

**Figure 3.13** The average conformations of TBP molecules in n-dodecane from 0.1 M to 1.0 M TBP/n-dodecane mixtures.
\[ K'_q = \frac{\gamma_{TBP}^{q-1} Y_{TBP}^{TBP}}{Y_{TBP}^{q-1}} K_q = \frac{[TBP_q]}{[TBP][TBP_{q-1}]} \]  

*Equation 3.3*

From here on we are referring to \( K'_q \) as dimerization (\( k_2 \)) and trimerization (\( k_3 \)) constants.

Using our own analyzing code and the criteria extracted from PMF studies, we were able to determine the exact concentrations of each TBP species from multiple unconstrained MD simulations over a wide range of TBP/n-dodecane mixture concentration from 0.1 M to 1.0 M. In this calculation, the TBP monomer concentration excludes UUU conformations as discussed above. The dimerization and trimerization constants of each concentration are listed in Table 3.6 below. We performed three independent simulations at each concentration to ensure reproducibility and statistical accuracy. There is no real trend to the self-association constants of TBP as the concentration of the mixture increases from 0.1 M to 1.0 M, which solidifies our criteria for identifying TBP dimers and trimers. The standard deviation values are relatively small at all concentrations except for the lowest concentration, 0.1 M. Such a relatively large deviation value at 0.1 M can be attributed to the small numbers of TBP molecules in the simulated system that contains just 16 TBP molecules and the low mixture concentration itself.
Table 3.6 The self-association constants of TBP in TBP/n-dodecane mixtures

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>dimerization constant (M⁻¹)</th>
<th>k₂</th>
<th>stdv</th>
<th>trimerization constant (M⁻¹)</th>
<th>k₃</th>
<th>stdv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run 1</td>
<td>Run 2</td>
<td>Run 3</td>
<td></td>
<td>Run 1</td>
<td>Run 2</td>
</tr>
<tr>
<td>0.10</td>
<td>1.70</td>
<td>1.50</td>
<td>1.44</td>
<td>1.55</td>
<td>0.14</td>
<td>0.35</td>
</tr>
<tr>
<td>0.20</td>
<td>1.49</td>
<td>1.61</td>
<td>1.61</td>
<td>1.57</td>
<td>0.07</td>
<td>0.45</td>
</tr>
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<td>0.40</td>
<td>1.57</td>
<td>1.48</td>
<td>1.61</td>
<td>1.55</td>
<td>0.07</td>
<td>0.51</td>
</tr>
<tr>
<td>0.60</td>
<td>1.57</td>
<td>1.50</td>
<td>1.52</td>
<td>1.53</td>
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<td>0.80</td>
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<td>1.55</td>
<td>1.58</td>
<td>1.56</td>
<td>0.02</td>
<td>0.58</td>
</tr>
<tr>
<td>1.00</td>
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<td>1.49</td>
<td>1.48</td>
<td>1.47</td>
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</tr>
<tr>
<td>average</td>
<td>1.54</td>
<td>0.07</td>
<td></td>
<td>average</td>
<td>0.56</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The average values we obtain from this study are $k_2 = 1.54 \pm 0.07 \text{ M}^{-1}$ and $k_3 = 0.56 \pm 0.09 \text{ M}^{-1}$. This new $k_2$ value is higher and new $k_3$ value is lower than the ones we estimated previously. This can be explained by the more stringent criteria for identifying TBP trimers extracted from their own PMF study rather than applied the same principles of TBP dimers for TBP trimers. This distinction decreases the amount of TBP trimers in the solution, subsequently increases the quantity of TBP dimers. Since we account for the existence of TBP trimers, our $k_2$ value is lower than the reported value of $2.6 \pm 0.1 \text{ M}^{-1}$ by Petkovic who assumed that all aggregated species are dimers.

3.5. Quantifying Dimer and Trimer Formation of Tri-n-butyl Phosphates in n-Dodecane: FTIR Experiment

In this work, we looked into the self-association of TBP in three different hydrocarbon solvents: n-octane, n-dodecane and n-hexadecane to study the effect of chain length on the self-association of TBP. This study also included iso-octane to investigate how a branched alkane would affect the behavior of TBP aggregates. The assumption, as stated earlier, is that the P=O groups are responsible for the self-association of TBP. Hence we
make the assumption that changes to the P=O peak in an absorption spectrum of TBP using FTIR would be due to P=O groups from several TBP molecules interacting. This would most likely be the case when using aliphatic solvents. These spectra can then be deconvoluted in order for quantitative analysis to be performed. Dyrssen and Petkovic concluded that there are three different frequencies corresponding to the P=O groups. Two of them were appointed to two rotational isomers of TBP monomer (Figure 3.14) and the third one to the TBP dimer. In this work, using Igor Pro (WaveMetrics, Lake Oswego, OR, USA) to deconvolute the FTIR spectra, we suggest that the inclusion of a fourth frequency that corresponds to the TBP trimers is not only possible but also necessary for fitting the spectra, especially for mixtures of higher concentrations of TBP. Furthermore, our computational study showed more than just two rotational isomers exist for TBP; however, using FTIR we can only distinguish between two types. It is recommended that both our experimental and computational studies be examined concurrently for a more comprehensive understanding of the self-association of TBP molecules.

![Figure 3.14 Schematic representation of TBP showing two different isomers of TBP molecule proposed by Dyrssen and Petkovic. In the figure R denotes a butyl chain (C₄H₉) and R' denotes a propyl chain (C₃H₇).](image)

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3.5.1. Experimental & Analysis Method

3.5.1.1. Materials

All chemicals were of 99% or higher purity and used without further purification. The TBP was obtained from Fluka, the n-octane from Sigma-Aldrich, the n-dodecane from Alfa Aesar, the n-hexadecane from Macron and the iso-octane (2,2,4-trimethylpentane) from EMD. We used a sodium chloride liquid cell (path length = 0.025 mm) purchased from Pike Technology for this quantitative study.

3.5.1.2. FTIR & the Beer-Lambert Law

Infrared spectroscopy is based on the response of an organic molecule to radiant energy. The molecule under investigation, TBP, absorbs the radiant energy and responds by vibrating at certain frequencies that correspond to specific bonds within the molecule. Vibrational response at these infrared frequencies can be transcribed into a spectrum in the range of 4000-400 cm\(^{-1}\). Samples were prepared gravimetrically using an analytical balance (Mettler Toledo) with TBP concentrations ranging from 0.01-1.0 M TBP in the respective solvents of n-octane, n-dodecane, n-hexadecane, and iso-octane. The TBP infrared spectrum was taken using Jasco 4100 (n-dodecane and iso-octane) and Jasco 4700 (n-octane and n-hexadecane) FTIR instruments. Two separate instruments were used due to availability but were shown to not affect the collected and normalized spectra to any significant extent. Each sample series was collected twice on different days. The samples were measured in the TBP absorption range of 1800-800 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\) with 48 scans taken per resolved spectrum. The absorbance of pure solvent was collected and used as a reference for all tested TBP concentrations. The liquid samples were placed in a
sodium chloride liquid cell which allowed for a fixed volume of sample and fixed path length. The cell path length was determined by measuring the absorbance of the empty cell with air being used as the reference and making use of the “fringing effect” of an empty cell\textsuperscript{89,90}. The path length was measured before and after each sample set to ensure that the sodium cell was not compromised by the chemicals. The fixed path length allows for a straightforward mathematical interpretation of peaks using the Beer-Lambert Law, \(A = \varepsilon dc\), where \(A\) is the total absorbance, \(\varepsilon\) is the species molar absorptivity, \(d\) is the sample thickness, and \(c\) is the sample concentration.

The Beer-Lambert Law is based on the concentration of a solute affecting the ability of the solution to absorb light. The relationship behaves linearly as long as the solute is simple, but as different forms of a molecule such as TBP exist in solution depending on concentration, the resulting IR peaks may come from the monomer, dimer and trimer variations within the TPB sample as well as rotational isomers. This complicates the relationship between concentration and absorbance and the Beer-Lambert equation quickly diverges from linearity and the spectrum peaks become less clearly resolved. One way to improve upon this limitation is to utilize computer software to deconvolute the total spectrum into individual peaks, which correspond to specific species or certain groups within the molecule and should display a linear relationship with concentration\textsuperscript{91}.

3.5.2. Results & Discussion

3.5.2.1. Self-Association of TBP in \(n\)-Dodecane Diluent

The collected spectra of TBP in \(n\)-dodecane from 0.1 M to 1.0 M (Figure 3.15) match well with the data from Levitskaia \textit{et al.}\textsuperscript{92} The TBP spectra collected in the other solvents
investigated in this study are very similar as each solvent is used as the reference in the respective study. As described below, we focused our analysis on the P=O stretch of TBP using the spectral region from 1250 cm\(^{-1}\) to 1310 cm\(^{-1}\).

![Concentration-dependent FTIR spectra of TBP in n-dodecane solutions. Important spectral regions for the TBP structure are indicated.](image)

The existence of multiple rotational isomers of some neutral organo-phosphoryl compounds, including TBP, have been proposed by various studies in the past\(^{77,78,83-86}\). Mortimer, in 1957, observed that the doublet of the P=O peak in the infrared spectra of trimethyl phosphate (TMP), triethyl phosphate (TEP) and triphenyl phosphate (TPP) in the liquid phase was missing from their solid phase spectra and hence concluded that the presence of more than one rotational isomer was the probable explanation for the splitting of the P=O frequency in the liquid phase\(^{85}\). Dyrssen et al. and Katzin confirmed the splitting in the P=O peak of pure TBP around the frequencies of 1270 cm\(^{-1}\) and 1280 cm\(^{-1}\) in two
separate studies\textsuperscript{84,86}. The doublet frequencies shifted to 1273 cm\textsuperscript{-1} and 1288 cm\textsuperscript{-1} for both 0.01 M TBP in n-hexane and 0.01 M TBP in n-dodecane. Dyrssen et al., once again, attributed this splitting to rotational isomerism. They further explained that the ester groups bound to the phosphorus can have two positions due to rotation around the phosphorus ester bonds. The TBP isomer with three ester groups pointing toward the P=O could reduce the P=O vibration due to the electrostatic interactions between the three hydrogen atoms on the first carbons in the butyl chains with the oxygen atom of the P=O ($M_1$ in Figure 3.14). The other TBP rotational isomer, in which the ester groups pointed away from the P=O, would have a higher P=O stretching frequency ($M_2$ in Figure 3.14)\textsuperscript{78}. Following these postulations, we assume TBPs exist primarily as monomer rather than aggregates at very low concentrations, in our case 0.01 M. By doing so, the resolved spectrum of TBP at this concentration is used to assign the frequencies of monomeric TBP isomers and other groups within the molecule.

We used the Igor Pro program (WaveMetrics, Lake Oswego, OR, USA) to deconvolute the FTIR spectra into a number of Lorentzian functions. The choice of using Lorentzian peak fitting instead of Gaussian or other types is supported by previous FTIR studies\textsuperscript{93-96}. At 0.01 M TBP, the Igor software automatically detected three peaks and produced a very poor fit to the experimental spectra (Figure 3.16). Therefore, it was necessary to add a fourth peak in order to improve the fit. In this case, we observe the same peaks as seen previously by several studies\textsuperscript{78,84,97} as shown in Figure 3.18, which displays the normalized infrared spectrum of 0.01 M TBP in n-dodecane and the deconvoluted absorbances of different species and groups in the TBP molecule in the
frequency range of 1310 cm$^{-1}$ to 1250 cm$^{-1}$. The sum of individual resolved absorbances gives the fitted total (as shown by the continuous red curve in Figure 3.18) that overlaps well with the original experimental absorbance (as shown by the continuous blue curve in Figure 3.18). Peak 1 and peak 4 had been previously assigned as CH$_2$ twist and bend, respectively$^{98-101}$. Peak 2 and peak 3 frequencies were well defined from previous studies as two different types of TBP monomers$^{77,78,84,85}$. For this study, we refer to peak 2 as monomer 2 ($M_2$) and peak 3 as monomer 1 ($M_1$). Due to the interactions between the butyl groups with the P=O group of $M_1$, vibration of the P=O group reduces, resulting in a lower frequency for this conformation as suggested by Dyrssen et al.$^{84}$ These electrostatic interactions also result in less available space around the P=O group for another monomer to come in and form dipole-dipole interactions, leading to $M_2$ being the more prominent isomer than $M_1$ in the self-association of TBPs.

As a validation of our procedure, different initial guesses for four peaks were also tested and the fitting algorithm always arrived at the same solutions of peak amplitude,
widths and locations. This is a clear indication that at least 4 peaks with their respective frequencies exist in this spectral window for 0.01M TBP in n-dodecane.

Figure 3.17 Normalized spectrum as a function of concentration of TBP in n-dodecane.

As the initial fit of the four Lorentzian functions to the spectra at a low concentration of 0.01 M TBP yielded peaks that match very closely with previous works,78,84,97 the frequencies of these four peaks were fixed in the remainder of the analysis of the other spectra at higher concentrations. For the deconvolution of spectra from more concentrated solutions the amplitudes of these peaks were allowed to vary. The shape of each Lorentzian function, reflected in the half-width at half-maximum (HWHM), was checked for every new fit to ensure that the peak shape remained consistent. Some broadening of the peak is expected as concentration increases. However, it is not necessary to fix the width parameter because this value reflects interaction energy which changes with aggregation. The HWHM of the CH\textsubscript{2} deformations changed less than 5% across the full concentration since they are farthest away from the P=O bond that mostly contributes to the dipole-dipole interaction with neighboring TBP molecules. As described below,
additional peaks were required to fit spectra at higher concentrations and once their position and shape was established the frequency and shape was maintained as with the first 4 peaks. This was done in order to minimize the number of parameters used to fit each spectrum.

As another validation of our procedure for adding one or more peaks as the concentration is increased, we compared the normalized spectra of all concentrations as shown in Figure 3.17 by dividing the whole spectra by its maximum value at each concentration. Since this figure clearly shows major changes in the spectra as a function of the concentration, this implies that there are other interactions in the solutions as the concentration increases. Not only the amplitudes, but also the locations of the peaks of the total spectra shifted. This led us to believe that other TBP species such as oligomers existed in the solution at higher concentrations as discussed below.

![Figure 3.18 Deconvolution of FTIR spectra at 0.01 M TBP in n-dodecane: red curve: fitted spectrum, blue curve: experimental data, dotted line: four individual resolved peaks. Peak 1: CH\textsubscript{2} twist, Peak 2: P=O stretching in M\textsubscript{2} ('binding' monomer), Peak 3: P=O stretching in M\textsubscript{1} ('non-binding' monomer), Peak 4: CH\textsubscript{2} bend.](image-url)
For the samples of TBP in n-dodecane at 0.06 M (Figure 3.19) and higher concentrations, the spectra are poorly resolved with just four peaks. Therefore, an additional peak was included while the frequencies and shapes of the four original peaks were maintained as described above. The best fit was obtained when a fifth Lorentzian peak, situated between the monomer peaks, was included at 1286 cm\(^{-1}\) (Figure 3.19). This frequency matches with the dimer peak that was determined in previous studies by Petkovic and coworkers\textsuperscript{77,78,84}. Hence, we designated this as the dimer peak (D) accounting for the presence of dimers in the solution. To verify the location, the fifth peak was moved by ± 2 wavenumbers in small increments, and new best fits were attempted. All of these alternative locations produced worse chi square values for the fit. This gave us confidence in the location of the dimer peak at 1286 cm\(^{-1}\).

All spectra for higher concentrations of TBP in n-dodecane, 0.2 M and higher, could be fitted with the 5 peaks described above. However, this produced an unphysical fit, discussed below in section 3.3. To improve the fit and produce physically meaningful results, an additional Lorentzian peak was included in the fitting routine, as described

![Figure 3.19 Deconvolution of FTIR spectra at 0.06 M TBP in n-dodecane: red curve: fitted spectrum, blue curve: normalized experiment data, dotted line: five individual resolved peaks. A = absorbance; d = cell thickness.](image_url)
above, and the best fit was found with this 6th peak located at 1282 cm\(^{-1}\). We designate this peak to TBP trimers (T) as seen in Figure 3.21. This figure shows the normalized spectrum of 0.31 M of TBP in n-dodecane and the deconvoluted peaks for each different species, including trimers, of the TBP molecule. When we include this trimer peak in lower concentrations than 0.20 M, negative absorbances are observed (trimer peak in Figure 3.20). Further tests to ensure that this peak and the trimer species are required to fit the spectra and describe the system are detailed below (section 3.5.2.3).

![Figure 3.20 The normalized infrared spectrum of 0.1M TBP in n-dodecane with negative A/d for trimer peak. Red curve: fitted spectrum; Blue curve: normalized experiment data; Dotted line: graphically resolved individual peaks. A = absorbance; d = cell thickness.](image)

The fitting procedure described above is carried out for the rest of the spectra in the concentration range up to 1.00 M TBP. The normalized absorbance of all species (\(M_1, M_2, D,\) and \(T\)) for the full studied concentration range can be found in the SI (Table 3.7 and Table 3.8).
Figure 3.21 Deconvolution of FTIR spectra at 0.31 M TBP in n-dodecane: red curve: fitted spectrum, blue curve: normalized experiment data, dotted line: five individual resolved peaks. A = absorbance; d = cell thickness.

Table 3.7 Normalized absorbances of TBP species in TBP/n-dodecane mixtures Run 1

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>M1 @ 1273.95</th>
<th>M2 @ 1289.57</th>
<th>D @ 1286.02</th>
<th>T @ 1282.63</th>
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<td>1.31</td>
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<td>0.00</td>
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<td>11.31</td>
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</tr>
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<td>31.28</td>
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### Table 3.8 Normalized absorbances of TBP species in TBP/n-dodecane mixtures Run 2

<table>
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<th>Conc. (M)</th>
<th>$M_1$ @ 1273.95</th>
<th>$M_2$ @ 1289.57</th>
<th>D @ 1286.02</th>
<th>T @ 1282.63</th>
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<td>80.84</td>
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</table>

#### 3.5.2.2. Determination of Equilibrium Constants for The Formation of Dimers and Trimers of TBP in n-Dodecane Diluent

Using MATLAB® (The MathWorks Inc., Natick, MA, 2000) and its built-in non-linear curve fit function, the amount of monomers, the dimerization and the trimerization constants were determined by solving a set of equations as described below. The Beer-Lambert equation can then be adapted for each species, specifically the TBP monomer ($M_1$ and $M_2$), dimer ($D$) and trimer ($T$):

\[
\frac{A_{M_1}}{d} = \varepsilon_{M_1}[M_1] \quad \text{ Equation 3.4}
\]

\[
\frac{A_{M_2}}{d} = \varepsilon_{M_2}[M_2] \quad \text{ Equation 3.5}
\]

As mentioned above, Dyrssen and Petkovic postulated that only one of the two isomers could participate in dimerization\textsuperscript{77,84}. We made the same assumption that the formation of TBP aggregates are by isomer 2 only ($M_2$ in Figure 3.14) since the
conformation of isomer 1 ($M_1$ in Figure 3.14) is sterically inhibited to accommodate another TBP molecule nearby. In addition, this analysis assumed TBP aggregation follows the step-wise self-association mechanism. Hence, the dimerization ($k_2$) and trimerization ($k_3$) constants can be calculated as:

$$k_2 = \frac{[D]}{[M_2]^2} \quad \text{Equation 3.6}$$

$$k_3 = \frac{[T]}{[M_2][D]} = \frac{[T]}{k_2[M_2]^3} \quad \text{Equation 3.7}$$

The normalized absorbances of TBP dimers and trimers can be written in terms of the TBP monomer concentration and the association constant as follows:

$$\frac{A_D}{d} = \varepsilon_D[D] = \varepsilon_D k_2 [M_2]^2 \quad \text{Equation 3.8}$$

$$\frac{A_T}{d} = \varepsilon_T[T] = \varepsilon_T k_2 k_3 [M_2]^3 \quad \text{Equation 3.9}$$

The mass balance for TBP total concentration is as shown:

$$[TBP]_{tot} = [M_1] + [M_2] + 2k_2[M_2]^2 + 3k_2k_3[M_2]^3 \quad \text{Equation 3.10}$$

Equations 3.4, 3.5, 3.8, 3.9 and 3.10, in which $\varepsilon_{M_1}, \varepsilon_{M_2}, \varepsilon_D, \varepsilon_T, k_2, k_3, M_1, M_2$ are unknowns, were solved simultaneously using the built-in nonlinear least-squares solver, slqnonline, in MATLAB® for all ten studied concentrations. The left-hand sides of these equations are experimental values. Initial guesses are provided for $\varepsilon_{M_1}, \varepsilon_{M_2}, \varepsilon_D, \varepsilon_T, k_2$ and $k_3$. Initial values for $M_1$ and $M_2$ are calculated from equations 1 and 2, respectively. The differences between the experimental data and the calculated data based on the fitted values are minimal, as seen in Table 3.9.
Table 3.9 Experimental values vs. fitted values for TBP in n-dodecane

<table>
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<tr>
<th>Total conc. exp. (M)</th>
<th>AM1/d exp.</th>
<th>AM1/d fit</th>
<th>AM2/d exp.</th>
<th>AM2/d fit</th>
<th>AD/d exp.</th>
<th>AD/d fit</th>
<th>AT/d exp.</th>
<th>AT/d fit</th>
<th>Total conc. fit (M)</th>
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<td>3.92</td>
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<td>104.76</td>
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For TBP in n-dodecane, we were able to arrive at the values of 1.68 ± 0.06 M⁻¹ and 0.78 ± 0.12 M⁻¹ for the dimerization constant and trimerization constant, respectively. Our k₂ value is lower than the previously reported value obtained by Petkovic. There are two probable explanations for this discrepancy. Firstly, the inclusion of TBP trimers in our analysis lowers the amount of TBP dimers, which thus decreases the k₂ value. In contrast, Petkovic assumed that any aggregating species is a dimer. Secondly, we used individual peaks from the deconvolution of the spectra, where the contribution of CH₂ deformation was removed, to quantify the amount of TBP monomers, dimers, and trimers peaks as seen in Figure 3.18, Figure 3.19, and Figure 3.21. In contrast, Petkovic used the total spectra instead of individual absorbances. Therefore, is it possible that they might have overestimated the amount of each TBP species especially dimers which could have contributed to a higher k₂ value.
The high quality of our data fitting and the repeatability of the experimental procedure are shown in Figure 3.22. The absorbance of each species was calculated using the fitted values in equations 3.4, 3.5, 3.8 and 3.9 and match well with experimental results (Figure 3.22A and Figure 3.22B). Moreover, Figure 3.22C plots the normalized absorbance of each species that exists in TBP/n-dodecane mixture as a function of TBP concentration found by deconvoluting each spectrum for two separate experimental series. The consistency between the collected data of two separate runs on different dates indicates the high reproducibility of this method.

![Figure 3.22](image)

*Figure 3.22 (A) Fitted normalized absorbance for monomers vs. experimental data. (B) Fitted normalized absorbance for dimers and trimers vs. experimental data. Legend for (A) and (B): Solid line: calculated from fitted parameters; x: experimental data; (C) The normalized absorbance of each species as a function of concentration over two runs. ●: Run 1; x: Run 2. A = absorbance; d = cell thickness; the color scheme for species as shown in legend.*

### 3.5.2.3. Investigation of TBP Trimers

Since previous studies have not included the presence of larger TBP aggregates than dimers in their analysis, the question of the actual existence of the TBP trimer arises. We
attempt to resolve this question by looking at the comparison between the fitted spectra of 1.0 M TBP in n-dodecane with (Figure 3.23A) and without (Figure 3.23B) the trimer peak. Both sets in Figure 3.23 include the two monomer peaks and the dimer peaks, similar to previous work. In our case, we observe that the total fit in both figures are almost identical and both match the experimental spectrum rather well. This observation, however, is not surprising since the amplitude of each peak is free to vary in order to minimize the disparity between theoretical and experimental spectra even though their frequencies are fixed. The most prominent difference between the two fits is the amplitude of the dimer peak. For the fit without trimers (Figure 3.23B), the absorbance of the dimer peak is almost twice compared to the same peak in the fit with trimers (Figure 3.23A) in order to compensate for the missing trimer peak. Furthermore, the amplitudes of the monomer peaks are significantly higher for the fit with trimers comparing to the fit without trimers.

![Figure 3.23](image)

*Figure 3.23 Fitted spectrum of 1.0 M TBP in n-dodecane mixture with (A) and without (B) the trimer peak at 1282.6 cm$^{-1}$. The peaks of CH$_2$ deformation are omitted for clarity.*

As a further test, the entire range of concentrations of TBP in n-dodecane without the trimer peak were fitted and the normalized absorbance of each species plotted as a function of total TBP concentration in Figure 3.24. The transitions at $\sim 0.5$ M in the trends of both isomers are notably unphysical for the sharp increase of $M_1$ isomers and decrease
of $M_2$ isomers. Moreover, the decrease in the amount of $M_2$ to almost zero at higher concentrations suggests that this fitting procedure might not be the best one to use. Since the amount of TBP dimer is unusually high and $M_2$ monomer is significantly low, the $k_2$ value obtained for this model is 14.5 M$^{-1}$, which is one order of magnitude higher than any previous studies reported in the literature. The possibility of this new trimer peak being another TBP dimer of a different conformation is also unlikely since this peak does not appear to any substantial degree until the concentration is above 0.2 M. This portion of our study has led us to believe that the TBP trimers are present in TBP/n-dodecane mixtures especially at high concentrations and should be accounted for in quantifying TBP self-association.

![Figure 3.24](image.png)

Figure 3.24 The normalized absorbance of each species as a function of concentrations fitted without accounting for the trimer peak at 1282.6 cm$^{-1}$.

### 3.5.2.4. Self-Association of TBP In Other Hydrocarbon Solvents

Using the same analytical procedure described above for TBP in n-dodecane mixtures, the behaviors of TBP molecules in iso-octane (Table 3.10 and Table 3.11), n-
octane (Table 3.12 and Table 3.13) and n-hexadecane (Table 3.14 and Table 3.15) over a wide range of TBP concentrations from 0.01 to 1.0 M were studied. Each experiment was repeated twice showing high degree of reproducibility. Figure 3.25 shows the frequencies of $M_1$, $M_2$, $D$, and $T$ for 0.3 M TBP concentration in each solvent listed above. We see some subtle changes in the locations of these peaks as the environment around the TBP molecules changes.
Table 3.10 Normalized absorbances of TBP species in TBP/iso-octane mixtures Run 1

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$M_1$ @ 1273.72</th>
<th>$M_2$ @ 1290.25</th>
<th>$D$ @ 1286.76</th>
<th>$T$ @ 1283.57</th>
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<td>61.74</td>
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Table 3.11 Normalized absorbances of TBP species in TBP/iso-octane mixtures Run 2

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Table 3.12 Normalized absorbances of TBP species in TBP/n-octane mixtures Run 1

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<th>( D ) @ 1286.75</th>
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Table 3.13 Normalized absorbances of TBP species in TBP/n-octane mixtures Run 2

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Table 3.14 Normalized absorbances of TBP species in TBP/hexadecane mixtures Run 1

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<th>Conc. (M)</th>
<th>M₁ @ 1273.57</th>
<th>M₂ @ 1289.14</th>
<th>D @ 1285.71</th>
<th>T @ 1282.77</th>
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Table 3.15 Normalized absorbances of TBP species in TBP/hexadecane mixtures Run 2

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<th>M₁ @ 1273.57</th>
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Table 3.16 Self-association constants of TBP in different solvents

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<th>Solvents</th>
<th>$P=O$ frequencies (cm$^{-1}$)</th>
<th>Dimerization constant (M$^{-1}$)</th>
<th>Trimerization constant (M$^{-1}$)</th>
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<td></td>
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<td>$M_2$</td>
<td></td>
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<td>iso-octane</td>
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<td>1289.6</td>
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<td>1.39 ± 0.05</td>
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The same algorithm was used to solve for the association constants in these solvents. Table 3.16 summaries the $P=O$ frequencies and the dimerization constant as well as the trimerization constant of TBP in all solvents analyzed in this work. The results show that when the solvent is a linear alkane, dimerization of TBPs (as indicated by $k_2$ value) in n-dodecane is less than that in shorter alkane solvent such as n-octane but greater than in longer alkane solvent such as that n-hexadecane. Moreover, as the alkane chain of the linear aliphatic solvent becomes longer, $k_3$ values increase. These trends are reflected in the amounts of dimers and trimers in different diluents as a function of concentration as shown in Figure 3.26. In all cases, the amounts of dimer and trimer increase as the concentration increases. The amount of dimer exhibits an exponential growth with a sharp decreasing turn around 0.1 - 0.2 M, reaching a plateau at high concentrations. However, the amount of trimer increases in a more linear fashion as the concentration increases in the range that we studied. These trends are also in good agreement with those observed in our separate MD simulation study.$^{21}$
We believe that the dipole-dipole interaction influences the self-association of TBP molecules resulting in the formation of dimers and trimers. In addition, the inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain play an important role in affecting the opposite trends in the association constants as a function of the chain length of the solvent. As a diluent, alkanes experience inter-molecular van der Waals forces giving rise to a greater boiling point when
such forces are strong\textsuperscript{102}. The strength of the van der Waals forces of hydrocarbons is determined by the surface area and the number of electrons surrounding each hydrocarbon chain of the diluent, which increases with its molecular weight. Therefore, as the alkane gets longer, its boiling point increases\textsuperscript{102}. Moreover, a linear alkane has a boiling point higher than a branched-chain alkane due to the greater surface area in contact between adjacent molecules\textsuperscript{102}. When TBP molecules are solvated in alkanes, inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain are stronger when the polar heads of TBP molecules are more clustered together, with their polar heads pointing away from the diluent. In the case of a trimer the polar TBP head groups are less exposed to the diluent than compared to the case of a dimer. As the alkane chain gets longer and more linear, inter-molecular van der Waals interactions between the butyl tails of each TBP molecule and the diluent hydrocarbon chain are stronger, which drives the formation of more trimers. This provides a possible explanation for the increasing trend of the trimerization constants (Table 3.16). As the diluent switch from linear alkanes to branched-chain alkanes the dimerization increases significantly as a result of the branched hydrocarbon being less able to solubilize TBP monomers owing to the decrease in van der Waals interactions. However, further studies are needed to improve the understanding of the chemical interactions in different solvents.
Figure 3.26 Mole percentage of TBP (A) dimers and (B) trimers as a function of concentration in different diluents: iso-octane, n-octane, n-dodecane and n-hexadecane. The average standard deviation is 1.0 % for dimer and 2.3 % for trimer.

3.6. Conclusion

In this chapter, we were able to verify and confirm the postulation of past studies that TBP has more than one rotational isomers. By utilizing our previously optimized force fields to perform gas phase simulations and PMF calculation of TBP monomer, we showed that TBP molecule has at least seven different rotational isomers of which the SSS, SSU, and SUU conformations are dominant and due to steric effect, no more than two, out of three, butyl tails of the TBP molecule can be pointing down at all time.
We investigated the self-association of TBP in n-dodecane by simulating different concentrations of TBP/n-dodecane mixtures ranging from 0.1 M to 1.0 M. When the mixture concentrations are higher than 0.4 M, the calculated CN of TBP molecule are greater than 1, indicating that dimers and larger oligomers exist. When the concentration reaches 0.8 M, the calculated CN of TBP molecules are greater than 2, indicating that trimers or larger oligomers exist at high concentrations. This suspicion led us to conduct a PMF study for TBP dimers and trimers in order to quantify their amount. We were able to visualize that TBP dimers adopt the anti-parallel orientation and TBP trimers prefer the triangular form over the linear form due to the fact that polar head groups of TBP are better shielded from the nonpolar environment of the n-dodecane solvent when they are in the triangular form.

The criteria extracted from the PMF study for TBP dimers and trimers were used to classify these complexes for the whole concentration range of TBP/n-dodecane mixtures. To our knowledge, we are the first group that rigorously establishes the criteria for recognizing the existence of both TBP dimers and trimers by performing PMF calculations. Our simulated TBP self-association values of $k_2 = 1.54 \pm 0.07$ M$^{-1}$ and $k_3 = 0.56 \pm 0.09$ M$^{-1}$ showed excellent agreement with our experimental study reported in a separate study$^{21}$. 
CHAPTER 4. Rate Theory on Water Exchange in Aqueous Uranyl Ion

4.1. Abstract

In this chapter, we report a classical rate theory approach to predict the exchange mechanism that occurs between water and aqueous uranyl ion. Using our water and ion-water polarizable force field and molecular dynamics techniques, we computed the potentials of mean force for the uranyl ion-water pair as a function of different pressures at ambient temperature. These potentials of mean force were used to calculate rate constants using transition rate theory; the transmission coefficients also were examined using the reactive flux method and Grote-Hynes approach. The computed activation volumes are positive; thus, the mechanism of this particular water-exchange is a dissociative process.

4.2. Introduction

Understanding the behavior of aqueous complexes such as uranyl ions in the condensed phase is fundamentally and technologically important because of its direct relevance to the nuclear fuel cycle. Knowledge of solvent-exchange and the kinetic properties of aqueous uranyl ions is essential for the development and improvement of solvent extraction processes used to recover these ions from spent nuclear fuels\textsuperscript{1-5}.

Significant progress has been made in this particular research area. Wipff and coworkers generated force field parameters for uranyl ions-water from free energy calculations, and reported on molecular dynamics (MD) simulation studies of the complexation and hydration behavior of aqueous uranyl ions\textsuperscript{103}. More recently, Kerisit and Liu modified Wipff’s ion-water potential parameters and carried out studies on the
structure, free energy, and kinetics of the uranyl ion using a variety of theoretical methods\textsuperscript{104}. Maginn and co-workers developed classical force field parameters for aqueous actinyl cations using quantum mechanical calculations and validated their results against static properties as well as the dynamical properties of the water–actinyl ion system\textsuperscript{105}.

The main goal of our work is to advance the understanding of the water-exchange mechanism around the actinyl ion. Knowledge of free energy profiles and rate theory evaluations are important for understanding a wide range of physical and chemical phenomena for these ionic systems. Information from those sources also provides a challenging test of the accuracy of the information derived from force field models. Our work is distinguished from earlier contributions by the methodology and to the extent to which we have exploited rate theory approaches. The most important values of this work are (1) polarization effects are explicitly included in the potential models, (2) pressure dependence and solvent response to the rate constant are evaluated, and (3) activation volume can be calculated from the rate constants as the function of pressures and this quantity can be compared directly to the experimental measurements.

4.3. Potential Models, Simulations, and Methods

For water-water interactions, we employed the Dang-Chang (DC) polarizable water model\textsuperscript{88}. Because of uncertainties in the hydration number and hydration energy\textsuperscript{104,105}, we expended substantial effort in developing the polarizable force field parameters for UO$_2^{2+}$-water interactions. The functional form that describes the UO$_2^{2+}$-water interactions is the same as used in the DC model as shown below. The total interaction energy of the system is summarized as follows:
\[ U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}} \quad \text{Equation 4.1} \]

\[ U_{\text{pair}} = \sum_i \sum_{j > i} \left( 4\varepsilon_i \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \frac{q_i q_j}{r_{ij}} \right) \quad \text{Equation 4.2} \]

and

\[ U_{\text{pol}} = -\sum_{i=1}^{N} \mu_i \cdot E_i^0 - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \mu_i \cdot T_{ij} \cdot \mu_j + \sum_{i=1}^{N} \frac{|\mu_i|^2}{2\alpha_i} \quad \text{Equation 4.3} \]

Here, \( r_{ij} \) is the distance between site \( i \) and \( j \), \( q \) is the charge, and \( \sigma \) and \( \varepsilon \) are the Lennard-Jones parameters, \( E_i^0 \) is the electric field at site \( i \) produced by the fixed charges in the system, \( \mu_i \) is the induced dipole moment at atom site \( i \), and \( T_{ij} \) is the dipole tensor. The first term in Equation 4.3 represents the charge-dipole interaction, the second term describes the dipole-dipole interaction, and the last term is the energy associated with the generation of the dipole moment \( \mu_i \). During molecular dynamics simulations, a standard iterative self-consistent field procedure is used to evaluate the induced dipoles.

We performed several MD simulations to optimize the Lennard-Jones potential and the polarizability parameters for the UO\(_2^{2+}\) molecule. The final parameters that reproduce the experimental hydration number and hydration enthalpy are summarized in Table 4.1, Table 4.2, Figure 4.1.
Table 4.1 Optimized potential parameters for water–water [9] and uranyl-water interactions used in the MD simulation. The terms $\sigma$ and $\varepsilon$ are the Lennard-Jones parameters, $q$ is atomic charge, and $\alpha$ is the molecular polarizability.

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>$\sigma$ (\text{Å})</th>
<th>$\varepsilon$ (kcal/mol)</th>
<th>q(e)</th>
<th>$\alpha$ (\text{Å}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>3.2215</td>
<td>0.1825</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>H</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5190</td>
<td>0.0000</td>
</tr>
<tr>
<td>M</td>
<td>0.0000</td>
<td>0.0000</td>
<td>−1.0380</td>
<td>1.4440</td>
</tr>
<tr>
<td>U</td>
<td>3.3498</td>
<td>0.0270</td>
<td>3.1250</td>
<td>1.0000</td>
</tr>
<tr>
<td>O(U)</td>
<td>3.2963</td>
<td>0.4380</td>
<td>−0.5625</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 4.2 Hydration properties of the UO$_2^{2+}$-H$_2$O.

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Hydration Enthalpy</th>
<th>First Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>$5.0 \pm 0.1$</td>
<td>$−406 \pm 3$ kcal/mol</td>
</tr>
<tr>
<td>Expt.</td>
<td>$4.9 \pm 0.4$</td>
<td>$−397$ to $418$ kcal/mol</td>
</tr>
</tbody>
</table>

Figure 4.1 Computed rate density function and corresponding running coordination number for U-O at ambient conditions.
Equation 4.4 was used to calculate the ion-water mean force as an average over the different solvent configurations:

\[ F(r) = \frac{1}{2} \langle \vec{r}_u \cdot (\vec{F}_A - \vec{F}_B) \rangle. \]  

Equation 4.4

In this expression, \( F_A \) and \( F_B \) are the forces acting on the solutes. The term, \( \vec{r}_u \), which is a unit vector along the A–B direction, is defined as:

\[ \vec{r}_u = \frac{\vec{r}_{AB}}{|\vec{r}_A - \vec{r}_B|}. \]  

Equation 4.5

The potential of mean force (PMF), \( W(r) \), is calculated as:

\[ W(r) = -\int_{r_o}^{r_e} \langle F(r) \rangle dr. \]  

Equation 4.6

We evaluated PMFs along the center-of-mass separation between the \( \text{UO}_2^{2+}-\text{H}_2\text{O} \) interactions with the separation between them incremented by 0.1 Å. At each center-of-mass separation, the average \( F(r) \) was determined from a 2-ns simulation time, preceded by a 500-ps equilibration period. The uncertainties of the PMFs were ±0.05 kcal/mol as estimated by determining the force averaged (the corresponding PMFs) over four equally spaced time frames during the production. The systems investigated consisted of one \( \text{UO}_2^{2+} \) in 1066 water molecules. All simulations were performed in an NVT ensemble at 300 K, with periodic boundary conditions applied in all three directions and a time step of 2 fs. To compute the \( \Delta V^\ddagger \), we carried out three studies at pressures of 0, 2, and 4 kbar, which correspond to cubic box lengths of 31.8, 31.2, and 30.7 Å, respectively. We used a modified version of the Amber 9 software package to perform all MD simulations; the Ewald
summation technique to handle long-range electrostatic interactions\textsuperscript{90}; and the SHAKE algorithm to fix the internal water and UO\textsubscript{2}\textsuperscript{2+} geometries\textsuperscript{91}.

4.4. Results and Discussions

![Graph showing PMFs for UO\textsubscript{2}\textsuperscript{2+}-H\textsubscript{2}O pair at three different pressures.]

**Figure 4.2** Computed PMFs for UO\textsubscript{2}\textsuperscript{2+}-H\textsubscript{2}O pair at three different pressures.

We start with the PMFs for the UO\textsubscript{2}\textsuperscript{2+}-H\textsubscript{2}O pair at pressures of 0, 2, and 4 kbar, and then continue with rate theory results using the transition state theory (TST)\textsuperscript{92}, reactive flux (RF)\textsuperscript{93}, Grote-Hynes (GH)\textsuperscript{94}, and Impey, Madden, and McDonald (IMM) methods\textsuperscript{106}. We end the section with the computed activation volume, \(\Delta V^\ddagger\). Figure 4.2 shows the computed PMF values obtained at 300 K for the three pressures normalized to the contact UO\textsubscript{2}\textsuperscript{2+}-H\textsubscript{2}O pair free energy minimum at 0 bar. As expected, the shapes of the computed PMFs are very similar, and the changes are small but noticeable. We observe two effects: (1) an increase in pressure stabilizes the contact UO\textsubscript{2}\textsuperscript{2+}-H\textsubscript{2}O pair and (2) the free energy barrier for escaping
the first hydration shell increases from 6.82 ± 0.05 kcal/mol at 0 bar to 7.20 ± 0.05 kcal/mol at 4 kbar. These changes are accompanied by a small change in the transition state distance from 3.25 Å to 3.24 Å. For a given PMF, the rate constant for the exchange process can be computed using TST as follows:

\[
k_{TST} = \sqrt{\frac{k_B T}{2}} \frac{(r^*)^2 e^{w(r)}}{r^2 e^{w(r)} dr}
\]

*Equation 4.7*

where \(r^*\) is defined as the position of the barrier top, \(\mu\) is the ion-water reduced mass, \(k_b\) is the Boltzmann constant, and \(T\) is the temperature. Using the computed PMFs and transition state distances, we computed the rate constant, \(k_{TST}\), for the exchange process using Equation 4.7; the results for \(k_{TST}\) are 1.48 \times 10^{-4}, 1.09 \times 10^{-4}, and 0.85 \times 10^{-4} \text{ ps}^{-1} at 0, 2, and 4 kbar, respectively. These results are summarized in Table 4.3 Rate theory results. We found \(k_{TST}\) increases with increasing pressure, and this trend would be expected by examining at the PMFs and the barrier heights. Equation 4.8 gives the pressure dependence of the rate constant at constant temperature:

\[
\Delta V^\ddagger = -RT \left( \frac{\partial \ln(k)}{\partial P} \right)_T
\]

*Equation 4.8*

where \(\Delta V^\ddagger\) is the activation volume, \(T\) is the temperature, \(R\) is the gas constant, \(k\) is the rate constant, and \(P\) is the pressure. An approximate solution to Equation 4.8 can be obtained using Equation 4.9:

\[
\ln \left( \frac{k_P}{k_o} \right) = \Delta V^\ddagger \frac{P}{RT}
\]

*Equation 4.9*
We use Equation 4.9 to calculate the activation volumes, where $k_p$ and $k_o$ are the rate constants at pressures $P$ and 0, respectively. When the computed rate constants were used, a positive activation volume (3.5 cm$^3$/mol) was obtained. These results establish that an exchange process with increasing pressure and increasing free energy at the barrier will lead to a positive activation volume (i.e., a dissociative mechanism).\(^9^8\)

### Table 4.3 Rate theory results

<table>
<thead>
<tr>
<th>UO$_2^{2+}$</th>
<th>Pressure/bar</th>
<th>$k_{\text{TST}}$/ps</th>
<th>$k_{\text{TST}K_{\text{RF}}}$/ps</th>
<th>$k_{\text{TST}K_{\text{GH}}}$/ps</th>
<th>$k_{\text{MM}}$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.48×10$^{-4}$</td>
<td>3.1×10$^{-5}$</td>
<td>3.6×10$^{-5}$</td>
<td>6.8×10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>1.09×10$^{-4}$</td>
<td>2.4×10$^{-5}$</td>
<td>1.6×10$^{-5}$</td>
<td>3.7×10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>0.85×10$^{-4}$</td>
<td>2.0×10$^{-5}$</td>
<td>1.1×10$^{-5}$</td>
<td>3.4×10$^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: The estimated error in transmission coefficients is ±0.01.

TST is known to significantly overestimate the values of rate constants. Because of the assumption that once the reactive species reach the transition state, they directly end up on the products side of the reaction without re-crossing to the reactants side. The RF method and GH theory are well known and popular corrections to TST that have been reported in the literature\(^9^9,^{10}^0\).

The RF method and GH theory approaches provide a transmission coefficient, $\kappa$, to correct the TST. In the RF method, the transmission coefficient, $K_{RF}$, is extracted from the plateau value of the time-dependent transmission coefficient as calculated using Equation 4.10:

$$k(t) = \frac{\langle \bar{r}(0) \ [r(t) - r^*] \rangle_c}{\langle \bar{r}(0) \ [r(0)]_c \rangle_c},$$

*Equation 4.10*
where \( \theta(x) \) is the Heaviside function, which is 1 if \( x \) is larger than 0 and 0 otherwise, and \( \dot{r}(0) \) is the initial ion-water velocity along the reaction coordinate. The subscript \( c \) means that the initial configurations have been generated in the constrained reaction coordinate ensemble. We constrained the reaction coordinate at its transition state value in the RF and GH approaches by removing the center-of-mass motion of each \( \text{UO}_2^{2+} \) and water molecules that were pre-selected to form a solute pair to perform the kinetics study in solution. To compute the time dependence transmission coefficient, we generated a series of starting configurations by running a simulation in which the distance between the \( \text{UO}_2^{2+} \) and a selected water molecule was constrained to be the transition state distance. We carried out a 10-ns simulation was carried out, and collected a configuration was collected every 4 ps to obtain 2500 configurations. Then, we ran each configuration both backward and forward for 2 ps, and the value of \( \kappa_{RF} \) was determined by averaging \( \kappa(t) \) over the last 0.5 ps of the forward and backward rate constants. In Figure 4.3, we present the computed time-dependent \( \kappa(t) \) at three different pressures. It is clear that the results converted well, and we observed that the rate constants decrease as pressure increases. The transmission coefficients \( \kappa_{RF} \), estimated as described above, are \( 2.1 \times 10^{-1} \), \( 2.2 \times 10^{-1} \), and \( 2.3 \times 10^{-1} \). The activation volume using the correct rate constants is \( 3.3 \text{ cm}^3/\text{mol} \), which has the same sign as the value extracted using \( \kappa^{\text{TST}} \). Thus, we conclude that the pressure dependence of both the barrier height and the transmission coefficient contribute minimally to the activation volume.
Figure 4.3 Computed time-dependent transmission coefficients, \( k(t) \), of UO\(_2^{2+}\)-H\(_2\)O pair in water from the RF method at three different pressures.

As mentioned above, we were interested in using GH theory to compute the exchange kinetic properties, such as the values for \( \kappa_{GH} \), of the UO\(_2^{2+}\)-H\(_2\)O pair, and then comparing the values with corresponding results obtained using the RF method and with experimental values. To accomplish this task, we computed the friction kernel using the trajectories at the barrier region in Equation 4.11 and Equation 4.12:

\[
 k(t) = \frac{1}{k_bT} \left\langle R(t, r^*) \times R(0, r^*) \right\rangle
\]

Equation 4.11

\[
 R(t, r) = F(t, r) \left\langle F(t, r) \right\rangle
\]

Equation 4.12

where \( r^* \) is the position of the barrier maximum, \( \mu \) is the reduced mass, \( k_b \) is the Boltzmann constant, and \( T \) is the temperature. The GH theory transmission coefficient that accounts for re-crossings at the barrier, \( \kappa_{GH} \), can be expressed using Equation 4.13\textsuperscript{101}. 

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\[ GH = GH + \int_0^t \frac{dt}{s} \left( \frac{1}{e^{s GH t}} \right) \]

Equation 4.13

Figure 4.4 Computed time-dependent friction kernels, \( \zeta(t) \), of UO\(_{2}^{2}\)-H\(_{2}\)O pair in water from the GH theory at three different pressures.

The GH theory transmission coefficient involves the frequency component of the time-dependent friction coefficient, \( \zeta(t) \), at the Laplace frequency, \( \omega_b \kappa_{GH} \), relevant in the barrier region. The term \( \omega_b \) is the barrier frequency obtained by fitting the PMF in the barrier region to an inverted parabola. Figure 4.4 shows the un-normalized, time-dependent friction kernels of the UO\(_{2}^{2}\)-H\(_{2}\)O pair as the function of pressures. In all cases, there are two distinct decay time scales; the first one rapidly decays for about 0.1 ps, and the second time scale lasts for a few picoseconds with a longer decay time. We can conclude from these data that the oscillating \( \zeta(t) \) reflects the barrier heights of the computed PMFs. We observed that the value of \( \omega_b \) decreases from 27 ps\(^{-1}\) to 25 ps\(^{-1}\) as the system pressure increases from 0 bar to 4 kbar. Transmission coefficients computed using GH theory are provided in Table 4.3. The computed values for \( \kappa_{GH} \) using these results are \( 2.4 \times 10^{-1}, 1.5 \times \)
$10^{-1}$, and $1.3 \times 10^{-1}$ for three pressures, respectively. The activation volume using the computed $\kappa_{GH}$ value is 7.3 cm$^3$/mol, which has the same sign as the value extracted using $k^{TST}$. However, its value is significantly larger, indicating that solvent effects are of importance.

In addition to the RF and GH methods, we also used the IMM method in our study$^{106}$. The IMM method allows the residence time of a solvent molecule in the first solvation shell of another molecule (i.e., UO$_2^{2+}$) to be calculated, and the inversion of the residence time is the rate constant. We used Equation 14 to determine the normalized time-correlation function of the population of solvent molecules in the first solvation shell of the UO$_2^{2+}$.

$$P(t) = \frac{< n_{\alpha}(t_i, t_f, t^*) >}{< n_{\alpha}(t_i, t_i, t^*) >} \quad \alpha, t_i$$  \hspace{1cm} \text{Equation 4.14}

The term $n_{\alpha}$ is number of solvent molecules. It is assigned a value of 1 if a solvent molecule is found in the first solvation shell at both the initial time, $t_i$, and the final time, $t_f$, and if it does not leave the shell for a continuous period of time longer than $t^* = 2$ ps. To ignore transient escapes from the first solvation shell, $t^*$ is used. The function $< \cdots >_{\alpha, t_i}$ in Equation 4.14 indicates averaging over solvent molecules, $\alpha$, and initial times, $t_i$. The term $P(t)$ is approximated as the exponential decay function $\exp(-t/\tau_p)$ so the residence time, $\tau_p$, can be determined using Equation 4.15:

$$\tau_p = \int_0^\infty P(t) \, dt = \int_0^\infty \exp(-t/\tau_p) \, dt$$  \hspace{1cm} \text{Equation 4.15}

In this study, we used $t^* = 2.0$ ps (i.e., the value originally proposed by Impey et al.)$^{106}$. In Figure 4.5 Computed time-correlation function, $P(t)$, as a function of pressure used to determine the residence time of an H2O molecule is in the first solvation shell of the UO22+
at three different pressures, we show the values of $P(t)$ as a function of the pressure obtained using the IMM method. The decay rate of $P(t)$ is much slower for the H$_2$O system at higher pressures than at lower pressures. This result would be expected because the fluid is denser at higher pressures. This finding essentially means that the value of $\tau_p$ for H$_2$O in the first solvation shell of the UO$_2^{2+}$ (i.e., $\tau_p$) is smaller at lower pressures. This is justified quantitatively by integrating $P(t)$, which gives us $\tau_p$ values of 15, 27, and 29 ns for pressures of 0, 2, and 4 kbar, respectively. The corresponding rate constants are $6.8 \times 10^{-5}$, $3.7 \times 10^{-5}$ and $3.4 \times 10^{-5}$/ps. A comparison of the computed resident times for UO$_2^{2+}$ in water using the RF, GH, and IMM methods are provided in Table 4.3. The observed trends are very consistent; however, the numerical values obtained using the IMM method are consistently higher.

Figure 4.5 Computed time-correlation function, $P(t)$, as a function of pressure used to determine the residence time of an H$_2$O molecule is in the first solvation shell of the UO$_2^{2+}$ at three different pressures
We end this section by discussing the performance of the different rate theory methods. Throughout this study, we have recognized the value of the rate theory approach. With the correction provided in Table 4.3, agreement with the experimental results reported by Grenthe and co-workers\textsuperscript{107} using $^{17}$O NMR measurements ($k = 1.4 \times 10^6$/s) is significantly improved. One of the shortcomings of our MD simulations (i.e., values a factor of 10 less than found in experimental data) is probably due to our choice of the reaction coordinate. Maginn and co-workers\textsuperscript{105} discussed the shortcomings of this system in their recently published paper. We realize that the value of the rate constant is quite small (i.e. $\kappa = 0.2$) because of the significant amount of recrossing. We are planning to extend the rate theory approach to investigate rare events of water exchange by exploring many different metastable states of the ion–solvent coordination number\textsuperscript{103}. One of the alternate reaction coordinates could be defined as the number of solvent molecules in the first solvation shell of a uranyl ion. This approach can improve the recrossing issue and, therefore, may improve the rate theory results. As mentioned above, our molecular models for water molecules and uranyl ion are nonflexible, which may contribute to the simulation shortcomings.

4.5. Conclusion

Through MD simulations using polarizable force field models, we studied in detail the water-exchange mechanism around aqueous uranyl ions. We computed PMFs and estimated rate constants using three different rate theories: TST, GH theory, and the RF method. In addition, we employed the IMM method to compute the residence time directly.
and the corresponding exchange rate constants. We investigated the pressure dependence of rate constants to understand the water-exchange mechanism in the first solvation shell.

Our findings show that the free energy barrier heights increase as pressure increases, and as a result, the TST rate constants decrease as pressure increases. Transmission coefficients computed using GH theory and the RF method increase as pressure increases. Rate constants calculated using GH theory and the RF method decrease as pressure increases. The activation volume, which is a key indicator of the exchange mechanism, was found to be positive from TST, indicating a dissociative mechanism for this particular uranyl ion. Similar findings from the use of GH theory and the RF method yield positive activation volumes, thus indicating a dissociative mechanism.
CHAPTER 5. Microscopic Behaviors of TBP, n-Dodecane and Their Mixtures at Air/Liquid and Liquid/Liquid Interfaces

5.1. Abstract

In solvent extraction processes for recovering metal ions from used nuclear fuel, as well as other industrial applications, a better understanding of the metal complex phase transfer phenomenon would greatly aid ligand design and process optimization. We have approached this challenge by utilizing classical molecular dynamics simulations technique to gain visual appreciation of the vapor/liquid and liquid/liquid interface between TBP and n-dodecane with air and water. In this study, we successfully reparameterized polarizable force fields for TBP and n-dodecane that accurately reproduced several of their thermophysical properties such as: density, heat of vaporization, and dipole moment. Our models were able to predict the surface and interfacial tension of different systems when compared to experimental results also performed by us. Through this study, we gained numerous atomistic understanding of the behaviors of TBP and n-dodecane at the interface against air and water, useful in further computational studies of such systems.

5.2. Introduction

There have been numerous efforts in the computational field to probe the transport of the metal complex from the aqueous to organic phase. However, most of these studies were carried out using non-polarizable force fields or just by simply turn on polarization for the molecules. We propose that in order to accurately study interfacial behaviors of the solvent extraction systems, especially when the extraction of
uranyl by TBP is mainly governed by electrostatic interactions, carefully reparametrized polarizable force fields should be employed. This principle is supported by several studies by Dang et al. who developed the first rigid, four-site polarizable model for water\textsuperscript{50,110}. When investigating the liquid-liquid interface between water and chloroform, Dang and coworkers concluded that the interfacial equilibrium properties change significantly by the omission of the polarization term in the potential models. This exclusion weakens the interactions between the water molecules, at the same time increases the average bulk density of chloroform\textsuperscript{49}.

Following our previous work\textsuperscript{21,29,30,111} of focusing on rigorous re-parameterization and validation, in this study we achieved satisfactory polarizable force fields for TBP and n-dodecane by optimizing the Lennard-Jones potentials parameters and the atomistic partial charges to reproduce their experimental bulk density, heat of vaporization, and dipole moment. Surface and interfacial tensions of liquid/vapor and liquid/liquid interfaces were calculated and compared with literature values as means of validation for the optimized polarizable force fields. We also carried out surface/interfacial tension measurements using a force tensiometer and the Du Nouy Ring principle. To gain insights into microscopic behaviors of TBP and n-dodecane molecules at the liquid/vapor and liquid/liquid interfaces, various equilibrium simulations were carried out to determine their density, dipole moment, orientation and chain length (for n-dodecane) profiles.
5.3. Potential Models, Computational and Experimental Details

5.3.1. Polarizable Potential Models

For non-additive polarizable potential models, the total interaction energy of the system can be written as

\[ U_{tot} = U_{pair} + U_{pol} \]  \hspace{1cm} \textit{Equation 5.1}\]

where \( U_{pair} \) is the pairwise additive part of the potential which sums up the Lennard-Jones and Coulomb interactions.

\[ U_{pair} = \sum_i \sum_j \left\{ 4 \varepsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + q_i q_j \]  \hspace{1cm} \textit{Equation 5.2}\]

In Equation 5.2, \( r_{ij} \) is the distance between atom site \( i \) and \( j \); \( q \) is the atomic charge; \( \sigma \) and \( \varepsilon \) are the Lennard-Jones parameters. The cross interaction between different molecules are obtained via the Lorentz-Berthelot combining rule.

\[ U_{pol}, \text{ the second term of Equation 5.1, represents the non-additive polarization energy and is given by} \]

\[ U_{pol} = - \sum_{i=1}^{N} \mu_i \cdot E_i^0 - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1, i\neq j}^{N} \mu_i \cdot T_{ij} \cdot \mu_j + \sum_{i=1}^{N} \frac{\mu_i^2}{2\alpha_i} \]  \hspace{1cm} \textit{Equation 5.3}\]

in which \( E_i^0 \) is the electric field at site \( i \), produced by the fixed charges in the system; \( \mu_i \) is the induced dipole moment at atom site \( i \), \( T_{ij} \) is the dipole tensor, and \( \alpha \) is the atomic polarizability. The \( U_{pol} \) expression in Equation 5.3 describes the charge-dipole interaction by the first term, the dipole-dipole interaction by second term, and the generation of the dipole moment by the last term.
The additional energy term, $U_{\text{pot}}$, in the calculation of the total interaction energy of the system, $U_{\text{tot}}$, was not included in our previous additive potential models. Hence, reparameterization was performed for our previously optimized additive force fields of TBP and n-dodecane. This reparameterization process is more intensive than for our previous study. Specifically, besides adjusting the LJ parameters, $\epsilon$ and $\sigma$, of the O2 and P atoms of TBP and of the C atoms of n-dodecane (Figure 5.1) to match the experimental bulk densities and vaporization enthalpies, the atomic partial charges ($q$) were also scaled simultaneously to reproduce their literature value of the dipole moment (Table 5.1).

For water-water interaction, we employ the polarizable water model from Dang et al. from 1997\textsuperscript{50}. This model is one of the first rigid, four-site polarizable models developed for water. It is capable of reproducing many thermophysical properties such as liquid density, heat of vaporization, dipole moment and self-diffusion coefficient of water. Moreover, it is able to capture different behaviors of water with changes in the environments (i.e., cluster, liquid, and liquid/vapor). This model also predicts the water surface tension to be 63 mN/m, in reasonable agreement with experimental value of 71.99 $\pm$ 0.36 mN/m\textsuperscript{116}. 
Table 5.1 Potential parameters for TBP and n-dodecane used in the MD simulations. $\sigma$ and $\varepsilon$ are the Lennard-Jones parameters, $q$ is the atomic charge, and $\alpha$ is the atomic polarizability.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Partial charge ($q$)</th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon$ (kcal/mol)</th>
<th>$\alpha$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TBP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.8836</td>
<td>3.7261</td>
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</tr>
<tr>
<td>P</td>
<td>1.7551</td>
<td>2.6495</td>
<td>0.0200</td>
<td>1.538</td>
</tr>
<tr>
<td>O</td>
<td>-0.6232</td>
<td>3.0000</td>
<td>0.1700</td>
<td>0.465</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1851</td>
<td>3.3997</td>
<td>0.1094</td>
<td>0.777</td>
</tr>
<tr>
<td>Cb</td>
<td>-0.0917</td>
<td>3.3997</td>
<td>0.1094</td>
<td>0.777</td>
</tr>
<tr>
<td>Cc</td>
<td>-0.0892</td>
<td>3.3997</td>
<td>0.1094</td>
<td>0.777</td>
</tr>
<tr>
<td>Cd</td>
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<td>3.3997</td>
<td>0.1094</td>
<td>0.777</td>
</tr>
<tr>
<td>H\textsubscript{a}</td>
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<td>2.4714</td>
<td>0.0157</td>
<td>0.172</td>
</tr>
<tr>
<td>H\textsubscript{b}</td>
<td>0.0620</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.172</td>
</tr>
<tr>
<td>H\textsubscript{c}</td>
<td>0.0459</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.172</td>
</tr>
<tr>
<td>H\textsubscript{d}</td>
<td>0.0383</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.172</td>
</tr>
<tr>
<td><strong>n-dodecane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>-0.0829</td>
<td>3.3106</td>
<td>0.1194</td>
<td>0.878</td>
</tr>
<tr>
<td>Cb</td>
<td>-0.0724</td>
<td>3.3106</td>
<td>0.1194</td>
<td>0.878</td>
</tr>
<tr>
<td>Cc</td>
<td>-0.0715</td>
<td>3.3106</td>
<td>0.1194</td>
<td>0.878</td>
</tr>
<tr>
<td>H\textsubscript{a}</td>
<td>0.0285</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.135</td>
</tr>
<tr>
<td>H\textsubscript{b}</td>
<td>0.0348</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.135</td>
</tr>
<tr>
<td>H\textsubscript{c}</td>
<td>0.0357</td>
<td>2.6495</td>
<td>0.0157</td>
<td>0.135</td>
</tr>
</tbody>
</table>

5.3.2. Simulation Methods

Similar to our previous studies, all parameters related to the bond length stretching, bond angle bending, dihedral angle torsion, and initial non-bonded interactions were taken from the original GAFF$^{52}$ parameter set for TBP and n-dodecane, which are schematically

Figure 5.1 Schematic of (A) TBP and (B) n-dodecane molecules
represented in Figure 1. The initial partial electric charges of atoms of TBP and n-dodecane molecules were obtained from the AM1-BCC model using the antechamber package that is implemented in AmberTool.

In this study, we are interested in reproducing the thermophysical properties and exploring the microscopic behaviors of TBP and n-dodecane in different environments: bulk liquid, liquid/vapor interface, and liquid/liquid interface. The bulk liquid simulations of pure TBP and n-dodecane were carried out as part of the reparameterization process. Simulations of their mixtures serve the purpose of validating the accuracy of the force fields to model the interaction between TBP and n-dodecane in solution. We investigated three different concentrations of TBP in n-dodecane: 0.1 M, 0.5 M and 1.0 M (Table 5.2). Liquid/vapor interface and liquid/liquid interface simulations were conducted in order to calculate their surface and interfacial tensions. More importantly, we quantitatively examined the behaviors of these molecules beyond their bulk liquid phase by looking at their density, orientation and dipole moment profiles. The simulation details for each system are described below.

5.3.2.1. Liquid TBP, n-Dodecane, and Mixtures

The MD simulations on liquid TBP and n-dodecane were performed on systems consisting of 500 molecules in cubic cells with initial cubic sizes of 63 Å and 57 Å for TBP and n-dodecane, respectively. All simulations were performed using the modified parallel version of Sander in AMBER 9. Packmol software was used to generate the initial configurations of the studied systems. Equations of motion were integrated with the velocity Verlet algorithm with a time step of 2 fs and a cutoff of 13 Å. Long range
electrostatics beyond the cutoff was treated by the particle-mesh Ewald (PME) method. Amber default scaling factors of 1/2 for van der Waals and of 1/1.2 for electrostatics were applied to the calculation of the non-bonded interactions for pairs of atoms in TBP and n-dodecane separated by three bonds (1−4 interaction). Bonds involving hydrogen atoms were constrained using the SHAKE algorithm with a tolerance of $10^{-5}$. Three-dimensional cubic periodic boundary conditions were applied. Both translational and rotational center of mass motions of the molecules were removed every 1000 steps (1 ps). The initial systems were minimized using the steepest decent algorithm to remove bad contacts. Then, each system underwent a heating process in which its temperature was increased gradually from 0 to 400 K over 1 ns. All systems were then cooled to room temperature over 0.5 ns. The isothermal–isobaric (NPT) ensemble coupled with a Langevin thermostat and Berendsen barostat was used to converge the system densities, followed by the canonical ensemble (NVT) where temperature was controlled by coupling to an external thermal bath. Liquid properties calculations of TBP and n-dodecane were carried out at 298.15 K.

Similar procedures were carried out for mixtures of TBP and n-dodecane. The concentrations of the mixtures were controlled by changing the numbers of TBP and n-dodecane molecules while keeping the system volume constant. The numbers of molecules and sizes of these systems are described in Table 5.2.
Table 5.2 Studied systems

<table>
<thead>
<tr>
<th>TBP concentration (M)</th>
<th>number of TBP molecules</th>
<th>number of n-dodecane molecules</th>
<th>initial cubic box size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 (pure n-dodecane)</td>
<td>0</td>
<td>500</td>
<td>57</td>
</tr>
<tr>
<td>0.1</td>
<td>12</td>
<td>498</td>
<td>58</td>
</tr>
<tr>
<td>0.5</td>
<td>58</td>
<td>436</td>
<td>58</td>
</tr>
<tr>
<td>1.0</td>
<td>116</td>
<td>367</td>
<td>58</td>
</tr>
<tr>
<td>3.6 (pure TBP)</td>
<td>500</td>
<td>0</td>
<td>63</td>
</tr>
</tbody>
</table>

5.3.2.2. Liquid-Vapor Interfaces of TBP, n-Dodecane, and Their Mixtures

![Figure 5.2 A schematic representation of the liquid/vapor interfacial simulation box. The liquid phase of TBP/n-dodecane/mixtures is in the middle of the box and sandwiched between two sections of vapor. The z axis is chosen to be perpendicular to the interface.](image)

The liquid-vapor interfaces of TBP, n-dodecane, and mixtures were constructed by placing the equilibrated boxes of bulk liquid, obtained from the simulations in section 2.2.1 into simulation cells with the cubic sizes tripled in the z direction (Figure 5.2). This results in simulation cells of 183 Å x 61 Å x 61 Å and 172 Å x 57 Å x 57 Å, roughly, for TBP and n-dodecane, respectively. Mixtures of TBP in n-dodecane simulation cells have similar dimension to pure n-dodecane simulation cell. Two liquid/vapor interfaces are created for each system and the interfaces are perpendicular to the z-axis. The whole systems were
equilibrated via NPT for density convergence before switching to NVT for the calculation of surface tension.

5.3.2.3. Liquid-Liquid Interfaces of TBP, n-Dodecane, and Their Mixtures with Water

In order to simulate the liquid-liquid interfaces of the systems of interest, we first equilibrated a cubic simulation box of 6350 water molecules with the dimension of 58 Å. Since the interfacial area of the TBP, n-dodecane, and their mixtures are slightly different from that of the water box, a series of short simulations were carried out to adjust their interfacial area while maintaining the equilibrated volume (i.e. reducing x and y from 61 Å to 58 Å and increasing z to 67 Å for pure TBP). The initial configuration of the liquid-liquid interface was obtained by joining the two equilibrated bulk liquid slabs together (Figure 5.3). The interface is chosen to be perpendicular to the z-axis. The systems were first minimized to remove any excess initial configuration strains, then followed by equilibration and production via NPT and NVT ensembles, respectively. Please note the plots of different property profiles of the liquid/liquid interfaces in later sections are shifted in the z direction for better visualization.
5.3.3. Surface/Interfacial Tension Experiments

The surface/interfacial tension measurements were carried out using a Sigma 700 force tensiometer, which makes use of the Du Nouy Ring method. The ring method has been discussed extensively elsewhere and proven to accurately produce surface and interfacial tensions when careful considerations are taken into account\textsuperscript{112-117}. It is recommended that "there is no motion of the ring except an infinitesimally slow upward motion". In our case, we found the pull rate of 5.0 mm/min gave the most satisfactory results for the studied systems (Figure 5.4). In order to minimize the wall effect on the tension values, the sizes of the liquid vessel and ring were selected so that their radius ratio was greater than the recommended minimum value of 3 (Table 5.3).

![Figure 5.4 Interfacial tension of unpurified n-dodecane/water interface as a function of pull rate](image)

Table 5.3 $\bar{R}$ and $D/R$ values for several surface/interfacial tension measurements. It is recommended that $\bar{R}$ is greater than 2 and $D/R$ is greater than 3. $\bar{R} = R\sqrt{(\rho_2 - \rho_1)g/\gamma_{12}}$

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$R$ (cm)</th>
<th>$D$ (cm)</th>
<th>$\rho_1 - \rho_2$</th>
<th>$\gamma_{12}$</th>
<th>$\bar{R}$</th>
<th>$D/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP</td>
<td>0.958</td>
<td>5.0</td>
<td>0.9685</td>
<td>23.30</td>
<td>6.11</td>
<td>5.219</td>
</tr>
<tr>
<td>water</td>
<td>0.958</td>
<td>5.0</td>
<td>0.9958</td>
<td>71.67</td>
<td>3.53</td>
<td>5.219</td>
</tr>
<tr>
<td>dodecane</td>
<td>0.958</td>
<td>5.0</td>
<td>0.7445</td>
<td>24.90</td>
<td>5.18</td>
<td>5.219</td>
</tr>
</tbody>
</table>
TBP was used as received from Sigma-Aldrich with > 99% purity. N-dodecane was obtained from Alfa Aesar and further purified using alumina columns as discussed in later section. Different concentration of TBP/n-dodecane mixtures were prepared gravimetrically using an analytical balance (Mettler Toledo). Ultra-pure filtered water was used for the aqueous phase. Experiments were carried out at 25 °C; temperature was controlled by a water bath that was connected to a water jacket around the sample vessel.

### 5.4. Results and Discussions

#### 5.4.1. Parameterization of TBP and n-Dodecane Polarizable Force Fields

Parameterizations of TBP and n-dodecane molecules are performed by, similar to our previous studies, adjusting the Lennard Jones potential parameters to match density and heat of vaporization simultaneously. Additionally, atomic partial charges are scaled to reproduce the experimental dipole moment. Table 5.4 summarizes the result of this procedure. As expected, density, heat of vaporization and dipole moment accurately reproduced experimental data and also matched well with previously parameterized non-polarizable models for pure TBP and n-dodecane.

In order to validate the accuracy of our force fields to model the interactions between TBP and n-dodecane, we calculated the densities of 0.1 M, 0.5 M, and 1.0 M of TBP/n-dodecane mixtures. Again, Table 5.4 shows good agreement between the mixtures’ densities and experimental values.
The self-association constants, specifically dimerization ($k_2$) and trimerization ($k_3$) constants, of TBP are additional great benchmarks for validating the force fields. Previously, we investigated the self-association behavior of TBP in n-dodecane solution experimentally via FTIR technique. Our simulated TBP self-association values showed excellent agreement with our experimental study. Thus, in this study, the criteria for identifying TBP dimers and trimers are adopted from our non-polarizable force field PMF studies. Specifically, two TBP molecules have to assume the antiparallel orientation as well as a distance around 5.25 Å and a P-O2-P-02 pseudo-dihedral angle range of 0° to 60° and 300° to 360° in order to be classify as a dimer. As for trimer, the third TBP molecule needs to be in a triangular form with an angle range of 125°-135° with the existing dimer, preserve the optimal distance of 5.25 Å as well as the antiparallel configuration between any two TBP molecules that are next to each other. The self-association constants are calculated to be $1.52 \pm 0.16 \text{ M}^{-1}$ for the dimerization constant and $0.39 \pm 0.18 \text{ M}^{-1}$ for the trimerization constant. These values agree well with both of our previous results from simulations using non-polarizable force fields and experimental results.

Another important property obtained from this portion of our study is the dipole moment of mixtures. Addition of TBP molecules to n-dodecane increases the total dipole of the mixture accordingly. We showed here a greater magnitude of variation over the concentration range when compared with a previous study of Khomami et al. It is also worth remarking that TBP’s permanent dipole, which is governed by the molecule’s conformations, is greater than its total dipole. This observation can be attributed to the fact
that TBP molecules tend to rearrange themselves via head-head interactions between the polar groups as shown in our previous study.

The comparable results between polarizable and non-polarizable force fields pose the question regarding the necessity of developing polarizable force fields. From our studies, including this manuscript, we can argue that for single-phase simulations, non-polarizable force fields, coupled with careful reparameterization, can produce satisfactory results. However, it has been recommended that the many-body polarization effect should be included in the interaction potentials to properly describe interfacial properties. Furthermore, TBP and water are highly polarizable liquids. We believe that our polarizable models will give a more accurate description of TBP behaviors in complex heterogeneous environments as demonstrated in later sections.

Table 5.4 Results comparing different properties of TBP, n-dodecane and their mixtures with experimental values

<table>
<thead>
<tr>
<th>Pure n-dodecane</th>
<th>Density (g/cm³)</th>
<th>Dipole Moment (D)</th>
<th>ΔH_vap (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Permanente</td>
<td>Total</td>
</tr>
<tr>
<td>Polarizable</td>
<td>.745 ± .001</td>
<td>0.094 ± .001</td>
<td>0.108 ± .001</td>
</tr>
<tr>
<td>Non-polarizable</td>
<td>.744 ± .007</td>
<td>NA</td>
<td>~ 0</td>
</tr>
<tr>
<td>Exp.</td>
<td>0.745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarizable</td>
<td>.751 ± .002</td>
<td>0.372 ± .003</td>
<td>0.400 ± .004</td>
</tr>
<tr>
<td>Exp.</td>
<td>.756</td>
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<td></td>
</tr>
<tr>
<td>0.5 M TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarizable</td>
<td>.775 ± .002</td>
<td>1.123 ± .003</td>
<td>1.083 ± .009</td>
</tr>
<tr>
<td>Exp.</td>
<td>.776</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 M TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarizable</td>
<td>.804 ± .002</td>
<td>2.268 ± .003</td>
<td>2.049 ± .009</td>
</tr>
<tr>
<td>Exp.</td>
<td>.805</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure TBP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarizable</td>
<td>.969 ± .002</td>
<td>3.93 ± .091</td>
<td>3.33 ± .006</td>
</tr>
<tr>
<td>Non-polarizable</td>
<td>.971 ± .007</td>
<td></td>
<td>3.58 ± .340</td>
</tr>
<tr>
<td>Exp.</td>
<td>0.973</td>
<td>3.25 to 3.33</td>
<td></td>
</tr>
</tbody>
</table>
5.4.2. Microscopic Behaviors of TBP, n-Dodecane, and Their Mixtures at The Liquid/Vapor Interfaces

To gain insights into the structural behaviors of TBP and n-dodecane molecules at the liquid/vapor interfaces, various MD simulations were carried out to first determine their density, dipole moment, orientation and chain length (for n-dodecane) profiles.

The orientation of TBP or n-dodecane is determined by calculating the angle between the P=O vector with respect to the interface according to the order parameter:

\[ S(z) = \langle (3 \cos^2 \theta - 1)/2 \rangle \]

*Equation 5.4*

where \( \theta \) is the angle between the phosphoryl group and z axis (perpendicular to the interface). A value of \( S(z) \) of 1 represents the parallel orientation while a value of 0.5 represents the perpendicular orientation. For n-dodecane, each chain is divided in half and the vector connecting the center of mass of one half to the center of mass of the other half is used. This method is suitable since the n-dodecane chain has an average length of 12.5 Å (Figure 5.5) when compared to its fully stretched length of ~15 Å in Figure 5.1B. The chain length of n-dodecane is calculated as the distance between two farthest hydrogens.

Several property profiles of TBP and n-dodecane as a function of the z-axis, normal to the interface, are shown in Figure 5.5 and Figure 5.6. These profiles are obtained by computing in slabs of 0.5 Å thickness parallel to the interface and averaged over 10 ns of simulation. The density profile of TBP is quite similar to the ones from previous studies with different force fields, including both non-polarizable and polarizable. There are two well-defined interfaces that are symmetric around the center of mass of the whole system of TBP and n-dodecane.
The density profiles are remarkably different when comparing pure n-dodecane (red curve of Figure 5.5) to pure TBP (red curve of Figure 5.6). The density profile of n-dodecane is rather smooth within the bulk region and only fluctuates at the two interfaces while TBP’s density profile oscillates periodically. This observation implies that TBP might possess a more ordered structure where the molecules arrange themselves head to head (phosphoryl group) and tail to tail (butyl group), almost sheet-like, which in turn affect the average bulk density even within the bulk region. This behavior can be due to the fact that TBP is a surfactant with both polar and non-polar regions thus some rearrangement within the bulk phase is necessary to minimize the system energy.
Figure 5.5 Density, dipole moment, orientation and chain length profiles of pure n-dodecane along the z-axis
As mention in previous section, it can be seen here again in Figure 5.6 that TBP’s permanent dipole is higher than its total dipole. These dipole profiles increase for TBP molecules that are close to the interfaces (at around 65 Å and 125 Å along the z-axis). This behavior is in relation to the change in orientation of the phosphoryl group. Within the bulk, TBPs have an order parameter of ~ 0.3 indicating random orientations. As they cross into the vapor phase, the phosphoryl groups appear to be more perpendicular to the interface which is reflected in the order parameter of 0.5. Interestingly, we observe the opposite behavior with n-dodecane in Figure 5. These molecules also exit in random
orientation (order parameter of 0.2) within the bulk but as they leave the solution, they
align themselves parallel to the interface (order parameter of ~ 0.9) in order to maximize
the van de Waal interactions. As expected of a nonpolar molecule, n-dodecane dipole
profiles are fairly constant along the z-axis.

To further test our model, we calculated the surface tension, $\gamma$, which is defined as
the difference between the pressure components in the direction parallel and
perpendicular to the interface:

$$\gamma = \frac{1}{2} \left( \frac{p_{yy} + p_{zz}}{2} - p_{xx} \right) L_x \quad \text{Equation 5.5}$$

In the above equation, $p_{\alpha\alpha}$ ($\alpha = x, y \text{ or } z$) is the $\alpha\alpha$ element of the pressure tensor and $L_z$ is
the linear dimension of the simulation cell in the z direction.

Table 5.5 reports the calculated surface tension of the studied systems from MD
simulations as well as the experimental results that were conducted using the tensiometer.
To verify the accuracy of our instrument, we measured the surface tension of pure water,
TBP and n-dodecane to compare with previous literature values. The tensiometer
produced the value of $71.65 \pm 0.01, 24.98 \pm 0.03$ and $27.71 \pm 0.04$ mN/m for water, n-
dodecane, and TBP, respectively. The literature values for these three liquids are $71.99 \pm
0.36, 24.9$ and $27.20 \pm 0.50$ mN/m\textsuperscript{118,119}. Thus, we are confident that our results for
mixtures will also be accurate.
Table 5.5 Comparison of surface tension obtained via MD simulations and experiments

<table>
<thead>
<tr>
<th></th>
<th>Surface tension (mN/m)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>Exp.</td>
</tr>
<tr>
<td>0.00 M</td>
<td>20.86 ± 0.44</td>
<td>24.98 ± 0.03</td>
</tr>
<tr>
<td>0.10 M</td>
<td>21.06 ± 0.48</td>
<td>25.09 ± 0.02</td>
</tr>
<tr>
<td>0.05 M</td>
<td>21.21 ± 0.86</td>
<td>24.87 ± 0.02</td>
</tr>
<tr>
<td>1.00 M</td>
<td>22.66 ± 0.55</td>
<td>24.88 ± 0.01</td>
</tr>
<tr>
<td>3.65 M</td>
<td>26.78 ± 1.10</td>
<td>27.71 ± 0.04</td>
</tr>
</tbody>
</table>

To calculate the surface tension from MD simulations, we ran each set three times for at least 20 ns each time starting from pre-equilibrated phases as described in earlier sections. As an example, the surface tension as a function of time of pure TBP is presented in Figure 5.7. It shows that the surface tension of TBP does not converge until after being simulated for about 20 ns, making this calculation rather expensive. Nonetheless, our calculated surface tension of pure TBP of 26.78 ± 1.10 mN/m matches well with the experimental value (Table 5.5), confirming the quality of our TBP model. In the case of n-dodecane, the calculated surface tension is 20.86 ± 0.44 mN/m, in reasonable agreement with the experimental value of 24.98 ± 0.03 mN/m.

Figure 5.7 The computed surface tension of TBP at 298 K as a function of time.
It is interesting to observe that the addition of TBP up to 1.0 M does not affect the surface tension of the n-dodecane/TBP solutions and both MD simulations and experiments are able to capture this behavior (Table 5.5). It can be postulated that, based on the results from experiments solely, the added TBP disperse randomly throughout the n-dodecane medium, hence no change in the surface tension can be detected. With the assistance from MD simulations, we can comprehend this behavior visually. The plot of Figure 5.8 compares the density profile along the z-axis of five different concentrations ranging from pure n-dodecane (0.0M) to pure TBP (3.65 M).

![Figure 5.8 Density profile along the z-axis of TBP, n-dodecane, and their mixtures](image)

From the density profile, the bulk density and interfacial thickness could be obtained (see Table 5.4) by fitting it to a hyperbolic tangent functional form:

$$\rho(z) = \frac{1}{2}(\rho_L + \rho_V) - \frac{1}{2}(\rho_L - \rho_V) \tanh\left(\frac{z - z_o}{d}\right)$$  \hspace{1cm} \text{Equation 5.6}

In this equation, $\rho_L$ and $\rho_V$ are the liquid and vapor density; $z_o$ is the position of the Gibbs diving surface; and $d$ is the estimated thickness of the interface.

The best-fitted curves estimate the liquid densities of 0.746 g/cm$^3$ for n-dodecane and of 0.962 g/cm$^3$ for TBP. These values match very closely to the bulk densities of both.
molecules at 298 K. Their mixtures’ densities, correspondingly, matched well with experimental data. The fits also produce an interfacial width of 2.88 Å for n-dodecane and of 3.31 Å for TBP. The addition of TBP to n-dodecane solution slightly decreases its interfacial width.

It can be seen that when up to 1.0 M of TBP is added to n-dodecane solutions, the average densities of the solutions increase accordingly (Table 5.6). However, the added amount of TBP was not enough to alter the density profile of n-dodecane. It appears that TBP was dispersed randomly within the bulk of n-dodecane rather than adopting the ordered structure observed in pure (3.6 M) TBP. This is also reflected in the minimal effect of the addition of TBP on the surface thickness of the mixtures (Table 5.6). Furthermore, the surface thicknesses and the interfacial shapes of the studied systems indicate that the liquid-vapor interfaces are neither smooth nor sharp, microscopically.

<table>
<thead>
<tr>
<th>Liquid density (g/cm³)</th>
<th>Interfacial width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
</tr>
<tr>
<td>0.00 M</td>
<td>0.746</td>
</tr>
<tr>
<td>0.10 M</td>
<td>0.750</td>
</tr>
<tr>
<td>0.05 M</td>
<td>0.773</td>
</tr>
<tr>
<td>1.00 M</td>
<td>0.806</td>
</tr>
<tr>
<td>3.65 M</td>
<td>0.962</td>
</tr>
</tbody>
</table>

The discrepancies observed for the surface tension of the mixtures comparing simulations and experiments can be attributed to the underestimation of the surface...
tension of pure n-dodecane since, again, the mixture’s surface tension is governed by n-dodecane for, at least, up to 1.0 M TBP concentration.

5.4.3. Microscopic Behaviors of TBP, n-Dodecane, and Their Mixtures at The Liquid/Liquid Interfaces with Water

Studies similar to those reported in Section 5.4.2 were carried out with the incorporation of water as the second liquid phase replacing the vapor phase. Our goal was to study the structural behaviors of TBP and n-dodecane as they come in contact with a highly polar medium such as water.

We looked at profiles for several variables of the TBP/water interface along the z-axis (Figure 5.9). The most apparent change for TBP is the total dipole moment (DM) profile when it is compared to the one of liquid/vapor interface (green curve of Figure 5.6). Within the bulk phase, TBP’s DM still has the average value of 3.2 D. However, their total DM gradually increases as they move from their bulk into the interface region and then, obtains the maximum value of ~ 5.5 D as they approach the bulk water phase. This observation clearly demonstrates the inducing strength of the polar water molecule since the permanent and induced DM of TBP are comparable to that of the liquid/vapor interface (not shown). It also reinforces the recommendation of utilizing polarizable force fields to capture interfacial behaviors.
Figure 5.9 Pure TBP/water interface profile along the z-axis. Red colored curves represent TBP; black colored curves represent water.

Since n-dodecane is a nonpolar molecule, it is as expected that there are not many interactions happening at its interface with water as shown in Figure 5.10. One characteristic that is worth mentioning is that the n-dodecane molecules no longer align themselves parallel to the interface as in the case of liquid/vapor interface. In order to minimize the hydrophobic interactions with water, n-dodecane would cross the interface “head on” with a right angle, reflected in the order parameter of ~ 0.4. However, this
behavior is not seen at both liquid-liquid interfaces, i.e. the orientation profile is non-symmetrical, and the only conclusion one can draw is that the n-dodecane molecules are not parallel with the interface.

Figure 5.10 Pure n-dodecane/water interface along the z-axis. Red colored curves represent n-dodecane; black colored curves represent water.

The density profiles of TBP and n-dodecane/water interfaces are also fitted using the hyperbolic tangent functional form shown in section 5.4.2 (Eq. 2) and presented in Table 5.7. The liquid density of n-dodecane produced by the fit no longer matches well with its literature or simulated liquid/vapor density value. Instead, the liquid density of n-dodecane increases almost 10% indicating some shrinkage of the oil phase. This behavior is expected and triggered by the hydrophobicity of n-dodecane. The same trend is observed
for all mixtures of up to 1.0 M TBP concentration; however, the addition of TBP indeed lessens the strained interactions between n-dodecane and water at the interface, resulting in a lesser degree of shrinkage in the volume of the mixtures. The interfacial thicknesses (Table 5.7) also decrease by roughly 50% in all systems comparing to the surface thicknesses listed in Table 5.4 for liquid/vapor interfaces. In the case of pure TBP/water liquid/liquid interface, the liquid density of TBP decreases while the water interfacial thickness is of the same as its liquid-vapor thickness. These observations suggest that there are interactions between TBP and water at the interface due to the amphiphilicity of TBP.

Both experiments and MD simulations are also carried out to determine the interfacial tension of the biphasic systems of interest. The interfacial tension measurements were conducted experimentally using the force tensiometer. Previous studies have observed that many stock alkanes suffer from amphiphilic impurities\textsuperscript{119}. The effect is minimal for surface tension measurements as shown in Figure 5.11A where the values remain constant and independent of the number of purifying cycles using an alumina column. However, Figure 5.11B shows significant changes in interfacial tension of the oil-water as a function of purifying cycles due to the high affinity toward the oil-water interface of the impurities. In our study, n-dodecane was purified 4 times using an alumina column. TBP, already a polar molecule, was used as received as minor impurities was assumed not to affect the surface tension to any significant level.
The interfacial tensions of TBP and n-dodecane with water observed using the force tensiometer are $7.82 \pm 0.28$ and $50.74 \pm 0.08$ mN/m, respectively. These values compare favorably with literature values of $8.01$ mN/m for TPB\textsuperscript{118} and $52.34$ (at $22 \, ^\circ C$) mN/m for n-dodecane\textsuperscript{119,120}. The measured interfacial tensions of TBP/n-dodecane mixtures are listed in Table 5.7. It can be seen that TBP dominates the interfacial tension measurements as small additions to the n-dodecane mixture lowers the interfacial tension significantly. Only $0.1$ M of added TBP reduces the interfacial tension between n-dodecane and water by more than $60\%$. However, the effect weakens as more of this surfactant is added to the mixture indicating interfacial saturation of TBP is reached.
We computed the interfacial tensions of liquid/liquid interfaces via MD simulations using Eq. 2 shown in section 5.4.2 and the results are listed in Table 5.7. It can be seen that MD simulations can satisfactorily reproduce the interfacial tensions of the two limiting systems (pure DOD-WAT and pure TBP-WAT). However, MD simulations inadequately replicate the interfacial tension values for mixtures of TBP/n-dodecane. Even though the interfacial tensions follow the correct downward trend as more TBP is added to the solutions, the absolute values are far from satisfactory when being compared to experimental data. Since we already validated the interactions between TBP and n-dodecane by computing their mixtures’ densities and self-association constant, we suspect that these shortcomings are stemming from a different error source besides our models. This observation led us to pursue an additional investigation into the starting configuration of interfacial tension calculation (section 5.4.4).

Table 5.7 Liquid density, surface thickness and interfacial tension of TBP in n-dodecane as a function of TBP concentration.

<table>
<thead>
<tr>
<th></th>
<th>Organic Phase</th>
<th>Aqueous Phase</th>
<th>Interfacial tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid density (g/cm³)</td>
<td>Interfacial thickness (Å)</td>
<td>Liquid density (g/cm³)</td>
</tr>
<tr>
<td>Pure DOD - WAT</td>
<td>0.810</td>
<td>1.71</td>
<td>0.994</td>
</tr>
<tr>
<td>0.1 M - WAT</td>
<td>0.766</td>
<td>1.28</td>
<td>0.994</td>
</tr>
<tr>
<td>0.5 M - WAT</td>
<td>0.782</td>
<td>1.28</td>
<td>0.994</td>
</tr>
<tr>
<td>1.0 M - WAT</td>
<td>0.799</td>
<td>0.79</td>
<td>0.994</td>
</tr>
<tr>
<td>Pure TBP - WAT</td>
<td>0.958</td>
<td>1.45</td>
<td>0.994</td>
</tr>
</tbody>
</table>

*calculated using pre-equilibrated organic and aqueous phases as initial configurations (configuration 1 in section 5.4.4)
5.4.4. The Effect of Initial Configuration of the System on the Calculation of Interfacial Tensions at the Liquid/Liquid Interfaces

As mentioned in previous section, the calculations of surface/interfacial tensions are very expensive computationally. Additionally, it is shown in Table 5.7 that simulations with pre-equilibrated organic and aqueous phases as initial configuration fail to reproduce the experimental interfacial tension. Our goal was to investigate whether a computational method using different starting configuration can balance result accuracy and computational expenses. In order to carry out this investigation, we started out with four different initial configurations of the 1.0 M TBP in n-dodecane with water system:

Configuration 1: Contact of the pre-equilibrated organic and aqueous phases (Figure 5.12).
Configuration 2: All TBP molecules are purposely placed at one interface (Figure 5.13).
Configuration 3: Random configuration of all molecules and let phase separation occur spontaneously (Figure 5.14).
Configuration 4: All TBP molecules are purposely placed at two interfaces (Figure 5.15).
Figure 5.12 System of separately pre-equilibrated of organic and aqueous phases. Red: water molecules; cyan: n-dodecane molecules; CPK presentation: TBP molecules. Top: initial configuration. Bottom: final configuration.

Figure 5.13 System of TBP molecules placed at one interface. Top: initial configuration. Bottom: final configuration.
Figure 5.14 System of mixing TBP, n-dodecane and water randomly. Top: initial configuration. Bottom: final configuration.

Figure 5.15 System of TBP molecules placed at two separate interfaces. Top: initial configuration. Bottom: final configuration.
Each configuration (conf.) was simulated for an extended amount of time. Specifically, conf. 1 and conf. 2 were simulated for 20 ns. Conf. 3 was simulated for 10 ns after phase separation was achieved which took 60 ns. Finally, conf. 4 was simulated for 30 ns. The comparisons of their interfacial tensions are shown in Table 5.8 below:

<table>
<thead>
<tr>
<th>Interfacial Tension (mN/m) from MD</th>
<th>Experimental value = 10.70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration 1</td>
<td>43.74</td>
</tr>
<tr>
<td>Configuration 2</td>
<td>35.43</td>
</tr>
<tr>
<td>Configuration 3</td>
<td>20.50</td>
</tr>
<tr>
<td>Configuration 4</td>
<td>18.83</td>
</tr>
</tbody>
</table>

It is evident from Table 5.8 that initial configuration has a vast effect on the interfacial tension (IT) of the system. The IT of conf. 2 decreases by almost 20% comparing to conf. 1 due to the accelerated amount of TBP concentrated at the interface. When comparing the final stage of conf. 2 to conf. 3 and conf. 4, it can be seen that many TBP molecules move into the aqueous phase from conf. 2 whereas for conf. 3 and 4, they remain that the interface. This distribution aids greatly in the reduction of the IT values of the two phases. Conf. 3 and conf. 4 generate very similar IT values due to the resemblance of their final stages. However, it took configure 3 60 ns to achieve phase separation before IT calculation could be performed.

These shortcomings in IT calculations due to initial configurations could be more accurately attributed to the equilibration issue that polarizable force fields often deal with. Theoretically, if all initial configurations were simulated for an extended amount of time, they should arrive at the same final configuration and yield similar IT values. However, the
computational expenses for these polarizable force field MD simulations are still high, both power and time. Thus, from this investigation, we recommend that IT of surfactant systems should be calculated with an initial configuration that best estimates the final configuration (configuration 4).

Finally, we show the equilibrium interface of 1.0 M TBP in n-dodecane and water of configuration 4 in Figure 5.16. It can be seen that TBP concentrates at the interface to minimize their potential energy as well as to lessen the interfacial tension between the two liquids, as oppose to distributing randomly within the bulk phase of n-dodecane in the case of liquid/vapor interfaces (Figure 5.16).

![Figure 5.16 The density profiles of 1.0 M TBP/water interface along the z-axis of configuration 4. Red/blue curve is the density of TBP/n-dodecane molecules within the solution. Green curve is the density of the 1.0 M mixture.](image-url)
5.5. Conclusion

In this work, by coupling classical molecular dynamics simulation technique with experiments, we have constructed polarizable force fields for TBP and n-dodecane molecules, two of the main components of PUREX type processes. By adjusting the Lennard-Jones parameters and atomic charges, our models were able to reproduce many thermophysical properties such as densities, heat of vaporizations and dipole moments. It was shown that TBP's permanent dipole moment is greater than its total dipole moment. To validate our force fields’ capability of modeling the interactions between TBP and n-dodecane molecules we calculated the densities and self-association constants of TBP/n-dodecane mixtures for up to 1.0 M of TBP concentration and produced satisfactory results. Surface/interfacial tension calculations of TBP and n-dodecane were compared to experimental values obtained from using a Sigma 700 force tensiometer. Our polarizable force fields were able to replicate surface tension values that are within 4% error for pure TBP and 17% error for pure n-dodecane. They correctly predicted the unaffected surface tension values of TBP/n-dodecane mixtures for up to 1.0 M of TBP as similarly demonstrated via experiments.

To gain insights into the microscopic behaviors of TBP and n-dodecane molecules at the liquid/vapor and liquid/liquid interfaces, various MD simulations were carried out to determine their density, dipole moment, orientation and chain length (for n-dodecane) profiles. These calculations showed that TBP tends to possess a more order structure even within the bulk region due to its amphiphilicity. N-dodecane, on the other hand, only rearranged themselves at the interfaces. The dipole moment profile of TBP fluctuated and
increased as it approached the liquid/vapor interface, in relation to the change in orientation of the phosphoryl head group to be perpendicular to that interface. This behavior of TBP persisted, but with greater magnitude for the case of liquid/liquid interface which demonstrated the inducing strength of the highly polar water molecule. Since n-dodecane is a nonpolar molecule, it is as expected that there were not many interactions happening at the interfaces. One interesting observation was that n-dodecane aligned themselves parallel to the liquid/vapor interface to maximize its van der Waal interactions but conformed to a more random, or possibly perpendicular orientation to minimize the hydrophobic interactions with water.

A case study to investigate the effects of initial configurations on the calculation of interfacial tensions provided distinctive responses from the interfacial tension values. This shortcoming in this kind of calculations due to initial configurations could be more accurately attributed to the equilibration issue that polarizable force fields often deal with. Thus, from this investigation, we recommend that, to balance result accuracy and computational expense, interfacial tension calculations of surfactant systems to be computed using the best-estimated final stage as the initial configuration.

Through this work, we are confidently presenting high quality polarizable force fields for TBP and n-dodecane molecules, two of the main components in the PUREX process. Together with our previously developed model for uranyl ion\textsuperscript{30}, the insights into the microscopic behaviors of these molecules at the liquid/vapor and liquid/liquid interfaces gained from this study will greatly aid the elucidation of the phase transfer mechanism of the metal complexes. This study paves the way for our next effort which will
be focusing on understanding the kinetic of phase transfer phenomena involved in the solvent extraction process.
CHAPTER 6. Conclusions and Future Work

6.1. Conclusion

We have successfully parameterized new sets of non-polarizable force fields for TBP and n-dodecane molecules using the AMBER force field (Chapter 2). Dipole moment and self-diffusion coefficient were used as means to validate the optimized parameter sets. The values resulting from our optimized parameters show better accuracy than the ones from the default GAFF when compared with experimental values. By utilizing our previously optimized force fields to perform gas phase simulations and PMF calculation of TBP monomer, we were able to verify and confirm the postulation of past studies that TBP has more than one rotational isomers (Chapter 3). We investigated the self-association of TBP in n-dodecane by simulating different concentrations of TBP/n-dodecane mixtures ranging from 0.1 M to 1.0 M as well as conducting a PMF study for TBP dimers and trimers in order to quantify their amount in mixtures. We were able to visualize that TBP dimers adopt the anti-parallel orientation and TBP trimers prefer the triangular form over the linear form due to the fact that polar head groups of TBP are better shielded from the nonpolar environment of the n-dodecane solvent when they are in the triangular form. The criteria extracted from the PMF study for TBP dimers and trimers were used to classify these complexes for the whole concentration range of TBP/n-dodecane mixtures. To our knowledge, we are the first group that rigorously establishes the criteria for recognizing the existence of both TBP dimers and trimers by performing PMF calculations. Our
simulated TBP self-association values of $k_2 = 1.54 \pm 0.07 \, \text{M}^{-1}$ and $k_3 = 0.56 \pm 0.09 \, \text{M}^{-1}$ showed excellent agreement with our experimental study reported in a separate study\textsuperscript{21}.

In Chapter 4, through MD simulations using polarizable force field models, we studied in detail the water-exchange mechanism around aqueous uranyl ions. We computed PMFs and estimated rate constants using three different rate theories: TST, GH theory, and the RF method. In addition, we employed the IMM method to compute the residence time directly and the corresponding exchange rate constants. We investigated the pressure dependence of rate constants to understand the water-exchange mechanism in the first solvation shell.

Finally, in Chapter 5, by coupling classical molecular dynamics simulation technique with experiments, we have constructed polarizable force fields for TBP and n-dodecane molecules. By adjusting the Lennard-Jones parameters and atomic charges, our models were able to reproduce many thermophysical properties such as densities, heat of vaporizations and dipole moments. To validate our force fields' capability of modeling the interactions between TBP and n-dodecane molecules we calculated the densities and self-association constants of TBP/n-dodecane mixtures for up to 1.0 M of TBP concentration and produced satisfactory results. Surface/interfacial tension calculations of TBP and n-dodecane were compared to experimental values obtained from using a Sigma 700 force tensiometer. Our polarizable force fields were able to replicate surface tension values that are within 4% error for pure TBP and 17% error for pure n-dodecane. They correctly predicted the unaffected surface tension values of TBP/n-dodecane mixtures for up to 1.0 M of TBP as similarly demonstrated via experiments.
6.2. Future Work

The work carried out in this dissertation hopes to improve the association between the computational and experimental fields regarding a better understanding of the treatment of used nuclear fuel. By contributing both non-polarizable and polarizable force fields for n-dodecane, TBP, and uranyl ion, hopefully additional MD simulations and experiments will be conducted to yield additional information on the mechanism of the metal ion extraction and third phase formation.

One immediate study that can be carried out is to perform extended, unrestrained MD simulations identify stable complexes of the system. For this study, the MD simulations conditions, such as temperature and concentrations, will mirror the PUREX process. The distribution ratio of uranyl, nitric acid and water between aqueous and organic phase can be quantified using MD simulations and compared with experiments using neutron activation analysis. The agreement between MD simulations and experimental results will allow us to elucidate the molecular-level behavior of the system and answer some of the most fundamental questions:

1. What is the driving force of the dehydration of $\text{UO}_2\cdot5\text{H}_2\text{O}^{2+}$?
2. How do TBP and nitrate complex with uranyl ions after their dehydration process?
3. What factors govern the competition between the extraction of uranyl, nitric acid and water by TBP?
4. Which complexes are the most stable: TBP-water, TBP-acid or TBP-uranyl-acid?
After the determination of stable complexes, PMF studies can be performed by transferring them across the aqueous/organic interface. The insight gains from this study will aid with the understanding of the kinetics of phase transfer mechanism.

Finally, MD simulations of high concentration of acid and metal ions can be carried out in order to observe the formation of third phase. As discussed earlier, the chemical origin of the third phase formation phenomenon is still a matter of debate. Does third phase form by following the “particle growth model” or the “particle interaction model”? Whether “super-aggregates” of 40 TBP molecules can exist in this heavy organic phase and why? The completion of this specific aim will greatly help with addressing these questions.
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