

Rheological and Tribological Characterization of Ionic Liquid Water-based Lubricants

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Declaration of originality

I hereby declare this thesis titled, “Rheological and Tribological Characterization of Ionic Liquid Water-based Lubricants”, and the work presented in it are my own. This work was done while I was pursuing my candidature for the Doctor of Philosophy degree at the University of Sydney. This work is an original contribution to the field with the exception of quoting from the work of others, for which the source is always provided. No part of this thesis has previously been submitted for the award of a degree or any other qualification in any university or other research institution. I have acknowledged all main sources of help.

Yang Feng

Abstract

Research on environmentally friendly replacements for petroleum-based lubricants has become necessary due to the rising awareness of sustainability and limited sources of petroleum-based oils. Water-based lubricants (WBLs) are potentially good alternatives in some industrial applications such as metalworking, metal deformation and machinery. However, water alone is insufficient as a lubricant for these applications, necessitating the addition of additives in various forms to enhance lubrication performance. This study investigates WBLs containing amino acid ionic liquids (AAILs) using both molecular dynamics (MD) simulations and experimental methods.

Rheological studies on tetrabutylphosphonium AA (P_{4444} -AA) WBLs, employing non-equilibrium and equilibrium MD simulations, reveal that the addition of AAIL additives to water increases both shear viscosity and zero-shear viscosity. Experimental viscosity measurements validate these simulation results, demonstrating a correlation between AAIL concentration and WBL viscosity. This indicates that the viscosity of AAIL WBLs can be tailored by adjusting the concentration of AAIL additives. Moreover, AAIL WBLs with different types of AA anions exhibit similar viscosities, suggesting that viscosity alone does not explain the distinct tribological behaviours reported in the previous literature.

Investigations into the lubrication mechanism of AAIL-WBLs using reactive MD simulations demonstrate a significant reduction in the coefficient of friction of up to 34% upon the introduction of AAILs. This reduction is attributed to the formation of hydration shells around the amino acid anions, creating a chemically adsorbed tribofilm on iron oxide surfaces, and P_{4444} cations establishing a load-bearing layer in the middle regions of the lubricant. This dual-layer structure, supported by hydration lubrication, effectively maintains lubricant fluidity while bearing substantial loads. Comparing the tribological performance of AAIL-WBLs with

different AA anions, P₄₄₄₄-Trp WBLs exhibit lower COF than other AAIL-WBLs. The formation of thicker and more stable hydrated AA adsorption layers in P₄₄₄₄-Trp WBLs contributes to their superior tribological behaviour.

To further optimize the lubrication performance of P₄₄₄₄-Trp WBLs to match that of industrial oil-based cutting fluids while maintaining their environmentally friendly characteristics, P₄₄₄₄-Trp additives were incorporated into glycerol aqueous solutions to create new P₄₄₄₄-Trp WBLs. These WBLs were then benchmarked against commercialized oil-based cutting fluids in terms of their tribological properties under various conditions. The results indicate that at a concentration of 20 wt%, P₄₄₄₄-Trp WBLs achieve a significant reduction in friction and wear, comparable to commercial oil-based cutting fluids. Introducing a 10 wt% glycerol to the AAIL WBLs further enhances friction and wear reduction, surpassing the performance of commercial oil-based cutting fluids. These superior lubrication performances were observed across all tested conditions, encompassing different lubrication regimes. The underlying lubrication mechanism involves a combination of the layered structure of the lubricant and improved viscosity. Additionally, anticorrosion studies reveal that increasing the concentration of P₄₄₄₄-Trp additives reduces the corrosion level, with complete elimination at 20 wt% concentration of P₄₄₄₄-Trp.

This comprehensive study of AAIL WBLs' rheological and tribological behaviours highlights their promise as eco-friendly lubricants, contributing to the advancement of a circular economy in industries reliant on lubrication.

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List of Publications

By the time of thesis submission, the research resulted in two published journal papers and two presented conference papers. Two additional manuscripts based on the content of Chapters 5 and 6 have been prepared and are ready for submission.

List of Published Papers

- Feng, Y., & Jabbarzadeh, A. (2024). Rheological properties of water-based amino acid ionic liquids. *Physics of Fluids*, **36** (1).
- Feng, Y., & Jabbarzadeh, A. (2024). Unravelling Molecular Origins of Improved Tribological Properties of Amino Acid Ionic Liquid Water-Based Lubricants. *Tribology International*, **201**, 110268.

For both of these two published papers, I co-designed the study with Associate Professor Ahmad Jabbarzadeh, analysed the data and wrote the drafts of the manuscript.

List of Presented Conference Papers

- Feng, Y., Jabbarzadeh A, "Water-based Amino-Acid Ionic Lubricants Show Improved Rheology over a Wide Range of Shear Rates", AKRC2023, Dec 2023
- Feng, Y., Jabbarzadeh A, Molecular dynamics simulation study on the rheological behaviour of water-based amino acid ionic liquid lubricants, 23rd Australasian Fluid Mechanics Conference, Dec 2022.

Nomenclature

$\mathbf{a}_i$	Acceleration of the particle
U_{angle}	Angle potential energy
K_{angle}	Bending constant for angle
$K_{dihedral}$	Bending constant for dihedral
k_B	Boltzmann's constant
BO'_{ij}	Bond order
U_{bond}	Bond potential energy
C_0, C_1, C_2	Coefficients for cosine terms
f_1, f_2, f_3, f_4, f_5	Correction factors
C	Coulomb's constant
W	Damping factor for the strength of the pressure coupling
Q	Damping factor for the strength of the temperature coupling
D_B, D_C	Diameter of measuring bob and cup
$U_{dihedral}$	Dihedral potential energy
$U_{Coulombic}$	Electrostatic potential energy
k	Ellipticity parameter
E_{bond}	Energy associated with bond formation (ReaxFF)
$E_{Coulomb}$	Energy associated with the electrostatic interaction (ReaxFF)
$E_{specific}$	Energy associated with the of specific interactions (ReaxFF)
E_{vdW}	Energy associated with the van der Waals interaction (ReaxFF)
$K_{improper}$	Energy constant for improper
$E_{torsion}$	Energy of four-body torsional strain (ReaxFF)
E_{over}	Energy of over-coordination penalty (ReaxFF)

E_{lp}	Energy of the lone pair (ReaxFF)
E_{angle}	Energy of three-body valence angle strain (ReaxFF)
E_{under}	Energy of under-coordination stability (ReaxFF)
N_1	First normal stress difference
$\mathbf{F}_i$	Force of the atom
$\mathbf{F}_f$	Friction force
$U_{improper}$	Improper potential energy
$U_{intermolecular}$	intermolecular (nonbonded) potential energy of the system
r_{ij}	Interparticle pairwise distance
$U_{intramolecular}$	Intramolecular (bonded) potential energy of the system
U_{LJ}	Lennard-Jones (LJ) potential energy
m_i	Mass of the atom
$\mathbf{M}$	Measured torque
h_0	Minimum film thickness
$\mathbf{p}_i$	Momentum of the particle
n	Multiplicity
$\mathbf{F}_N$	Normal load
$\mathbf{W}$	Normal load (Hamrock and Dowson equation)
Val_i	Number of bonding electrons
N	Number of particles
$n_{LP,opt}$	Optimal number of lone pairs
q_i, q_j	Partial charges
$\mathbf{u}_{i\alpha}, \mathbf{u}_{i\beta}$	Peculiar velocity components
$\mathbf{r}_i$	Position momentum of the atom

$\mathbf{r}$	Position vector of the atom
U	Potential energy
p_{val}	Pre-defined parameter for angle energy
p_{boc}	Pre-defined parameter for bond energy
p_{lp}	Pre-defined parameter for long pair energy
p_{ovun}	Pre-defined parameter for overcoordination energy
p_{tor}	Pre-defined parameter for torsion energy
p_{vdw}	Pre-defined parameter for vaal dee Waal interaction
P	Pressure
R'	Reduced radius of curvature
E'	Reduced young's modulus
R	Regression coefficient
R_q, R_{q1}, R_{q2}	Root-mean-square roughness
$\mathbf{F}_L$	Shaft applied load
K_{bond}	Spring constant
T	Temperature
t	Time
Δt	Time interval
V_1, V_2, V_3	Torsion coefficients
$U_{torsion}$	Torsion potential energy
U_{total}	Total potential energy of a molecular system
E_{system}	Total potential energy of the system (ReaxFF)
a	Transition parameter between the Newtonian and power-law region
$\mathbf{e}_x$	Unit vector

r_{vdw}	Vaal dee Waals radius
$U_{van\ der\ Waals}$	Van der Waals potential energy
D_{ij}	Van der Waals well depth
U	Velocity of entraining surfaces (Hamrock and Dowson equation)
$\mathbf{v}_i$	Velocity of the atom
V	Volume of the simulation box
$D_e^\sigma, D_e^\pi, D_e^{\pi\pi}$	Well depth parameters for bond

Greek Symbols

θ_{ijk}	Bending angle
λ	Characteristic time
μ	Coefficient of friction
ε	Dielectric constant
φ_{ijkl}	Dihedral angle
η_0	Dynamic viscosity (Hamrock and Dowson equation)
$\dot{\xi}$	Dynamical force
$C_{q_i q_j}$	Energy-conversion constant
$\dot{\gamma}_E$	Eyring rate
γ_i	Friction coefficient
σ_{ij}	Interparticle distance
λ	Lambda ratio
ζ	Nosé–Hoover thermostat coefficient

Δ'_i	Overcoordination numbers
α	Pressure viscosity index
ω	Rotational velocity
$\dot{\gamma}$	Shear rate
γ_w	Shielding factor vaal dee Waals interaction
$\sigma_{xy}, \sigma_{yz}, \sigma_{xz}$	Stress tensor element
$\dot{\gamma}_c$	The critical shear rate for the onset shear thinning
η_∞	Viscosity at infinite shear rates
$\eta_{xy}, \eta_{yz}, \eta_{xz}$	Viscosity components
ϵ_{ij}	Well depth for the interaction between atom
α_{ij}	Well width factor for vaal dee Waals interaction
η_0	Zero-shear viscosity

Superscripts

$\sigma, \pi, \pi\pi$	Bond type indices
-----------------------	-------------------

Subscripts

x, y, z	Direction identifier in Cartesian coordinates
i, j	Particle indices
α, β	Plane indices for stress tensor calculations

Acronyms

AAILs	Amino acid ionic liquids
AAs	Amino Acids
ACFs	Autocorrelation functions
Ala	Alanine
BF₄	Tetrafluoroborate
BMIM	1-butyl-3-methylimidazolium
BTAH	Benzotriazole
C₂C₁C₁im	1-ethyl-3-methyl imidazolium
C₄C₁C₁im	1-methyl-3-n-butyl-imidazolium
CDs	Carbon dots
CDs-IL	Carbon dots ionic liquids
CG	Conjugate Gradient
CHARMM	Chemistry at Harvard Macromolecular Mechanics
CMC	Carboxymethyl chitosan
CODs	Graphene quantum dots
COF	Coefficient of friction
COMB	Charge optimised many-body
Deca	Decanoate
DFT	Density Functional Theory
EAM	Embedded atom model
EEM	Electronegativity-Equalisation method
EMD-GK	Green-Kubo Equilibrium Molecular Dynamics
GAFF	General AMBER force field

Glu	Glutamic
Gly	Glycine
GO	Graphene oxide
GROMOS	GRONingen MOlecular Simulation
His	Histidine
IBC	Isolated boundary conditions
Ile	Isoleucine
ILs	Ionic liquids
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
Leu	leucine
LJ	Lennard-Jones
Lys	Lysine
Lys	Lysine
MC	Monte Carlo
MD	Molecular dynamics
MM	Molecular mechanics
MQL	Minimum quantity lubrication
MSD	Mean squared displacement
MSM	Multi-level summation method
MWF	Metalworking fluids
N₄₄₄₄	Tetrabutylammonium
N₄₄₄₄	Tetrabutylammonium
N₄₄₄₄OH	Tetrabutylammonium hydroxide
NEMD	Non-Equilibrium Molecular Dynamics
NPT	Isothermal-isobaric

NVE	Microcanonical
NVT	Canonical
OPLS	Optimised Potentials for Liquid Simulations
P₄₄₄₄	Tetrabutylphosphonium
P₄₄₄₄OH	Tetrabutylphosphonium hydroxide
P6,6,6,14	Tetraalkylphosphonium
PAO	Poly α -olefins
PBC	Periodic boundary conditions
PES	Potential energy surface
PF₆	Hexafluorophosphate
Phe	Phenylalanine
PPPM	Particle-particle particle-mesh
Pro	Proline
QAAA	Quaternary ammonium amino acids
Qeq	Charge Equilibration
RDF	Radial distribution function
ReaxFF	Reactive force-field
REBO	Reactive empirical bond order
RTILs	Room temperature ionic liquids
SBO	Sum of π -bond orders
SDS	Sodium dodecyl sulphate
Ser	Serine
Si₃N₄	Silicon nitride
THTDP	Trihexyltetradecylphosphonium
TiO₂	Titanium dioxide

TIP3P	Transferable intermolecular potential with 3 points
Trp	Tryptophan
Tyr	Tyrosine
Val	Valine
WBLs	Water-based lubricants
XPS	Photoelectron spectroscopy
ZnO	Zinc oxide
μVT	Grand canonical

Chapter 1: A Review on Ionic Liquid Water-based Lubricants: Development and Performances

1.1 Introduction

In the world of material science, tribology stands as a pivotal field of investigation. It is the study of friction, wear and lubrication phenomena for interacting surfaces in relative motion [1]. The word *tribology* was coined by Peter Jost in his publication of the Jost Report [2] in 1966. Since then, the term *tribology* has garnered significant attention and is now widely employed in various scientific and engineering disciplines. The report underscored the significant cost of friction, wear and corrosion to the UK economy, amounting to 1.1-1.4% of the GDP [2]. Furthermore, the report proposed that the judicious application of fundamental tribological principles could potentially save the UK economy an estimated £515 million per year [2][3]. Similarly, it has been reported that the cost of inadequate understanding or application of tribology principles was estimated to be as high as 6% of the GDP in the United States[3][4]. In summary, all of these figures show the significant importance of studying tribology.

A primary objective in tribology, yet one of the most significant challenges for researchers, is the minimisation of friction and wear across various applications. Approximately 20% of the world's total energy consumption is attributed to the detrimental effects of friction and wear within sectors such as transportation, manufacturing, power generation, and residential consumption [5]. To mitigate these adverse effects, the most prevalent strategy involves the application of lubrication. Reduced friction and wear is achieved by introducing a suitable lubricant between interacting surfaces. Lubricants can be classified into three primary categories based on their physical states: solid, gaseous, and liquid. Each category possesses distinct properties, rendering them suitable for diverse applications [6]. Solid lubricants, such as powders, graphite, molybdenum disulfide, polymers, and soft metals, are solid substances employed to provide lubrication [7]. Gaseous lubricants commonly include air, steam, and

metal vapour [8]. Liquid lubricants, encompassing petroleum oils, bio-derived oils, and water, are the most widely utilised options in industrial settings [6][9].

1.2 Liquid Lubricants

Liquid lubricants are widely employed in industrial machinery, offering several advantages over solid and gaseous lubricants, including heat dissipation, wear debris removal, and forming a liquid seal between contacting surfaces [10]. As early as 3500 B.C.E, the ancient Egyptians and Sumerians started to use bitumen, a viscous liquid produced through the distillation of petroleum, as the lubricant to extend the life of their tools [6][10]. Throughout the centuries, petroleum-based oils have risen to prominence as the industry's preferred liquid lubricant. This is mainly attributed to their excellent performance and cost-effectiveness in production. However, the current ratio of oil reserves to production indicates that global oil reserves may be depleted within the next 50 years [11]. The finite nature of petroleum-based lubricants renders them unsustainable. Moreover, their production and use contribute significantly to carbon emissions, exacerbating environmental concerns. In response to growing sustainability awareness, researchers have intensified efforts to develop environmentally friendly and efficient alternatives to petroleum-based oils for industrial lubrication. As the most abundant liquid on earth, water has emerged as a promising candidate.

1.3 Water-Based Lubricants

Like petroleum-based oils, water has been used as a lubricant since ancient times. However, water development as a lubricant has been constrained due to its known poor tribological performance compared to petroleum-based oil. Consequently, researchers have shifted their focus toward incorporating various additives into water to create water-based lubricants (WBLs) that exhibit improved tribological properties, including reduced friction, wear resistance, oxidation resistance, and corrosion resistance [12]. In general, additives for WBLs can be

classified into two primary categories: solid particles and water-soluble organic compounds [13].

Solid particles as additives for WBLs are usually nanoparticles which include graphene, copper, titanium dioxide (TiO_2), and many others [14-20][279][280]. In an experimental study conducted by Qiang *et al.* [14], graphene quantum dots (GQDs) were synthesised and utilised as lubricant additives for water. The study revealed that when the concentration of GQDs in water reached 4 mg/ml, it exhibited superior tribological performance, characterised by a 42.5% reduction in the coefficient of friction and a 58.5% decrease in the wear rate compared to pure water. Gu *et al.* [17] synthesised the TiO_2 nanoparticles dual-coated with silane coupling agent (KH-570) and OP-10 and employed them as lubricant additives for water. The experimental results demonstrated that dual-coated TiO_2 nanoparticles can significantly enhance the load-bearing capacity of pure water. Additionally, they contribute to the reduction of friction and improve the anti-wear properties of water.

Among water-soluble compounds used as additives, ionic liquids have undoubtedly gained significant interest. The exploration of ionic liquids as lubricants or additives in lubricants is a relatively new field, initiated by the pioneering study conducted by Ye *et al.* [21] in 2001 [22]. This suggests that this area of research holds significant potential for future breakthroughs.

1.4 Ionic Liquid WBLs

Ionic liquids (ILs) are typically compounds entirely made up of ions with a melting point below 100 °C [23]. Theoretically, using different types of anion and cation, more than one million combinations can form an ionic liquid [24][25]. Some combinations of anions and cations in ILs can result in desirable properties such as excellent thermal stability, high combustible temperature, negligible vapour pressure, and good miscibility with water and organic substances [21,26-32]. Furthermore, ILs can enhance the performance of lubricants under severe conditions, including extreme pressure and temperature, which are challenging

scenarios for some oils, greases and solid lubricants [31]. Most importantly, most ILs are organic, green, and sustainable compounds that pose no harm to the environment. This environmentally friendly characteristic further underscores their potential as additives to WBLs to replace petroleum-based lubricants.

In general, the most commonly used cations in forming ILs include imidazolium, pyridinium, ammonium, and phosphonium. On the other hand, the selection of anions can be highly diverse, given the thousands of options available [6]. The extensive variety of ion types and the molecular structure of ILs provide them with a unique flexibility. This allows for the modulation of their physical and chemical properties by selecting the specific ion types and the modification of ions, which make them excellent candidates for lubricants and lubricant additives [25]. Some specific properties of ILs can be determined by the ion type [25]. For instance, all imidazolium-based ILs exhibit low melting points and demonstrate exceptional chemical and electrochemical stability [33]. Furthermore, ion modification can improve the physical and chemical properties. This can be achieved by adjusting the length of the regulatory chain, altering the substituent number, and choosing different function groups [25].

1.4.1 ILs as base lubricants

Until now, approximately four hundred ILs have been studied as base lubricant or lubricant additives in various friction systems [25]. For ILs as base lubricants, a study conducted by Reeves *et al.* [34] has shown that ILs lubricants have improved properties compared to traditional lubricants. Four types of ILs, which are salicylate, saccharinate, benzoate and 1-decyl-3-methylimidazolium bis (trifluoromethyl sulfonylimide), designated as C₁₀mimTf₂Nm, are chosen to be anions and combined with Tetraalkylphosphonium cations (P_{6,6,6,14}) to obtain the IL lubricants. Friction tests have been conducted on these IL lubricants and some natural oils (canola oil, soybean oil, and safflower oil) and petroleum-based oils (gear oil and motor oil). The results indicated that IL lubricants exhibit a lower coefficient of friction (COF) than

conventional oils, especially for the [P_{6,6,6,14}] [salicylate] IL lubricant. Yao *et al.* [35] conducted experiments on 1-alkyl-3-octylimidazolium hexafluorophosphate ILs and evaluated their tribological behaviours at both room temperature and high temperature (150 °C) conditions. The results demonstrated that these ILs with long alkyl side chains significantly reduce friction and exhibit exceptional anti-wear properties, particularly under high-temperature and high-load conditions.

1.4.2 ILs as WBLs additives

Other than using the ILs as a base lubricant, ILs can also be used as additives to water to create the IL WBLs. The preparation of IL-WBLs is generally straightforward and cost-effective, making them promising candidates for various industrial applications, including metalworking (e.g., cutting, milling, turning), metal deformation (e.g., cold and hot rolling, extrusion, drawing), and machinery applications (e.g., bearings, gearboxes).

As previously mentioned, WBLs offer several advantages over petroleum-based oils, such as excellent environmental friendliness, exceptional cooling capabilities, non-flammability, and low cost [36, 37]. Therefore, many industrial applications can be for fire-resistant hydraulic and metalworking fluids [37-42]. However, many commercially available products, including water-glycol hydraulic fluid, water-in-oil emulsion, and synthetic cutting fluid, exhibit poor performance and anti-wear properties at extreme pressures [43-46]. This significantly limits their applicability in certain industrial processes. For instance, WBLs are often insufficient in metal-cutting operations like broaching and gear hobbing. Despite the environmental and safety issues associated with petroleum-based cutting fluids, including misting, fire hazards, and pollution, they continue to be the preferred choice due to their superior lubricity [37]. Therefore, while WBLs offer several advantages, there is a strong emphasis on enhancing their tribological properties to expand their suitability for a broader range of industrial applications. Incorporating ILs as additives into water presents a promising avenue to address this challenge.

In the study by Sol *et al.* [42], dry machining was highlighted as a more environmentally friendly alternative to mineral oil-based and other halogen-containing working fluids [47, 48, 49]. However, dry machining is often accompanied by drawbacks, such as increased contact temperature and stresses due to high friction, which reduces the tool's life span. Their study revealed that the addition of 1 wt% of Trihexyltetradecylphosphonium decanoate ([THTDP] [Deca]) ILs to distilled water results in a 70% reduction of COF compared to pure water. This performance is comparable to the mineral oil-based cutting fluids, suggesting that [THTDP] [Deca] is an efficient additive for WBLs in aluminium machining operations. A similar result has been reported on the minimum quantity lubrication (MQL) machining process for titanium, which was conducted by Davis *et al.* [50]. MQL is a relatively new technique that has been developed in the last few years [51]. It refers to supplying the minimum amount of lubricant (in millilitres per hour (mL/h)) to the cutting area with an air stream [52] [53]. The concept of MQL aims to reduce lubricant waste and improve lubrication efficiency, promoting sustainability. Therefore, one of the main focuses of studying MQL is finding environmentally friendly lubrication to achieve sustainability goals. Davis *et al.* [50] prepared a water-based cutting fluid containing 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] [PF₆]) ILs. The results demonstrated that these ILs WBLs reduce tool wear by more than 60% compared to dry conditions.

Beyond their applications as cutting fluids, researchers also investigate the tribological behaviours and properties of different types of IL WBLs in various tribo-pairs. These tribo-systems often represent metal deformation and machinery applications involving different interacting surfaces. For example, silicon nitride (Si₃N₄), a structural ceramic widely used in bearing applications, is popular due to its excellent wear and corrosion resistance, lightweight, and high strength [54]. In the study conducted by Phillips *et al.* [55], two types of ILs additives for water, 1-methyl-3-n-butyl-imidazolium hexafluoro phosphate ([C₄C₁C₁im] [PF₆]) and 1-

ethyl-3-methyl imidazolium tetrafluoroborate ($[C_2C_1C_1im][BF_4]$), were evaluated for their lubricating effects for Si_3N_4/Si_3N_4 contact. The results highlighted that the addition of 2 wt% $[C_4C_1C_1im][PF_6]$ or $[C_2C_1C_1im][BF_4]$ significantly reduced the running-in period of COF measurement and the COF values. In another study with a tribo-system involving Si_3N_4/Si_3N_4 contact, a similar improvement of running-in period and COF was also observed when phosphazene-based ILs were used as additives in water [56].

In addition to the Si_3N_4 , various traditional metals employed in industrial applications, such as bearing steel, copper, and aluminium alloy, have also been chosen as the tribo-pairs in the IL WBLs tribo-system in some studies[57][58][59][60][61][62][63][64]. For example, Tang *et al.* [63] explored the application of carbon dots (CDs), synthesised with ILs to formulate carbon dots ionic liquids (CDs-IL) additive for WBLs. They tested the friction and wear behaviours of ILs, CDs and CDs-IL in the steel/steel contact to evaluate the potential reduction in wear and friction offered by these additives. From comparing the performance of these additives, it was found that CDs-IL demonstrated the best results in terms of reducing friction and wear [63]. This improvement was attributed to the synergistic effect between the CDs and IL [63]. Fan *et al.* [64] conducted tribological experiments on water with benzotriazole tetrabutylammonium ($[N_{4444}][BTA]$) and benzotriazole tetrabutylphosphonium ($[P_{4444}][BTA]$) additives in various contacts including steel/steel, steel/aluminium and steel/copper. The findings suggest that these additives can significantly improve the friction reduction and anti-wear properties of water for these tested tribo-contacts [64]. Moreover, while many ILs have complex structures that require intricate synthesis routes and conditions [25], limiting their practical applications, the preparation of IL-WBLs in Fan *et al.*'s study was remarkably simple. The WBLs were prepared in situ by adding equal molar ratios of benzotriazole (BTAH) and tetrabutylammonium hydroxide ($N_{4444}OH$) or tetrabutylphosphonium hydroxide ($P_{4444}OH$) in water and stirring the solutions at 25°C until the ILs were fully dissolved, resulting in a clear liquid [64]. The

simplicity of WBL preparation is particularly promising as it demonstrates high efficiency in production. It provides more convenient, environmentally friendly, and cost-saving methods that could benefit industrial applications. In addition to tribological properties, Fan *et al.*'s study also conducted corrosion tests since water corrosion on metal surfaces is a significant drawback and restricts its use as a lubricant on such surfaces. The results demonstrated that adding IL additives to WBLs significantly enhances their corrosion resistance, making them more suitable for metal surface applications.

A similar finding has been seen from a tribological study on WBLs with amino acid ionic liquids (AAILs) by Yang *et al.* [65]. The preparation of AAIL-WBLs was equally simple, and the results indicated reductions in COF and wear. Moreover, corrosion tests revealed improved corrosion resistance with the addition of AAILs. The study also conducted biodegradation and soil phytotoxicity tests, demonstrating excellent antibacterial properties and low toxicity on plants [65]. The promising results of this study ignited our interest and motivated our continued research into AAIL WBLs.

1.5 Amino Acid

Amino Acids (AAs) are organic or carbon-based compounds that contain both amino ($-NH_2$) and acid groups [66]. Over 500 amino acids exist in nature, but the most common and essential ones are the 20 α -AAs incorporated into proteins found in the human body [67]. These α -AAs possess a carboxyl ($-COOH$) as the acid group, and their basic structure is shown in Figure 1.1.

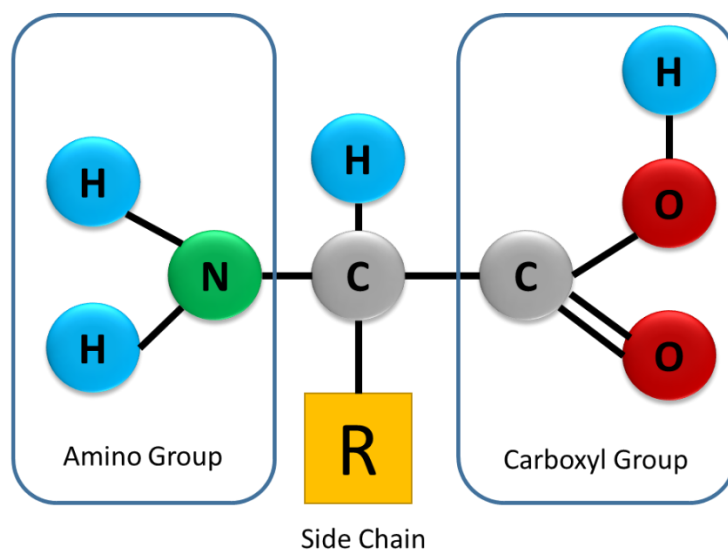


Figure 1.1: Illustration of Amino Acid (AA)

Except for the amino and carboxyl, the R group or side chain of AAs is the most critical determinant of their chemical and physical properties. The nature of the R group influences the polarity and hydrophobicity of amino acids, with some being nonpolar and hydrophobic while others are polar and hydrophilic. Additionally, certain AAs are basic, whereas others are acidic [68]. The 20 common proteinogenic AAs are presented in Figure 1.2 [68].

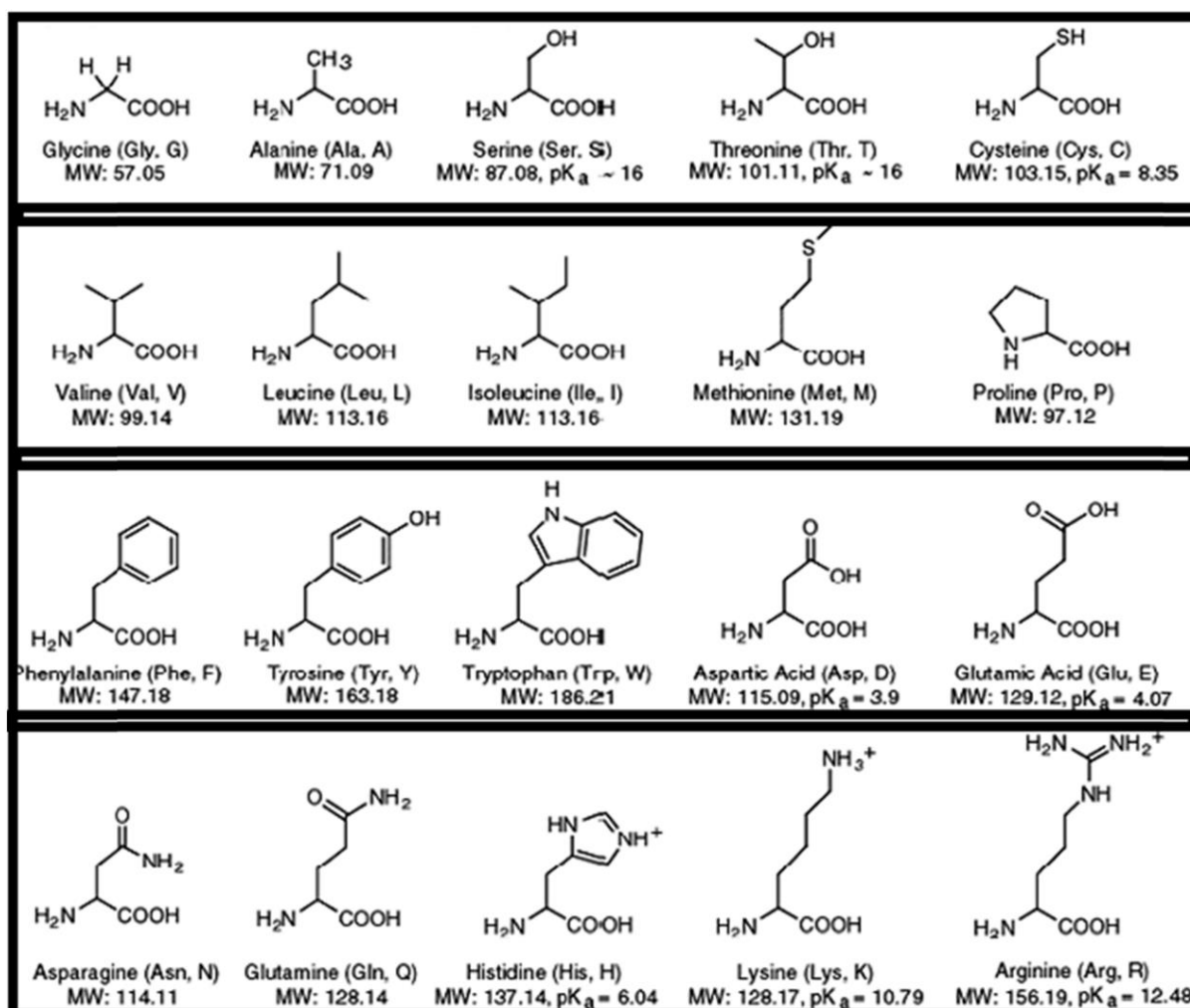


Figure 1.2: Twenty common proteinogenic AAs. pK_a is the negative base-10 logarithm of the acid dissociation constant (*K*_a) of a solution. $pK_a = -\log_{10} K_a$. (Figure adapted from reference [68])

AAs are widely acknowledged for their crucial role in facilitating life on Earth. When incorporated into proteins, AA residues make up the second-largest component of human muscles and other tissues, with water being the predominant component. Moreover, these AAs participate actively in transporting neurotransmitters and their biosynthesis, further underscoring their importance in biological systems [69]. Consequently, it has a wide range of applications in various industries including medical, healthcare, and food sectors [70][71][72][73].

Since AAs are fully biodegradable, researchers have investigated their potential applications in various industries. For example, AAs have been widely studied as a type of biosurfactant,

which is a green and sustainable surface active agent [75][76][77][78]. Hentrich *et al.* [74] published a series of findings that have significantly impacted the industry. They were the first to file a patent on the applications of acyl sarcosinate and acyl aspartate as surfactants in domestic goods such as shampoos, detergents and all kinds of toothpaste [75]. The applications of AA surfactants exhibit excellent adhesive properties across various surfaces, and this characteristic has inspired researchers to explore their potential in lubricant applications. For example, the lubricating properties of amphoteric-type AA surfactants, such as glutamic acid, have been studied [79].

1.5.1 Amino acid ionic liquids (AAILs)

Many studies and examples of ILs serving as lubricants or lubricant additives have been explored in previous sections, all of which suggest that ILs hold significant promise as lubricants. Consequently, it would be intriguing to investigate the performance AAILs in terms of their lubrication behaviours. Room temperature AAILs were first synthesised in 2005 by Fukumoto *et al.* [80]. Room temperature ionic liquids (RTILs) have predominantly been designed using a variety of cationic derivatives due to the convenience of their chemical modification [81][82][83]. However, comparatively less information is available about the influence of anion structure on the properties of RTILs. Therefore, to develop the task-specific RTILs, Fukumoto *et al.* have focused on investigating AAs as ILs because they can behave as anions with various characteristics from the effects of the different structures of AA anions. They synthesised the AAILs by coupling the imidazolium cation with 20 different natural AAs and provided the results for the thermal properties and ionic conductivity of these AAs [80]. In the same year, Tao *et al.* [84] synthesised a new family of ILs, in which the cations are directly derived from the natural AA and α -AA ester salts. These studies collectively demonstrate the versatility of AAs, which can be readily converted into both anions and cations due to their inherent amino and carboxylic groups. Moreover, the functional side chains of AAs

can impart a variety of properties to the resulting ILs [80][84][85]. It is also worth mentioning that the great merit of the AAs is their low cost. It is easy to obtain large amounts of pure AA at low cost [86]. This economic factor enhances the industrial potential of AAILs.

1.5.2 AAIL lubricants

To date, research on AAILs as lubricants remains relatively limited. In addition to Yang *et al.*'s study [65] on investigating the tribological behaviour of water with AAILs additives, which has been mentioned in the previous section, Zhu *et al.* [87] prepared a group of quaternary ammonium AAILs (QAAA ILs) by coupling tetrabutylammonium (N_{4444}) cation with fourteen types of natural AAs as base lubricant and investigated the tribological behaviours under various contacts. The results display that N_{4444} -AA IL lubricants have extremely low COF and excellent anti-wear properties under all different contacts. In the other study conducted by Mu *et al.* [88], they synthesised a green lubricant by dissolving lignin in [choline][AA] ILs. Similarly, this novel lubricant shows excellent performance in friction and wear reduction.

1.6 Phosphonium IL Lubricant

As highlighted in previous sections, ILs considered for lubrication applications offer a diverse range of anions, encompassing organic and inorganic options. Conversely, the cations most commonly encountered in ILs are ammonium-, phosphonium-, imidazolium-, or pyridinium-based [89]. Among these cations, phosphonium ILs have attracted significant attention in recent studies. Phosphonium cations have a general chemical formula $[PR_4]^+$ which is shown in Figure 1.3. They typically possess four R-groups or side chains, which can be hydrogen, alkyl, aryl, ester, or halide groups [89]. For example, tetrabutylphosphonium (P_{4444}) features four alkyl chains with four carbons ($-C_4H_9$) as its R-groups.

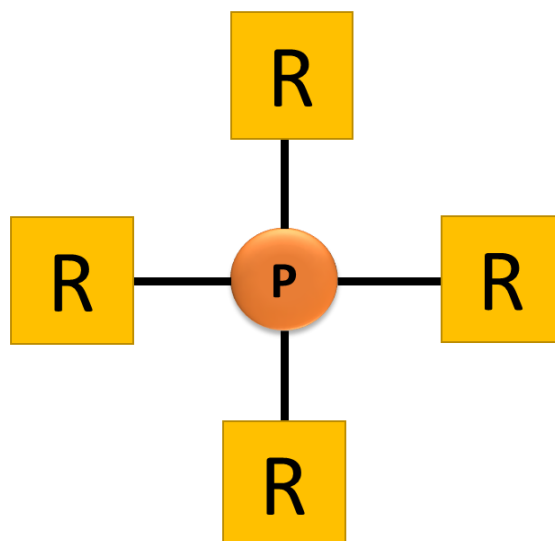


Figure 1.3: Illustration of phosphonium cation

Phosphonium-based ILs offer several advantages over other cationic options. Studies have demonstrated that phosphonium-based ILs exhibit lower wear and friction compared to synthetic and petroleum-based oils, as well as ammonium and imidazolium ILs [89][90][91][92][93][94]. The absence of acidic protons in phosphonium-based IL contributes to their enhanced stability in strongly basic media and superior thermal stability compared to their ammonium counterparts [95][96][97]. Furthermore, phosphonium ILs have been reported to exhibit superior resistance to both corrosion and tribo-corrosion [98][99][100]. In addition, a variety of halogen-free phosphonium-based ILs have been developed, which are environmentally friendly [101][102][103]. They can be extracted from bio-based feedstock [104] and are biodegradable [105][106][107]. In industrial processes, phosphonium-based ILs have been found to have applications in lubrication due to the advantages mentioned above. The other important reasons to consider phosphonium-based IL is its high availability and low cost [101]. Phosphonium salts are already manufactured on a multi-ton scale, which means they can meet the demands of industrial applications [108].

1.7 Computational Studies in IL WBLs

The majority of studies on IL WBLs employ experimental methods to examine and investigate their tribological properties. The studies discussed in previous sections are all experimental based, focusing on measuring the tribological properties of IL WBLs. When comparing these studies, it becomes evident that tribological properties vary significantly with the specific combination of cations and anions in ILs. Given that the performance of IL-WBLs in different applications depends on these properties, the ultimate goal for many researchers studying IL-WBLs is to identify the optimal combination of cations and anions that can maximise lubrication performance.

Finding the cation and anions for ILs is still a trial-and-error process [89], making experimental investigations sometimes inefficient in terms of time and cost. Beyond exploring the relationship between IL selection and lubrication performance, a comprehensive understanding of the lubrication mechanism of IL-WBLs is equally crucial. While experimental studies can provide valuable insights, they often fail to provide a complete picture of the underlying mechanisms. Some studies have utilised X-ray photoelectron spectroscopy (XPS) to analyse the elemental distribution and bond energy of the wear scar's surface [65][87], in conjunction with the results from friction and wear tests to propose the 'possible' lubrication mechanism. However, these proposed mechanisms require further validation to confirm their accuracy. Traditional experimental methods are limited in their ability to capture the behaviours of cations and anions within IL WBLs. Therefore, complementary methods are necessary to elucidate these mechanisms.

Atomistic simulations serve as indispensable numerical tools in exploring various material properties, including magnetic, electronic, chemical, and mechanical properties [89]. These simulations offer a practical approach to exploring the relationships between the atomic-scale structure and the properties of molecular systems. By examining the system at the atomic level,

these simulations can reveal how the arrangement and interactions of individual atoms influence the overall behaviour of the system. Furthermore, these simulations can serve as a valuable complement to experimental techniques [89]. They can help narrow down the number of formulations requiring physical testing by analysing atomic-level properties and predicting the behaviour of molecular systems, saving considerable time, effort, and resources. Atomistic simulations can provide insights into how changes at the atomic level can affect the properties of the system. This can guide the design of new materials or modifications to existing ones, helping to achieve desired properties more efficiently. Currently, there are many different types of atomistic simulation methods available, such as molecular mechanics (MM), Monte Carlo (MC), and molecular dynamics (MD) simulation methods. [109][110][111][112].

Among these methods, MD simulations are particularly promising for studying IL lubricants, as they enable the computation of various physico-chemical properties of ILs under different temperature and stress conditions, including density, viscosity, diffusion coefficients, and thermal conductivity. More importantly, MD simulations provide detailed information about the atomic-scale mechanisms that underlie the observed properties and behaviours of ILs. This can include insights into the structure and dynamics of ILs, the interactions between ions, and the response of the system to external stimuli. A more in-depth discussion of MD simulation methodology will be presented in Chapter 2.

MD simulation is a powerful tool for investigating lubricant properties in many studies [281][282]. Most of these studies focus on investigating physico-chemical properties of bulk lubricants, including rheological and structural properties under various operational conditions, such as temperatures, shear rates, and pressures [113][114][115][116][117]. However, in real-world applications, lubricants often interact with solid surfaces and are confined to a thin layer between these surfaces during operation. This confinement and interaction with solid surfaces can influence tribological properties, such as friction and wear. Consequently, some studies

have explored the tribological behaviour of confined lubricants between different contact surfaces [118][119][120][121][122][123].

1.8 Motivation

Based on the valuable insights from the literature review in this chapter, there are a few highlights that become our motivation for studying the WBLs:

-The primary motivation for this research is rooted in the urgent need to find environmentally friendly alternatives to oil-based lubricants. Traditional lubricants, although practical and effective, pose significant environmental challenges. Their production and disposal processes often lead to pollution, contributing to the global environmental crisis. As such, there is a pressing need to explore and develop alternatives that are both effective and environmentally friendly. WBLs present a promising solution to this problem. However, despite their potential, the research on WBLs, particularly those based on AAIL additives, is still in its early stage. Many important properties of AAIL WBLs remain unexplored, limiting our understanding and application of these promising materials. Therefore, it is necessary to study it.

-One of the unexplored properties is the rheological behaviour of AAIL WBLs. Rheological properties, which describe how fluid flows under applied forces, are crucial for understanding how a lubricant will perform in real-world applications. Despite its importance, the rheological behaviour of AAIL WBLs remains largely unknown. In Chapter 3 of this thesis, we delve into this critical aspect. We employ experimental methods and MD simulations to explore the rheological behaviours of AAIL WBLs. This comprehensive approach allows us to gain a deeper understanding of these behaviours, paving the way for developing more effective WBLs.

-Understanding the lubrication mechanism of WBLs is another crucial aspect of this research. The lubrication mechanism describes how a lubricant reduces friction and wear between surfaces. A thorough understanding of this mechanism is essential for optimising future WBL

designs. However, due to experimental limitations, the complete picture of the lubrication mechanism of AAIL WBLs remains elusive. Therefore, in Chapter 4, we explore this mechanism at the molecular level using MD simulations. This approach allows us to overcome the limitations of experimental methods and gain a more complete understanding of the lubrication mechanism of AAIL WBLs.

-One of the significant advantages of AAIL additives is the wide array of AA options they offer. Investigating the tribological performance of various types of AAIL WBLs is crucial for providing informed guidance on their design. Furthermore, studying the tribological behaviours of different AAIL WBLs can offer a deeper understanding of their underlying lubrication mechanisms. This aspect of the study is presented in Chapter 5.

-WBL studies should ideally be application-driven. However, due to the relatively new nature of WBL research, most current studies primarily focus on improving the incorporation of additives into base lubricants. There is often a lack of discussion regarding whether the enhanced lubrication performance of WBLs can effectively replace actual industrial oil-based lubricants in practical applications. Chapter 6 of this thesis addresses this by analysing the optimisation of AAIL WBLs to achieve lubrication performance comparable to oil-based lubricants. The tribological properties of AAIL WBLs were benchmarked against commercial oil-based lubricant products using experimental methods.

-Lubrication studies should always be application-driven. This means that the performance of a lubricant should be evaluated under conditions that closely resemble its intended applications. A challenge of applying WBLs is tribological performance under different conditions. Industrial lubrication applications often require a wide range of velocities, pressures, and temperatures and involve lubrication in different contacts. These conditions have not yet been thoroughly investigated for AAIL WBLs. Therefore, in Chapter 6, the lubrication performance

of AAIL WBLs under various conditions has been investigated. This approach provides a comprehensive guideline for the application of AAIL WBLs.

-In general, this study provides a systematic methodology for studying AAIL WBLs both experimentally and through MD simulations. It serves as a guideline for future lubrication system studies, promoting a more integrated and comprehensive approach to lubricant research. By combining experimental methods with MD simulations, we can overcome the limitations of each approach and gain a more complete understanding of AAIL WBLs.

In conclusion, this study offers a comprehensive exploration of AAIL WBLs. It provides a complete picture of their properties and potential applications, contributing significantly to the field of environmentally friendly lubrication systems. Through this research, we hope to pave the way for developing more effective and environmentally friendly lubricants, contributing to a more sustainable future.

Chapter 2: General Methodology of Molecular Dynamics Simulation

2.1 Introduction

Molecular Dynamics (MD) simulation is a powerful and insightful computational simulation technique used to study the physical movements of atoms and molecules in molecular systems. By employing a general model of the physical principles that dictate interatomic interactions, these simulations can forecast the trajectories of each atom within the system over a specified time period [124]. This allows for a detailed exploration of dynamic processes at the atomic level. The MD simulation was initially developed in the early 1950s, with the first simulations of simple gases conducted by Berni Alder and Thomas Wainwright in the late 1950s [125][126]. Over the past seven decades, the field of MD simulations has experienced rapid advancements. It has found extensive applications in many research areas, such as materials science, biochemistry, biophysics, and engineering.

In essence, the concept of MD simulation is analogous to experimental methods. In MD simulations, a model system comprising a specific number of particles is initially prepared, similar to preparing a material sample in an experiment. Subsequently, the forces exerted on each atom by all other atoms are calculated. The spatial position and velocity of each atom are then determined using Newton's laws of motion as a function of time, emulating the connection of a sample to measuring equipment and the execution of an experiment. During the simulation, properties of interest are recorded over a specified time interval, similar to experimental procedures. To achieve accurate output results, both experiments and MD simulations require an extended duration for averaging [127].

This chapter delves into the fundamental methodology of MD simulations, covering various aspects. The force field, which is the molecular mechanics model used to calculate the interaction between particles, is presented in section 2.2. The basic algorithm for MD simulation is outlined in section 2.3. In section 2.4, the ensembles employed in MD simulations are explored. Furthermore, the thermostats and barostats which associated with the ensembles

are addressed in sections 2.5 and 2.6 correspondingly. At the end of this chapter, the principles of boundary conditions and the energy minimisation process are described in sections 2.7 and 2.8 respectively.

2.2 Force Fields

In MD simulations, the interactions between atoms are modelled using force fields, which consist of mathematical functions and associated parameters. The force field model is usually calibrated to align with the outcomes derived from quantum mechanical calculations and specific experimental measurements [126]. The dynamic behaviour of particles is governed by the cumulative forces acting upon them, as articulated by Newton's second law of motion. These forces are linked to the interaction energy between the atoms, commonly referred to as potential energy. The relationship between force $\mathbf{F}$ and potential energy U is described in Eq.2.1, where $\mathbf{r}$ is the coordinate of the atom position.

$$\mathbf{F}(\mathbf{r}) = -\frac{dU(\mathbf{r})}{d\mathbf{r}} \quad (2.1)$$

The potential energy of a molecular system usually consists of intramolecular and intermolecular interactions, as shown by Eq.2.2.

$$U_{total} = U_{intramolecular(bonded)} + U_{intermolecular(nonbonded)} \quad (2.2)$$

Intramolecular interactions encompass the bonded interactions within a molecule, including bond stretching, angle bending, and torsional interactions. In contrast, intermolecular interactions refer to the non-bonded forces between molecules, such as van der Waals forces and electrostatic interactions. Many force fields have been developed, and they can be classified into two main categories: classical force field and reactive force field. In the classical force field, the connections between atoms are either fixed or allowed to vibrate around average values, typically the bond length between atoms. Examples of classical force fields are

Chemistry at Harvard Macromolecular Mechanics (CHARMM) [128], GRONingen MOlecular Simulation (GROMOS) [129], Optimised Potentials for Liquid Simulations (OPLS) [130], General AMBER force field (GAFF) [131]. However, due to the nature of fixed bonding of the classical force field, they are not compatible with simulating complex interactions between atoms, which involve chemical reactions. In order to simulate chemical reactions, the reactive force fields such as the embedded atom model (EAM) [132][133], charge optimised many-body (COMB) [134], reactive empirical bond order (REBO) [135][136] and ReaxFF [137] have been developed. Reactive force fields are bond order-based force fields that allow for continuous bond breaking and formation to achieve simulating systems involving chemical reactions. The following sections will delve into classical and reactive force field methodologies.

2.2.1 Classical force field

As highlighted in Eq.2.2, the potential energy of a molecular system consists of two primary components: intramolecular (bonded) energy and intermolecular (non-bonded) energy. The components for intramolecular and intermolecular energy in the classical force field are described in Eq.2.3 and Eq.2.4.

$$U_{intramolecular(bonded)} = U_{bond} + U_{angle} + U_{torsion} + U_{dihedral} + U_{improper} \quad (2.3)$$

$$U_{intermolecular(non-bonded)} = U_{van\ der\ Waals} + U_{Coulombic} \quad (2.4)$$

2.2.1.1 Intramolecular energy

Intramolecular energy is associated with multi-body interactions of atoms connected through the covalent body within a molecule. This typically includes contributions from bond stretching, angle bending, torsional interactions, dihedral angles, and improper torsions.

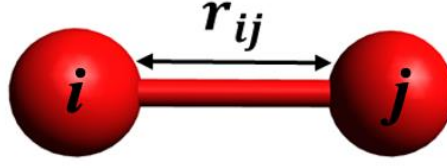


Figure 2.1: Illustration of a stretching bond between two atoms

Figure 2.1 illustrates a basic model of two adjacent atoms, i and j , connected by a covalent bond. Bond stretching, the deformation of this bond from its equilibrium length, can be described by a harmonic function as shown in Eq.2.5,

$$U_{bond} = K_{bond}(r_{ij} - r_0)^2 \quad (2.5)$$

where K_{bond} is the spring constant, r_{ij} is the instantaneous distance between atoms i and j , and r_0 is the equilibrium bond length. This indicates that the bond model is only suitable for a system with bond stretching in equilibrium states and bonds remaining intact [138].

$$U_{angle} = K_{angle}(\theta_{ijk} - \theta_0)^2 \quad (2.6)$$

Similarly to the bond potential, Eq.2.6 describes a harmonic potential for the bending angle, a three-body interaction formed between three bonded atoms i, j, k (Figure 2.2). In Eq.2.6, the K_{angle} is the bending constant, θ_{ijk} is the bending angle formed between bonded atoms i, j, k , and θ_0 is the equilibrium angle.

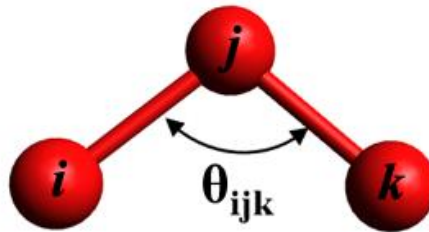


Figure 2.2: Illustration of a bending angle bond between three atoms

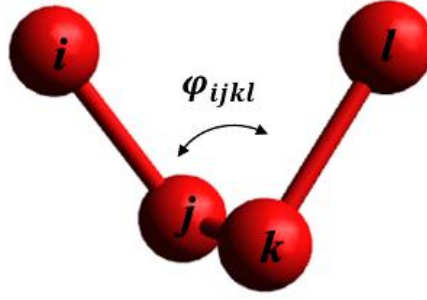


Figure 2.3: Illustration of a dihedral between four atoms

Furthermore, dihedral angle potential is a four-body potential that is formed by four bonded atoms i, j, k and l . It describes the angular spring between the planes defined by atoms i, j, k and atoms j, k, l (Shown in Figure 2.3). This dihedral is crucial because it can significantly influence the three-dimensional conformation of the molecule. Variations in the dihedral angle can lead to different spatial arrangements of the atoms, resulting in distinct molecular conformations [138]. Various functions can describe the dihedral angle potential. For example, the cosine potential [139] can be described in Eq.2.7,

$$U_{dihedral} = K_{dihedral} [1 + \cos(n\varphi_{ijkl} - \varphi_0)] \quad (2.7)$$

where the $K_{dihedral}$ is the bending constant, n is the multiplicity representing the periodicity, φ_{ijkl} is the dihedral angle, and φ_0 is the equilibrium value of the dihedral.

Meanwhile, the improper torsion potential, another four-body potential, is used to describe out-of-plane motions formed by three atoms centred around a fourth atom. One function that can describe the improper torsion is the Fourier potential [140], which is given by Eq.2.8,

$$U_{improper} = K_{improper} [C_0 + C_1 \cos(\omega) + C_2 \cos(2\omega)] \quad (2.8)$$

where $K_{improper}$ is the energy constant, C_0 , C_1 , and C_2 are real coefficients for cosine terms #0, #1 and #2, and the ω is the angle between the atom i, j, k and l .

2.2.1.2 Intermolecular energy

Intermolecular potentials typically consist of two components: the van der Waals potential and the electrostatic potential. The van der Waals potential describes the attractive and repulsive interactions between two nonbonded atoms. The 12-6 Lennard-Jones (LJ) potential [141] is a widely used potential to represent van der Waals interactions, expressed by in Eq.2.9,

$$U_{LJ} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (2.9)$$

where ϵ_{ij} is the well depth for the interaction between atoms i and j , and σ_{ij} is the distance between these atoms. To describe ϵ_{ij} and σ_{ij} for different pairs of atoms, the combining rules of Lorentz-Berthlot are used [142][143]. The well depth ϵ_{ij} for a pair of atoms i and j can be obtained from the geometric mean, which is shown in Eq.2.10.

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}} \quad (2.10)$$

The σ_{ij} can also be determined by the geometric mean (Eq.2.11), which is given by,

$$\sigma_{ij} = (\sigma_i \sigma_j)^{\frac{1}{2}} \quad (2.11)$$

or the arithmetic average (Eq.2.12).

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (2.12)$$

When using the 12-6 LJ potential on specific fluid models, it can accurately capture many fluid properties such as diffusion coefficient, viscosity [144][145], and surface tension [146].

Long-range Coulombic potential is typically used to capture the electrostatic interaction between two charged atoms. It can be expressed by Eq.2.13,

$$U_{coulombic} = \frac{C_{q_i q_j}}{\epsilon r} \quad (2.13)$$

where C is the energy conversion constant, q_i and q_j are the partial charges on the atoms i and j , and ϵ is the dielectric constant.

To reduce computational costs, intermolecular potentials are often implemented with a cutoff distance. However, the long-range electrostatic interaction may not be accurately captured within this cutoff distance. To address this, additional reciprocal space-based truncation methods, such as the Ewald algorithm [147][148], particle-particle particle-mesh (PPPM) algorithm [149][150], and multi-level summation method (MSM) [151] are required. For instance, the PPPM method applies a three-dimensional grid to particles beyond the cutoff distance and calculates the charge density at each grid point. Subsequently, the fast Fourier transform is applied to the three-dimensional grid to determine the electric field efficiently [150].

2.2.2 Reactive force field

Unlike classical force fields, reactive force fields can dynamically capture the bond breaking and formation in the system and are used to simulate complex systems involving chemical reactions. Among those reactive force field potentials that have been mentioned in the previous section, the ReaxFF is the most common one which has been widely used [137][138][152][153]. The total potential energy of ReaxFF can be expressed in Eq.2.14 [137][152].

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{lp} + E_{angle} + E_{torsion} + E_{vdW} + E_{Coulomb} + E_{specific} \quad (2.14)$$

In Eq.2.14, E_{system} is the total potential energy of the system. E_{bond} represents the energy associated with bond formation between atoms. E_{over} and E_{under} are the energies of an over-coordination penalty and under-coordination stability, respectively, associated with the atomic valence rules. E_{lp} is the energy of the lone pair. E_{angle} and $E_{torsion}$ are the energies of three-body valence angle strain and four-body torsional strain. These energy terms are functions of the

bond order and are calculated for every pair of atoms at each time step. In addition to these energies associated with bond order, E_{vdW} and $E_{Coulumb}$ represent the non-bonding energies associated with the van der Waals and electrostatic interactions. Lastly, $E_{specific}$ refers to the energies of specific interactions such as conjugation, hydrogen binding and C₂ correction.

ReaxFF is a force field based on the concept of bond order. The bond order can be determined from the interatomic distance from Eq.2.15, as shown below [137][152].

$$\begin{aligned} BO'_{ij} &= BO'_{ij}{}^{\sigma} + BO'_{ij}{}^{\pi} + BO'_{ij}{}^{\pi\pi} \\ &= \exp[P_{bo1} \cdot (\frac{r_{ij}}{r_o^{\sigma}})^{P_{bo2}}] + \exp[P_{bo3} \cdot (\frac{r_{ij}}{r_o^{\pi}})^{P_{bo4}}] + \exp[P_{bo5} \cdot (\frac{r_{ij}}{r_o^{\pi\pi}})^{P_{bo6}}] \end{aligned} \quad (2.15)$$

In Eq.2.15, BO'_{ij} denotes the bond order between atoms i and j . The system bond order is the sum of the bond order of σ bond, π bond and double- π bond. r_{ij} is the interatomic distance between atoms i and j , and r_o represents the equilibrium bond length. P_{bo} is the parameter used to model the bonds.

2.2.2.1 Bond energy

In ReaxFF, a dynamic correction is applied to the bond order, allowing for the formation of additional bonds by available lone pairs while preventing atoms from exceeding their maximum bonding capacity. To achieve this, overcoordination numbers Δ'_i and $\Delta'_i{}^{boc}$ are defined as in Eq.2.16 and Eq.2.17,

$$\Delta'_i = -Val_i + \sum_{j=1}^{neighbours(i)} BO'_{ij} \quad (2.16)$$

$$\Delta'_i{}^{boc} = -(Val_i + n_{LP,opt}) + \sum_{j=1}^{neighbours(i)} BO'_{ij} \quad (2.17)$$

where Val_i is the bonding electron of atom i , and $n_{LP,opt}$ is the optimal number of lone pairs.

These overcoordination numbers describe the difference between the total bond order around

an atom and the number of bonding electrons. The correction factors f_1, f_2, f_3, f_4, f_5 can be calculated by Eq.2.18 to Eq.2.22,

$$f_1(\Delta'_i, \Delta'_j) = \frac{1}{2} \left(\frac{Val_i + f_2(\Delta'_i, \Delta'_j)}{Val_i + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} + \frac{Val_i + f_2(\Delta'_i, \Delta'_j)}{Val_i + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} \right) \quad (2.18)$$

$$f_2(\Delta'_i, \Delta'_j) = \exp(-p_{boc1}\Delta'_i) + \exp(-p_{boc1}\Delta'_j) \quad (2.19)$$

$$f_3(\Delta'_i, \Delta'_j) = -\frac{1}{p_{boc1}} \ln \left[\frac{\exp(-p_{boc2}\Delta'_i) + \exp(-p_{boc2}\Delta'_j)}{2} \right] \quad (2.20)$$

$$f_4(\Delta'_i{}^{boc}, BO'_{ij}) = \frac{1}{1 + \exp[-p_{boc3}(p_{boc4}BO'_{ij}BO'_{ij} - \Delta'_i{}^{boc}) + p_{boc5}]} \quad (2.21)$$

$$f_5(\Delta'_j{}^{boc}, BO'_{ij}) = \frac{1}{1 + \exp[-p_{boc3}(p_{boc4}BO'_{ij}BO'_{ij} - \Delta'_j{}^{boc}) + p_{boc5}]} \quad (2.22)$$

where $p_{boc1}, p_{boc2}, p_{boc3}, p_{boc4}, p_{boc5}$ are the pre-defined parameters.

The corrected σ , π and $\pi\pi$ bond order can be calculated as shown in Eq.2.23 to Eq.2.25, and the total corrected bond order is the sum of them which is shown in Eq.2.26.

$$BO_{ij}^\sigma = BO'_{ij}^\sigma \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i{}^{boc}, BO'_{ij}) \cdot f_5(\Delta'_j{}^{boc}, BO'_{ij}) \quad (2.23)$$

$$BO_{ij}^\pi = BO'_{ij}^\pi \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i{}^{boc}, BO'_{ij}) \cdot f_5(\Delta'_j{}^{boc}, BO'_{ij}) \quad (2.24)$$

$$BO_{ij}^{\pi\pi} = BO'_{ij}^{\pi\pi} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i{}^{boc}, BO'_{ij}) \cdot f_5(\Delta'_j{}^{boc}, BO'_{ij}) \quad (2.25)$$

$$BO_{ij} = BO_{ij}^\sigma + BO_{ij}^\pi + BO_{ij}^{\pi\pi} \quad (2.26)$$

The corrected over-coordination number can be obtained from the total corrected bond order by Eq.2.27.

$$\Delta_i = -Val_i + \sum_{j=1}^{neighbours(i)} BO_{ij} \quad (2.27)$$

It is also used to calculate the angle energy and torsion energy in the later sections.

The energies associated with bond formation and breaking are captured by using the Morse potential, which uses the corrected bond order BO_{ij} shown in Eq.2.28,

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp[p_{be1}(1 - (BO_{ij}^\sigma)^{p_{be2}})] - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi} \quad (2.28)$$

where D_e^σ , D_e^π and $D_e^{\pi\pi}$ are the well depth parameters of σ , π and π - π bonds. The parameters p_{be1} and p_{be2} are pre-defined.

2.2.2.2 Lone pair energy

During the simulation, the number of lone pairs on an atom can dynamically change due to changes in the number of bonds. This dynamic change in the optimal number of lone pairs is associated with an energy term that can be computed using Eq.2.29,

$$\Delta_i^e = -Val_i^e + \sum_{j=1}^{neighbours(i)} BO_{ij} \quad (2.29)$$

where Val_i^e is the total number of the electrons in its outer shell (Val_i^e is 6 for oxygen and 1 for hydrogen). Therefore, the Δ_i^e describes the difference between the Val_i^e and the total bond orders for that atom. After the Δ_i^e is obtained, the total number of lone pairs around the atom can be determined by Eq.2.30,

$$\Delta_i^{lp} = n_{lp,opt} - \text{int}\left(\frac{\Delta_i^e}{2}\right) + \exp\{-p_{lp1} \cdot \left[2 + \Delta_i^e - 2 \cdot \text{int}\left(\frac{\Delta_i^e}{2}\right)\right]^2\} \quad (2.30)$$

where the p_{lp1} is the pre-defined parameters. The lone pair energy is defined as the penalty energy associated with it, which is shown in Eq.2.31.

$$E_{lp} = \frac{p_{lp2} \Delta_i^{lp}}{1 + \exp(-75 \Delta_i^{lp})} \quad (2.31)$$

2.2.2.3 Overcoordination energy

For an atom, overcoordination happens when the number of bonds is more than its valency ($\Delta_i > 0$). The corrected overcoordination can be calculated by considering the deviation from the optimal number of lone pairs, as shown in Eq.2.32,

$$\Delta_i^{lpcorr} = \Delta_i - \frac{\Delta_i^{lp}}{1 + p_{ovun3} \cdot \exp(p_{ovun4} \cdot \{\sum_{j=1}^{neighbours(i)} (\Delta_i - \Delta_i^{lp})(BO_{ij}^{\pi} + BO_{ij}^{\pi\pi})\})} \quad (2.32)$$

The penalty energy from the overcoordination can be described by Eq.2.33 as follows,

$$E_{over} = \frac{\sum_{j=1}^{nbond} p_{ovun1} D_e^{\sigma} BO_{ij}}{\Delta_i^{lpcorr} + Val_i} \cdot \Delta_i^{lpcorr} \left[\frac{1}{1 + \exp(p_{ovun2} \cdot \Delta_i^{lpcorr})} \right] \quad (2.33)$$

where p_{ovun1} and p_{ovun2} are pre-defined parameters.

2.2.2.4 Undercoordination energy

In contrast to overcoordination energy, the undercoordination energy arises from the resonance of π -electrons between attached undercoordinated atomic centres. This undercoordination energy can be described by Eq.2.34, which is shown as follows,

$$E_{under} = -p_{ovun5} \cdot \frac{1 - \exp(p_{ovun6} \cdot \Delta_i^{lpcorr})}{1 + \exp(p_{ovun2} \cdot \Delta_i^{lpcorr})} \cdot \frac{1}{1 + p_{ovun7} \cdot \exp(p_{ovun8} \cdot \{\sum_{j=1}^{neighbours(i)} (\Delta_j - \Delta_j^{lp})(BO_{ij}^{\pi} + BO_{ij}^{\pi\pi})\})} \quad (2.34)$$

where p_{ovun6} , p_{ovun7} and p_{ovun8} are pre-defined parameters.

2.2.2.5 Angle energy

Similar to the bond energy, the valence angle energy can also be described by using the Morse potential, which is given in Eq.2.35,

$$E_{angle} = f_7(BO_{ij})f_7(BO_{jk})f_8(\Delta_j)\{p_{val1} - p_{val1}\exp[-p_{val2}(\theta_0 - \theta_{ijk})^2]\} \quad (2.35)$$

where p_{val1} and p_{val2} are the pre-defined parameters, and f_7 and f_8 are factors used to switch valence angle energy on and off, which are shown in Eq.2.36 and Eq.2.37.

$$f_7(BO_{ij}) = 1 - \exp(-p_{val3} \cdot BO_{ij}^{p_{val4}}) \quad (2.36)$$

$$f_8(\Delta_j) = p_{val5} - (p_{val5} - 1) \cdot \frac{2 + \exp(p_{val6}\Delta_j^{angle})}{1 + \exp(p_{val6}\Delta_j^{angle}) + \exp(-p_{val7}\Delta_j^{angle})} \quad (2.37)$$

The θ_{ijk} is the angle made by atoms i, j, k , with atom j as the central atom and the θ_0 is the equilibrium angle which relates to the sum of π -bond orders (SBO) around the atom j . For example, the θ_0 for configuration which has one π -bond is 109.47° . For the configuration of two π -bonds and three π -bonds, the θ_0 is 120° and 180° correspondingly. In addition to π -bonds on the central atom, lone pairs, overcoordination, and undercoordination can also influence equilibrium angles, as described by Eq.2.38.

$$\begin{aligned} SBO = & \sum_{j=1}^{neighbours(i)} (BO_{ij}^\pi + BO_{ij}^{\pi\pi}) + [1 - \prod_{n=1}^{neighbours(j)} \exp(-BO_{jn}^8)] \cdot [Val_j^{angle} \\ & - \sum_{j=1}^{neighbours(i)} (BO_{jn}) - p_{val8}n_{lp,j}] \end{aligned} \quad (2.38)$$

Because one atom cannot have more than 2 π -bonds, the SBO needs to be smaller than 2, which will be achieved by Eq.2.39

$$SBO_2 = \begin{cases} 0 & \text{if } SBO \leq 0 \\ SBO^{p_{val9}} & \text{if } 0 < SBO < 1 \\ 2 - (2 - SBO)^{p_{val9}} & \text{if } 1 < SBO < 2 \\ 2 & \text{if } SBO > 2 \end{cases} \quad (2.39)$$

The final equilibrium angle can be calculated by Eq.2.40.

$$\theta_0(BO) = \pi - \theta_{0,0}\{1 - \exp[-p_{val10}(2 - SBO_2)]\} \quad (2.40)$$

2.2.2.6 Torsion energy

With a similar concept as angle energy, torsion energy can be described by Eq. 2.41 as follows,

$$E_{dihedral} = f_{10}(BO_{ij}BO_{jk}BO_{kl})\sin\theta_{ijk} \cdot \sin\theta_{jkl} \left[\frac{1}{2}V_1(1 + \cos\phi_{ijkl}) + \frac{1}{2}V_2\exp\{p_{tor1} \cdot (BO_{jk}^\pi - 1 + f_{11}(\Delta_i\Delta_k))^2\} (1 - \cos 2\phi_{ijkl} + \frac{1}{2}V_1(1 + 3\cos\phi_{ijkl})) \right] \quad (2.41)$$

where p_{tor1} is the pre-defined parameter, V_1 , V_2 , V_3 are the torsion coefficients, and f_{10} and f_{11} can be described in Eq.2.42 and Eq.2.43.

$$f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) = [1 - \exp(-p_{tor2} \cdot BO_{ij})] \cdot [1 - \exp(-p_{tor2} \cdot BO_{jk})] \cdot [1 - \exp(-p_{tor2} \cdot BO_{kl})] \quad (2.42)$$

$$f_{11}(\Delta_j^{angle}, \Delta_k^{angle}) = \frac{2 + \exp[-p_{val6}(\Delta_j^{angle} + \Delta_k^{angle})]}{1 + \exp[-p_{val3}(\Delta_j^{angle} + \Delta_k^{angle})] + \exp[p_{val4}(\Delta_j^{angle} + \Delta_k^{angle})]} \quad (2.43)$$

2.2.2.7 Van der Waals energy

Similar to classical force fields, intermolecular interactions contribute to the overall energy of the system. The van der Waals interactions between all atom pairs can be described using a distance-corrected Morse potential, as shown in Eq.2.44,

$$E_{vdW} = Tap \cdot D_{ij} \left\{ \exp \left[\alpha_{ij} \left(1 - \frac{f_{13}(r_{ij})}{r_{vdw}} \right) \right] - 2 \exp \left[\frac{1}{2} \alpha_{ij} \left(1 - \frac{f_{13}(r_{ij})}{r_{vdw}} \right) \right] \right\} \quad (2.44)$$

where D_{ij} represents the van der Waals well depth, α_{ij} is used to control well width and r_{vdw} is the van der Waals radius. Tap is the taper correction used to avoid energy discontinuities when charged species move in and out of the cut-off radius of intermolecular interaction. It can be described in the 7th order Taper correction factor with the cut-off radius R_{cut} , which is shown in Eq.2.45.

$$\begin{aligned}
Tap_0 &= 1 \\
Tap_1 &= 0 \\
Tap_2 &= 0 \\
Tap_3 &= 0 \\
Tap_4 &= -\frac{35}{R_{cut}^4} \\
Tap_5 &= \frac{84}{R_{cut}^5} \\
Tap_6 &= -\frac{70}{R_{cut}^6} \\
Tap_7 &= \frac{20}{R_{cut}^7}
\end{aligned} \tag{2.45}$$

A shielded interatomic distance is calculated to prevent excessively high repulsions between bonded atoms and atoms that form an angle, which is presented in Eq.2.46,

$$f_{13}(r_{ij}) = \left[r_{ij}^{p_{vdw1}} + \left(\frac{1}{\gamma_w} \right)^{p_{vdw1}} \right]^{\frac{1}{p_{vdw1}}} \tag{2.46}$$

where p_{vdw1} is the pre-defined parameter and γ_w is the shielding factor.

2.2.2.8 Coulomb energy

The Coulomb's law is used to describe the energy from electrostatic interactions, which is shown in Eq.2.47,

$$E_{coulomb} = Tap \cdot C \cdot \frac{q_i q_j}{[r_{ij}^3 + (\frac{1}{\gamma_{ij}})^3]^{\frac{1}{3}}} \tag{2.47}$$

where the Tap is described in Eq.2.47 in the van der Waals energy section, C is the Coulomb's constant, and γ_{ij} is the shielding parameter, which is also similar to what has been discussed in the van der Waals energy section.

Atomic charges are calculated using the Electronegativity-Equilisation method (EEM) developed by Mortier *et al.* [154], which is similar to Charge Equilibration (Qeq) method [155] but avoids an iterative scheme for hydrogen charges, leading to more time-efficient simulations.

2.3 MD Algorithm

The MD simulation starts with initial conditions, including the initial velocities and positions. Then, the interactions between atoms result in forces acting on individual atoms, which are parameterised by the force fields. Once the forces acting on atoms are calculated, the dynamics of the entire system can be described by the constant change in velocities and positions of each atom, as determined by Newton's second law of motion.

In MD simulations, Newton's second law of motion is solved by obtaining the initial velocities and positions at the beginning of a small time step, followed by force and energy calculations, and finally, the final velocities and positions at the end of the time step. This procedure is then repeated for subsequent time steps, typically thousands of times in a simulation, to generate the time evolution of positions and velocities.

Newton's second law of motion can be expressed as in Eq.2.48,

$$\mathbf{a}_i = \frac{\mathbf{F}_i}{m_i} \quad (2.48)$$

where $\mathbf{a}_i$, $\mathbf{F}_i$ and m_i are the acceleration, force and mass of atom i . With the assumption that mass of the atom is a constant, and the force on the atom is related to its instantaneous velocity $\mathbf{v}_i$ and position $\mathbf{r}_i$ which is described in Eq.2.49.

$$\mathbf{F}_i = m_i \frac{d}{dt} \mathbf{v}_i = m_i \frac{d^2}{dt^2} \mathbf{r}_i \quad (2.49)$$

Because of the Electronegativity-Equilisation method and the complexity of solving these differential equations in a system that contains thousands of atoms, it is necessary to use a numerical solver to solve these motion equations.

2.3.1 Verlet algorithm

The Verlet algorithm [156] is a widely used method for solving Newton's equations of motion in MD simulations. Assuming the current time step is t and the time interval is Δt , the position of an atom at the subsequent time step ($t + \Delta t$) and the preceding time step ($t - \Delta t$) can be expressed using the Taylor expansion in Eq.2.50 and Eq.2.51.

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{d(t)}{dt} \Delta t + \frac{1}{2!} \frac{d^2}{dt^2} \mathbf{r}_i(t) \Delta t^2 + \frac{1}{3!} \frac{d^3}{dt^3} \mathbf{r}_i(t) \Delta t^3 + O(\Delta t^4) \quad (2.50)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \frac{d(t)}{dt} \Delta t + \frac{1}{2!} \frac{d^2}{dt^2} \mathbf{r}_i(t) \Delta t^2 - \frac{1}{3!} \frac{d^3}{dt^3} \mathbf{r}_i(t) \Delta t^3 + O(\Delta t^4) \quad (2.51)$$

Combining Eq.2.50 and Eq.2.51 leads to:

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{d^2}{dt^2} \mathbf{r}_i(t) \Delta t^2 + O(\Delta t^4) \quad (2.52)$$

The velocity can be obtained by subtracting Eq.2.51 from Eq.2.50.

$$\mathbf{v}(t) = \frac{d\mathbf{r}(t)}{dt} = \frac{[\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)]}{2\Delta t} + O(\Delta t^4) \quad (2.53)$$

Although the Verlet algorithm is a simple method to implement, it has some disadvantages that limits its capacity to calculate some of the system's properties. For example, the position of an atom is calculated at the time step $t + \Delta t$. However, the velocity is given for the time step t , resulting in a one-time step lag. Moreover, the atom positions must be stored for three consecutive time steps to calculate velocities. Alternative methods have been developed to address these shortcomings.

2.3.2 Verlet leapfrog algorithm

As an economical alternative to the basic Verlet algorithm, the Verlet leapfrog algorithm stores only one set of atom positions and velocities. It defines the positions at time t and velocities that are half a time step behind $\left(t + \frac{1}{2}\Delta t\right)$, which are presented in Eq.2.54 and Eq.2.55.

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 \quad (2.54)$$

$$\mathbf{v}_i\left(t + \frac{1}{2}\Delta t\right) = \mathbf{v}_i\left(t - \frac{1}{2}\Delta t\right) + \frac{\mathbf{F}_i(t)}{m_i}\Delta t \quad (2.55)$$

Then, the velocity at time step t can be calculated by Eq.2.56.

$$\mathbf{v}_i(t) = \frac{1}{2}[\mathbf{v}_i\left(t - \frac{1}{2}\Delta t\right) + \mathbf{v}_i\left(t + \frac{1}{2}\Delta t\right)] \quad (2.56)$$

2.3.3 Velocity verlet algorithm

The velocity Verlet algorithm, a combination of the basic Verlet and leapfrog algorithms, offers a more comprehensive approach. It allows the positions and velocities of atoms to be computed at the same instant time step. By using the positions and velocities at time t , the positions at time step $t + \Delta t$ can be calculated by Eq.2.57.

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\frac{\mathbf{F}_i(t)}{m_i}\Delta t^2 \quad (2.57)$$

Then, the velocities at time step $t + \Delta t$ can be obtained from Eq.2.58.

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}\frac{\mathbf{F}_i(t + \Delta t)}{m_i}\Delta t \quad (2.58)$$

As evident from the position and velocity equations, the velocity Verlet algorithm requires the storage of only one set of positions, velocities, and forces at any given time step. This efficiency in memory usage contributes to the algorithm's computational cost-effectiveness.

2.4 Ensembles

The term "ensemble" carries a statistical mechanics connotation, representing a large set of microstates that a system can occupy, each with a specific probability. The ensemble average provides the average value of a property across all these microstates, corresponding to experimentally observable quantities [158][159][160]. The ergodic hypothesis posits that the time average of a property in a lengthy MD simulation is equivalent to the ensemble average, assuming the system is ergodic [161].

In MD simulations, the ensemble typically refers to a specific set of conditions defining the macroscopic state of the simulated system. These conditions commonly include constraints on the system's total energy, volume, pressure, and temperature.

In general, the most common ensembles used in MD simulations are microcanonical (NVE), canonical (NVT), isothermal-isobaric (NPT) and grand canonical (μ VT). In the NVE ensemble, the number of particles (N), volume (V), and energy (E) are maintained constant. Therefore, it is usually used to simulate isolated systems that can not exchange heat and energy with the outer environment. The NVT ensemble keeps the number of particles (N), volume (V), and temperature (T) constant, allowing the system to exchange heat with the surroundings.

This ensemble is often employed when simulating systems at a fixed temperature, using a thermostat to control the temperature. The NPT ensemble maintains the number of particles (N), pressure (P), and temperature constant. This ensemble is more flexible than NVE and NVT, allowing the system to exchange heat and energy while adjusting its volume to maintain constant pressure. In addition to using a thermostat to maintain temperature, a barostat is typically employed in the NPT ensemble to ensure constant pressure. The μ VT ensemble fixes the chemical potential (μ), volume (V), and temperature (T), allowing for fluctuations in the number of particles. Unlike the other three ensembles, the μ VT ensemble represents an open system.

The choice of ensemble influences the properties that can be calculated from the simulation. For example, the NVE ensemble is well-suited for studying energy conservation, while the NVT and NPT ensembles are more relevant for conditions resembling laboratory experiments or natural processes where temperature and pressure remain constant.

2.5 Thermostat

As mentioned in the previous section, a thermostat is needed in NVT ensemble to keep the temperature constant. In MD simulation, the thermostat is a computational algorithm used to control the temperature of the system [162]. This is crucial for simulating systems under conditions where temperature is fixed.

Various thermostat algorithms are widely used, such as Berendsen [163], Andersen [164], Nosé–Hoover [165][166][167], and Langevin thermostats [168][169][170]. The thermostat usually adjusts the velocities of particles in the simulation to meet a desired temperature. For example, Berendsen Thermostat [163] rescales the velocities of particles to bring the system temperature gradually towards the target temperature. Andersen's thermostat [164] randomly selects particles and assigns them new velocities based on the desired temperature distribution, mimicking the effect of a heat bath. The Nosé-Hoover thermostat is one of the most widely used thermostats, introducing an additional degree of freedom to the system that interacts with the particles, thereby controlling the temperature. It introduces a dynamical factor ζ to modify the velocities of particles, which is shown in Eq.2.59 and Eq.2.60,

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \zeta \mathbf{p}_i \quad (2.59)$$

$$\dot{\zeta} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - 3Nk_B T \right) \quad (2.60)$$

where $\mathbf{p}_i$ is the momentum of the particle i , $\mathbf{F}_i$ is the force on the particle i , N is the number of particles, k_B is the Boltzmann's constant, T is the desired temperature, and the damping factor Q represents the strength of the temperature coupling.

The Langevin thermostat [168][169][170] introduces random forces and a friction term into the equations of motion, simulating the interaction with a heat bath with random forces and friction. It can be expressed in Eq.2.61,

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \gamma_i m_i \dot{\mathbf{r}}_i + \mathbf{R}_i(\mathbf{t}) \quad (2.61)$$

where $\mathbf{r}_i$ is the position of the particle, γ_i is the friction coefficient, and $\mathbf{R}_i(\mathbf{t})$ is a random force that follows a Gaussian distribution with mean zero and variance related to γ_i and the temperature. This method is particularly useful for systems with a small number of particles.

2.6 Barostat

In MD simulations, a barostat is a computational tool used to maintain constant pressure conditions within the simulated system. It functions by scaling the coordinates of each atom in the system and adjusting the volume of the simulation box, allowing the system to expand or contract in response to the internal pressures exerted by the particles. Similar to thermostats, there are also various algorithms for barostats. For example, the Nosé–Hoover barostat [171] is one such algorithm that provides additional control over pressure, complementing the temperature control offered by the Nosé–Hoover thermostat. It can be expressed as Eq.2.62 and Eq.2.63,

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{1}{3} \frac{d^2(\ln V)}{dt^2} \mathbf{p}_i \quad (2.62)$$

$$\frac{d^2 V}{dt^2} = \frac{1}{W} (P(t) - P_0) \quad (2.63)$$

where W is the damping factor that represents the strength of the pressure coupling, $P(t)$ is the pressure of the system at time t and P_0 is the desired pressure. The Nosé–Hoover thermostat

and barostat [172] are particularly useful as they enable systems simulations under constant temperature and pressure conditions, mirroring real-world experimental conditions. This deterministic method ensures the correct distribution of microstates in the NPT ensemble, providing a realistic simulation environment for studying molecular systems.

2.7 Boundary Conditions

In MD simulations, boundary conditions are crucial in defining how particles behave at the edges of the simulation box. These conditions significantly influence the physical properties and behaviour of the simulated system. Boundary conditions can generally be categorised into isolated boundary conditions (IBC) and periodic boundary conditions (PBC). IBCs are typically employed for studying systems such as clusters and molecules where the simulation box does not interact with its surroundings. Under IBC, particles that move beyond the boundaries of the simulation box do not interact with the particles within the box.

In practice, PBCs are the most commonly used boundary conditions, as they enable the simulation of bulk materials with a finite number of particles, such as liquids and solids. Figure 2.4 demonstrates that PBCs allow the simulation box to make identical copies of the simulation box in all dimensions.

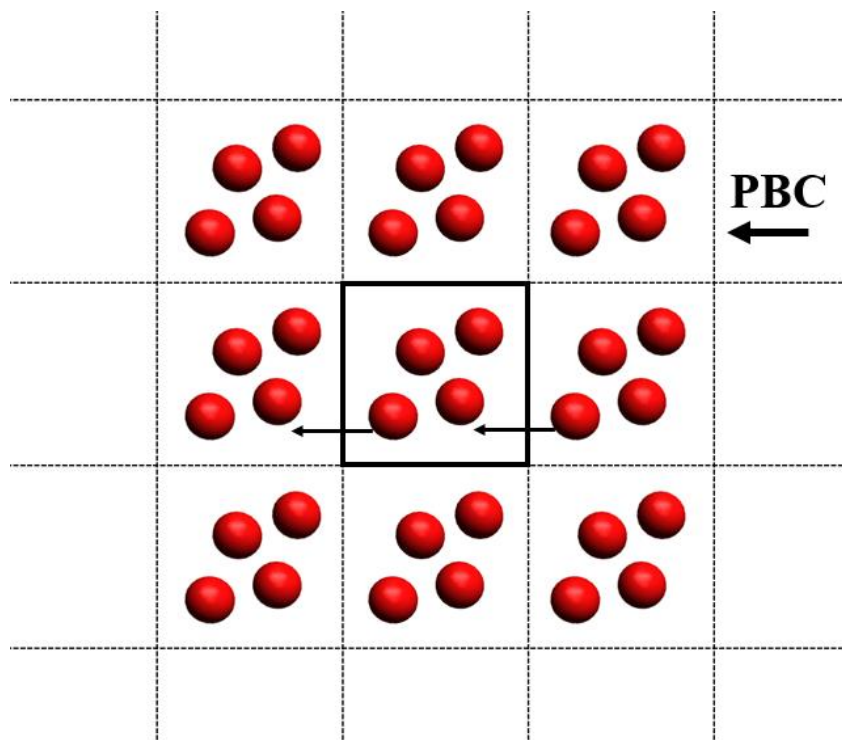


Figure 2.4: Periodic boundaries condition in a 2D system

When particles in the primary simulation box move, their corresponding particles in all replicated boxes move in unison, maintaining the same direction and velocity. During the simulation, as particles cross the boundary of the primary simulation box, their counterparts from the neighbouring replicated box on the opposite side enter the primary box, creating the effect of an infinite bulk simulation system.

While PBCs offer significant advantages, they are not without potential issues. For instance, particles in the primary simulation box may interact with all copies of particles from the replicated boxes [173]. Additionally, particles may interact with themselves if the dimensions of the simulation box are too small. Two primary practices are commonly employed to mitigate these challenges: the minimum image convention and the application of a cutoff radius. The minimum image convention ensures that each particle interacts only with the closest image of other particles, optimising computational efficiency. Implementing a cutoff radius guarantees that intermolecular interactions are captured and evaluated only when the distance between two particles is smaller than the cutoff radius, further reducing computational costs. The cutoff

radius should generally not exceed half the size of the simulation box to prevent particles from interacting with their own copies.

2.8 Energy Minimisation

In MD simulations, the potential energy of a system is a complex, multidimensional function of the atomic coordinates. This function, often referred to as the potential energy surface (PES), is high-dimensional because each atom can move in three dimensions, and the energy depends on the positions of all atoms [175]. The PES can be visualised as a landscape with valleys and hills, where each point represents a possible configuration of the system with a specific energy value. On the PES, the minimum points are of particular interest as they correspond to the stable states of the system. When the system starts with a configuration of high initial energy, energy minimisation is necessary to find the global and local lowest point on the PES, which refers to the most stable state. In general, finding the global minimum is computationally challenging. Therefore, optimisation algorithms are employed to efficiently search for a local minimum that is hopefully close to the global minimum. These algorithms navigate the PES by iteratively adjusting the atomic coordinates to move towards lower energy states [176].

In most of the energy minimisation methods, the slope of the PES at a given point is crucial for determining how to adjust the coordinates of the system to lower its energy. The gradient of the energy function represents this slope with respect to the coordinates. If the gradient at a point is positive, it suggests that the potential energy of the system can be lowered by decreasing the coordinate value. On the other hand, if the gradient is negative, the potential energy can be lowered by increasing the coordinate value. Eventually, the goal is to reach the point where the gradient is zero, which is the local minimum on the PES [175]. There are some methods that are widely used, including Newton-Raphson, steepest descent and conjugate gradient methods. In the Newton-Raphson method [177], both the first and second derivatives of the PES are used to find the minimum. It makes the energy minimisation process very fast

but computationally expensive. The steepest descent method takes steps proportional to the negative of the gradient of the PES. It's a quick way to move away from high-energy states but is inefficient for fine-tuning to the minimum because it can overshoot. The conjugate gradient method [178] is an improved version of the steepest descent method. It considers the gradients to avoid redundant movements, which are more efficient and converge faster to a local minimum, especially for systems with a large number of degrees of freedom.

Chapter 3: Investigation on Rheological Properties of Amino Acid Ionic Liquid Water-Based Lubricants

3.1 Introduction

As mentioned in the literature review in Chapter 1, ionic liquids (ILs) demonstrate significant potential as additives for water-based lubricants (WBLs) to improve tribological properties. However, many traditional ILs contain halogenic or sulfuric compounds, which can harm the environment. Given the emphasis on sustainability in this study, identifying environmentally friendly IL additives is crucial. Amino Acids (AAs) are organic compounds composed of amino and carboxylic acid groups. Most AAs contain only carbon, hydrogen, nitrogen, and oxygen, making them entirely biodegradable. They can be easily converted into both anions and cations, and the functional groups in their side chains can confer a variety of properties to the resulting ionic liquids. These features and other advantages discussed in Chapter 1 make amino acid ionic liquids (AAILs) promising candidates as WBL additives for further study.

While some aspects of the tribological behaviour of AAIL WBLs have been previously studied, their rheological behaviour remains unexplored. Ionic liquid lubricants can operate in both the hydrodynamic lubrication and boundary lubrication regimes. In the boundary lubrication regime, where the film thickness is on the order of a few nanometers, shear rates are incredibly high. For instance, a lubricant film of 2 nm thickness separating two sliding surfaces moving at 0.1–10 m/s experiences a shear rate of 10^8 – 10^{10} s⁻¹. Therefore, understanding the rheological behaviour of the lubricant over a wide range of shear rates is crucial. The mechanism by which AAILs function as effective lubricants depends on their viscosity, rheological behaviour, and interaction with the lubricated surfaces. In this chapter, we have employed molecular simulations, validated by experiments, to study the effect of AAILs on the rheological behaviour of WBLs.

Molecular simulation has emerged as a powerful tool for investigating lubricant properties (e.g. Ref.[113][114]) and provides valuable insights into lubricants' rheological, tribological and structural properties under various operational conditions, such as temperatures, shear rates and

pressures. Such insight is complementary to what we learn from experiments and can be used to explain the phenomena observed in ways that may not be possible or very challenging to obtain from experiments. Therefore, in this chapter, we have developed MD simulation models to study the influence of AAIL additives on the rheological properties of WBLs. Furthermore, we also conducted rheological experiments to validate the simulation results. The rheological and structural properties of tetrabutylphosphonium amino acid (P₄₄₄₄-AA) ionic liquids of different AA types and concentrations in water have been studied over a wide range of shear rates. The objectives of this chapter are *i*) to study AAILs' rheological properties, including zero-shear viscosity, shear viscosity and normal stress difference, for a wide range of shear rates; *ii*) to find the effects of AA type and concentration on these properties and behaviour; and *iii*) validate the molecular model by experiments.

3.2 Experimental Procedure

3.2.1 Material and AAIL WBLs preparation

The experimental method of preparing the tetrabutylphosphonium amino acid (P₄₄₄₄-Ser) WBLs was adapted from a previous study by Yang *et al.* [65] and Song *et al.* [174]. It is a straightforward in situ method. The L-Serine (Sigma-Aldrich, St. Louis, MO, USA, $\geq 99\%$ (HPLC)) was added into tetrabutylphosphonium hydroxide (Sigma-Aldrich, St. Louis, MO, USA, 40 wt %) to achieve the equimolar mixture. The distilled water was then added to the solution to obtain the P₄₄₄₄-AA WBLs in three different concentrations of 5, 7.5, and 10 wt%, and the solution was stirred for 24 hours. A distilled water sample is prepared as the reference group. The compositions for P₄₄₄₄-Ser in different concentrations and pure water are presented in Table 3.1.

	Serine (g)	Tetrabutylphosphonium, P ₄₄₄₄ (g)	Water (g)
Pure Water	0	0	50
5 wt% P₄₄₄₄-Ser WBL	0.72	1.78	47.5
7.5 wt% P₄₄₄₄-Ser WBL	1.08	2.67	46.25
10 wt% P₄₄₄₄-Ser WBL	1.43	3.57	45

Table 3.1: Components of pure water, 5, 7.5, and 10 wt% P₄₄₄₄-Ser WBLs

3.2.2 Experimental measurements

The zero-shear viscosity was measured by an Anton Paar MCR-302 rheometer (Anton Paar GmbH, Graz, Austria). The concentric cylinder (CC) system with a measuring bob (Diameter D_B = 26.651 mm) and cup (Diameter D_C = 28.922 mm) was used, as shown in Figure 3.1.

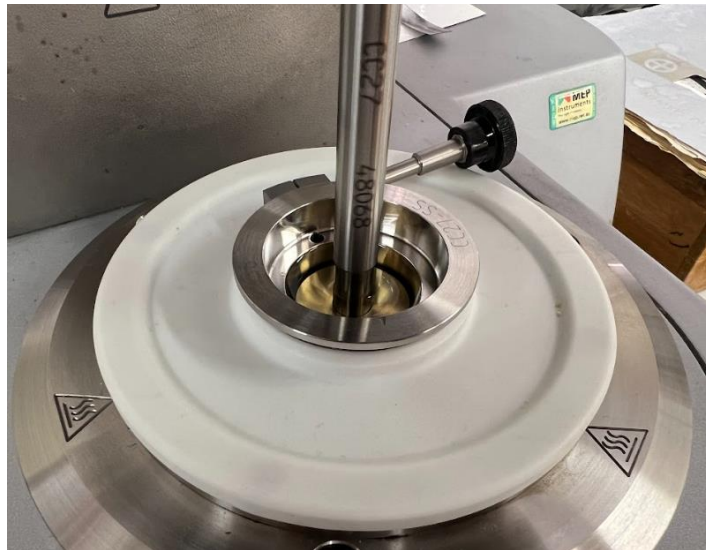


Figure 3.1: The concentric cylinder system with a measuring bob and cup for the viscosity measurement

The experiment was conducted at 20°C, and the temperature was controlled through a Peltier system integrated with the rheometer. The measuring cup was filled with 19 ml of P₄₄₄₄-Ser WBL sample and sheared at shear rates between 0 to 100 s⁻¹, and the viscosity was measured. The sampling started at the shear rate of 50 s⁻¹, where the viscosity data became stable and independent of the shear rate. The average viscosity between 50-100 s⁻¹ for each test was calculated as zero-shear viscosity. The reported data are the average of five independent tests on each concentration of P₄₄₄₄-Ser WBL and pure water.

3.3 Molecular Simulations Methodology

We have conducted MD simulations for the P₄₄₄₄-AA WBLs and pure water using Green-Kubo Equilibrium Molecular Dynamics (EMD-GK) and Non-Equilibrium Molecular Dynamics (NEMD) simulations, which will be described in detail here. All simulations are conducted by the Large-scale Atomic/Molecular Massively Parallel Simulator, LAMMPS [179]

3.3.1 Green-Kubo equilibrium molecular dynamics (EMD-GK)

Green-Kubo Equilibrium Molecular Dynamics (EMD-GK) [180][181] is a method based on the fluctuation-dissipation theorem and is used for calculating the zero-shear viscosity of a liquid. It has been observed that the EMD-GK method demonstrates optimal performance with fluids with a lower viscosity range, generally not exceeding 20 mPa·s. This characteristic poses a challenge for employing the EMD-GK method in high-pressure scenarios, where a lubricant's viscosity is expected to rise significantly [182]. The EMD-GK method is based on linear response theory and calculates the transport coefficients, such as viscosity, diffusion coefficients, and thermal conductivity. This is achieved by evaluating the integral of autocorrelation functions (ACFs) of these internal properties, and it is one of the popular methods to determine zero-shear viscosity [183]. In this method, the zero-shear viscosity is calculated from the integral given by Eq.3.1 [184].

$$\eta_{\alpha\beta}(t) = -\frac{V}{k_B T} \int_0^t [\sigma_{\alpha\beta}(0) \sigma_{\alpha\beta}(t')] dt' \quad (3.1)$$

In this equation, α and β are the Cartesian coordinates (x, y, z); $\sigma_{\alpha\beta}$ is the component of the stress tensor, V is the system volume, k_B is the Boltzmann constant, T is temperature, and t is time. The zero-shear viscosity can be obtained by evaluating and averaging the three viscosity components η_{xy} , η_{yz} , η_{xz} . These viscosity components are calculated from the given volume and temperature of the system, the Boltzmann constant and the ensemble average of the three off-diagonal stress tensor elements (σ_{xy} , σ_{yz} , σ_{xz}). In practice, the upper limit time t for the integral needs to be long enough to get the noise-free decay of the ACF and convergence of viscosity [185]. The components of the shear stress tensor are calculated using Irving-Kirkwood [186] formalism given in Eq.3.2 as,

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left(\sum_i^N m_i \mathbf{u}_{i\alpha} \mathbf{u}_{i\beta} + \sum_i^N \sum_{j>1}^N \mathbf{r}_{ij\alpha} \mathbf{F}_{ij\beta} \right) \quad (3.2)$$

where V is the volume of the simulation box, m is the mass of atom i , α and β are coordinates substituted by x, y or z in an orthogonal system. The $\mathbf{u}_{i\alpha}$ and $\mathbf{u}_{i\beta}$ are α and β components of peculiar velocity (velocity due to thermal fluctuations) of atom i . Also, $\mathbf{r}_{ij\alpha}$ and $\mathbf{F}_{ij\beta}$ are, respectively, the α component of the distance vector and β component of the pairwise force between atoms i and j . This method for calculating stress components is used in our previous molecular dynamics and particle-based simulation works. Non-equilibrium molecular dynamics (NEMD) [113][114][187][188].

3.3.2 Non-equilibrium molecular dynamics (NEMD)

Although The EMD-GK method is useful to get the viscosity at zero shear rate of fluids, viscosity is actually a shear-dependent property which can be calculated by using non-equilibrium Molecular Dynamics (NEMD) method. The method can also estimate the zero-

shear viscosity by checking the viscosity at low shear rates at the Newtonian regime, where viscosity is independent of the shear rate. The method's advantage is obtaining the full spectrum of rheological behaviour in Newtonian and non-Newtonian regimes. The SLLOD algorithm [189][190] under NVT (constant atoms, volume, and temperature) conditions is used in this study, where the motion is governed by Eq.3.3.

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \mathbf{e}_x \dot{\gamma} y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{e}_x p_{yi} \dot{\gamma} - \zeta \mathbf{p}_i\end{aligned}\quad (3.3)$$

Here $\mathbf{r}_i$, $\mathbf{p}_i$, $\mathbf{F}_i$ and m_i are the position, momenta, and acting force vector and mass of atom i , $\mathbf{e}_x$ is the unit vector in the x direction (flow direction), $\dot{\gamma}$ is the shear rate. Coefficient ζ is a Nosé–Hoover thermostat. For this thermostat, we used a damping constant of 10.

In NEMD simulation, the Lee-Edwards sliding brick boundary conditions [191] are usually used. They are a set of periodic boundary conditions used in MD simulations to impose a shear flow. This technique allows for the simulation of systems under translation invariant shear flow, which is particularly useful for studying the bulk rheology of complex fluids. Lees-Edwards sliding brick periodic boundary conditions, in combination with the SLLOD algorithm, can efficiently create a planar Couette shear flow simulation. Equations of motion are integrated by a leapfrog version of the Verlet algorithm with a time step of 1 fs. Simulations were conducted using LAMMPS domain decomposition parallel simulations on 96 CPUs with reasonable efficiency to speed up the calculations. In a steady planar Couette flow, the velocity profile is linear across the thickness of the sample [189]. Therefore, the shear rate ($\dot{\gamma}$) depends on shear velocity U_x that is applied at the top edge of the simulation box and the thickness of the sample in y direction h , as given by Eq.3.4.

$$\dot{\gamma} = \frac{2U_x}{h} \quad (3.4)$$

The shear viscosity is calculated from shear stress in the xy plane (σ_{xy}) and shear rate ($\dot{\gamma}$) by Eq.3.5, and its ensemble average is reported here.

$$\eta(t) = -\frac{\sigma_{xy}(t)}{\dot{\gamma}} \quad (3.5)$$

After simulations at different shear rates, the viscosity values are plotted versus the shear rates, and the Newtonian and shear thinning behaviour are evaluated.

3.4 Simulation Details

As mentioned previously, P₄₄₄₄-AA ionic liquids are chosen as additives to create models of water-based lubricants in this study. We have simulated three different types of amino acids, namely Serine (Ser), Phenylalanine (Phe), and Lysine (Lys), due to their previously demonstrated ability to improve the lubrication property of WBLs in experimental studies [65]. The molecular structure of these amino acids and P₄₄₄₄ are shown in Figure 3.2, and their molecular information can be found in Table A1 in the Appendix.

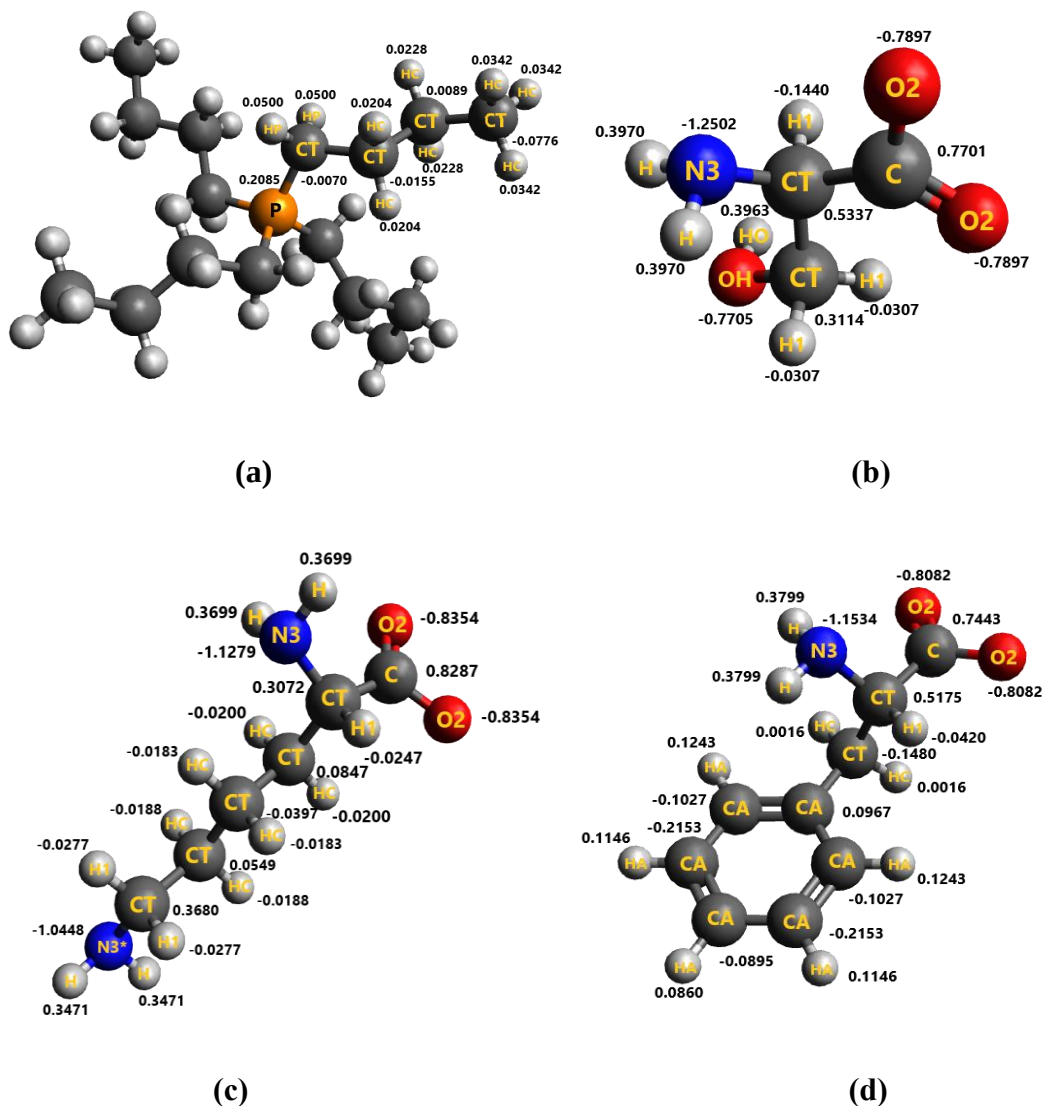


Figure 3.2: Structures and partial charges of (a) P_{4444} cation (b) Serine (Ser) (c) Lysine (Lys) (d) Phenylalanine (Phe) anion.

An all-atoms simulation potential model, namely, the Amber force field [193], is chosen for all simulations in this study. The potential energy E of the Amber force field was developed by Cornell *et al.* [193]. It contains two main parts, which are bonded interactions (bonds, angles and dihedrals) and nonbonded interactions (The van der Waals interactions and Coulombic interactions, which are given by Eq.3.6.

$$\begin{aligned}
E_{total} = & \sum_{bonds} K_r(r - r_0)^2 + \sum_{angles} K_\theta(\theta - \theta_0)^2 \\
& + \sum_{Dihedrals} \frac{K_\phi}{2}(1 + \cos(n\phi - \gamma)) + \sum_{i=1}^N \sum_{j=i+1}^N \left\{ 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\}
\end{aligned} \tag{3.6}$$

Mass, Charge and Lennard Jones(LJ) potential		
	O	H
Mass(amu)	15.994	1.008
Charge q(e)	-0.834	0.417
LJ ϵ (kcal/mol)	0.1521	0.0460
LJ σ (Å)	3.1507	0.4
Bond (O-H)		
K (kcal/mol/ Å ²)	450	
r ₀ (Å)	0.9572	
Angle (H-O-H)		
K _θ (kcal/mol)	55.0	
θ ₀ (degree)	104.52	

Table 3.2: Atomic masses, charges (q), Lennard Jones potential energy(ϵ) and distance(σ), O-H bond stiffness (K) and bond length (r_0), H-O-H bond angle stiffness(K_θ) and angle(θ_0) for TIP3P-CHARMM water model

The lubricant model consists of three compounds: water molecules, P₄₄₄₄ cations and AA anions. The water molecules are simulated by the TIP3P (transferable intermolecular potential with 3 points) model [194], which can provide high computational efficiency. In the TIP3P model,

each water molecule consists of one oxygen atom (O) at the centre and two hydrogen atoms (H) bonded to the O atom. The potential parameters from a modified TIP3P-CHARMM model [194], are used in this study. All parameters are presented in Table 3.2. To investigate the influence of AAIL additive, a pure water model is created as the control for comparison. The molecular structure of both ions, the P₄₄₄₄ cation and AA anions are created using Avogadro [195]. The water molecules, P₄₄₄₄ cations and AA anions are then packed together using Packmol [196], to create the P₄₄₄₄-AA WBLs with three different concentrations (5 wt%, 7.5 wt%, and 10 wt%). The force field parameters for P₄₄₄₄ cation and AA anions are adopted from a force field study for MD simulation of P₄₄₄₄-AA ionic liquids by Zhou *et al.* [197]. They developed the MD force field parameters based on the Amber force field, including the interatomic, bond, angle, dihedral and charge potentials for the P₄₄₄₄ cation and several different types of amino acid anions. They validated the force field against experimental results [197]. The number of water molecules and P₄₄₄₄-AA pairs for each system and concentration are presented in Table 3.3.

	Number of Atoms	Number of Water Molecules	Number of P₄₄₄₄- AA Pairs
Pure water	18600	6200	0
5 wt% P₄₄₄₄-Ser	17307	5439	15
7.5 wt% P₄₄₄₄-Ser	17868	5450	23
10 wt% P₄₄₄₄-Ser	18297	5439	30
10 wt% P₄₄₄₄-Lys	18290	5438	26
10 wt% P₄₄₄₄-Phe	18447	5499	26

Table 3.3: The number of water molecules and P₄₄₄₄-AA pairs for each system and concentration

3.5 Simulation Procedures

This study uses EMD-GK and NEMD with SLLOD simulations utilising the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [198].

The 12-6 Lennard Jones potential with a cutoff distance of 10 Å is used. The pairwise interaction calculation also considers long-range Coulomb electrostatic force with the same cutoff distance. The standard Ewald summation with a K-Space accuracy of 10^{-3} (relative RMS error in per-atom forces) is used for the long-range electrostatic force calculation. A harmonic style is used for the bond and angle potential, and the CHARMM style is used for the dihedral potential which are expressed in Eq.3.6.

All simulations start with an energy minimisation stage by applying the Conjugate Gradient (CG) algorithm. After that, the simulations are conducted for 5ps with an NVE ensemble with the Langevin thermostat. Such a step aims to reorient all atoms, which would help speed up the density equilibration stage [183].

For EMD-GK simulations, initially, the system is simulated for 10 ns under canonical (NVT) ensemble using a Nosé–Hoover thermostat at 293.15K to equilibrate the system. After the equilibration, the production and sampling stage is performed for 20 ns under the same NVT ensemble to calculate the viscosity and other properties. Based on the EMD-GK method mentioned in the previous section, the zero-shear viscosity is calculated by the running average integral of the autocorrelation function of the three stress tensors in the σ_{xx} , σ_{yy} and σ_{zz} directions. For NEMD simulation, the equilibrium stage is done for 3 ns in the NVT ensemble. The SLLOD algorithm is applied to the system with a given shear rate to achieve a Couette flow. Following the equilibrium stage, we calculate shear viscosity and other properties with the same ensemble over a 10 ns sampling stage. Here, we have calculated the ensemble average of the shear viscosity, the radial distribution function (RDF), and stress tensor components. The RDF will provide insight into the formation of the hydration shell. The first normal stress

difference is calculated using the normal stress tensor components in the three dimensions. The shear simulations are run under different shear rates between 10^9 to 10^{12} s^{-1} .

3.6 Results and Discussion

3.6.1 Shear viscosity

Figure 3.3 shows the calculated average shear viscosity as a function of the shear rate for pure water and three P₄₄₄₄-AA water-based lubricants with different concentrations of 5 wt%, 7.5 wt% and 10 wt% P₄₄₄₄ and Serine additives. The results are shown over a wide range of shear rates between 10^9 to 10^{12} s^{-1} . Figure 3.3 shows that all lubricants have a Newtonian plateau of relatively stable viscosity at the low shear rate region. An apparent shear thinning behaviour at higher shear rates follows this. The viscosity of P₄₄₄₄-Ser WBLs at all examined concentrations is higher than that of pure water.

This improved viscosity is more significant at lower shear rates and persists over a wide range of shear rates (up to $\sim 10^{11} \text{ s}^{-1}$). For example, at the shear rate of 10^9 s^{-1} , the viscosity of 5 wt% P₄₄₄₄-Ser WBL is 40% higher than pure water. Comparing the viscosity of P₄₄₄₄ -Ser WBLs with different concentrations of 5 to 10 wt% P₄₄₄₄-Ser shows the viscosity increases with the increase of concentration.

Some empirical and microscopic models can be applied to characterise this relationship between viscosity and applied shear rate which demonstrates both the Newtonian and non-Newtonian behaviours of AAIL WBLs [199]. We have fitted the obtained viscosity data points into a Cross model [200], given by Eq. 3.7 and shown them (solid lines) in Figure 3.3.

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c} \right)^m \right]^{-1} \quad (3.7)$$

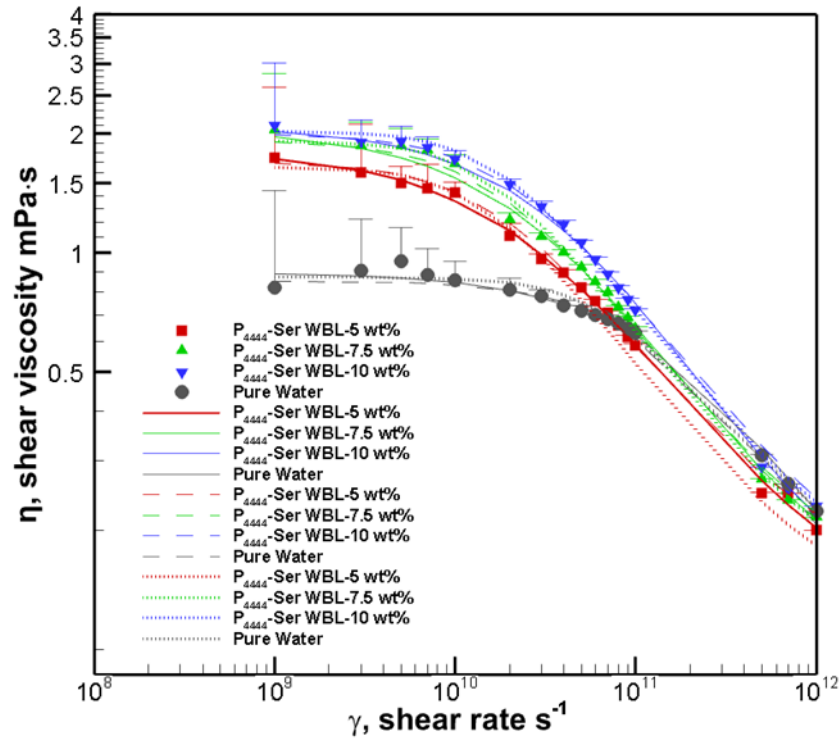


Figure 3.3: Shear viscosity versus shear rate (10^9 to 10^{12} s^{-1}) for pure water (circles), and P_{4444} -Ser AAIL water-based lubricant with 5wt% (squares), 7.5 wt% (triangles) and 10 wt% (deltas) concentration. The lines are the best fit ($R^2=98-99\%$) to the simulated data by the Cross model (solid lines) given by Eq.3.7 The Carreau-Yasuda model (dashed lines) by Eq.3.8, and the Eyring model by Eq.3.9 (dotted lines)

Cross Model Parameters					
	$\eta_0(\text{mPa.s})$	$\eta_\infty(\text{mPa.s})$	m	$\dot{\gamma}_c \text{ (1/s)}$	R^2
Water	0.91	0.0812	0.9635	1.97×10^{11}	0.983
5 wt% P_{4444} -Ser WBL	1.75	0.1124	0.8478	3.23×10^{10}	0.998
7.5 wt% P_{4444} -Ser WBL	2.05	0.1201	0.8756	3.31×10^{10}	0.993
10 wt% P_{4444} -Ser WBL	2.09	0.105	0.8992	4.36×10^{10}	0.998

Carreau-Yasuda Model Parameters					
	η_0 (mPa.s)	η_∞ (mPa.s)	n	λ (s)	R^2
Water	0.85	0.1232	0.02	7.51×10^{-12}	0.980
5 wt% P ₄₄₄₄ -Ser WBL	1.71	0.1321	0.27	5.10×10^{-11}	0.995
7.5 wt% P ₄₄₄₄ - Ser WBL	1.93	0.1112	0.29	5.23×10^{-11}	0.994
10 wt% P ₄₄₄₄ -Ser WBL	2.01	0.099	0.31	4.34×10^{-11}	0.998
Eyring Model Parameters					
	η_0 (mPa.s)	η_∞ (mPa.s)	$\dot{\gamma}_c$ (1/s)	R^2	
Water	0.87	0.1051	4.11×10^{10}	0.980	
5 wt% P ₄₄₄₄ -Ser WBL	1.65	0.1106	8.61×10^9	0.992	
7.5 wt% P ₄₄₄₄ - Ser WBL	1.92	0.1227	9.30×10^{10}	0.991	
10 wt% P ₄₄₄₄ -Ser WBL	2.03	0.1314	1.05×10^{10}	0.996	

Table 3.4: Parameters of Cross (page 58), Carreau-Yasuda and Eyring models obtained from fitting to simulation data for pure water and P₄₄₄₄-Ser WBLs with different concentrations (5 wt%, 7.5 wt% and 10 wt%)

In the Cross model, the η_0 , η_∞ , $\dot{\gamma}_c$ and m are, respectively, zero-shear viscosity, viscosity at infinite shear rates, the critical shear rate for the onset shear thinning, and shear thinning index. The parameters of the Cross model and the regression coefficient R^2 for water and P₄₄₄₄-Ser WBLs with different concentrations are presented in Table 3.4.

Besides the Cross model, the viscosity data points are also fitted into the Carreau-Yasuda [201], model given by Eq.3.8.

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty})[1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}} \quad (3.8)$$

And the Eyring Model [202] given by Eq.3.9.

$$\eta(\dot{\gamma}) = \eta_{\infty} + \frac{(\eta_0 - \eta_{\infty})\dot{\gamma}_E}{\dot{\gamma}} \sinh^{-1}(\dot{\gamma}/\dot{\gamma}_E) \quad (3.9)$$

In the Carreau-Yasuda model, the η_0 , η_{∞} , λ , n and a are, respectively, zero-shear viscosity, viscosity at infinite shear rates, characteristic time, the shear thinning index, and transition parameter between the Newtonian region and power-law region. In the Eyring model, the η_0 , η_{∞} are the zero-shear viscosity and the viscosity at infinite shear rates and $\dot{\gamma}_E$ refers to the Eyring rate.

In the Carreau-Yasuda model, $a=1.3$ is recommended [203]. The remaining parameters of the Carreau-Yasuda and Eyring models and R^2 are also presented in Table 3.4.

The R^2 values from Table 3.4 indicate the excellent fit of the simulation data to all three models. The Cross and Carreau-Yasuda models fit better than the Eyring model for this low-viscosity lubricant. The same behaviour is also reported in other studies, where high-viscosity liquids fit better with the Eyring model. It is evident from the model parameters in Table 3.4 that the m values for all P₄₄₄₄-Ser WBLs stay in the range of 0.8478 to 0.8992 and are very close to each other. Meanwhile, pure water has an m value of 0.9635, higher than P₄₄₄₄-Ser WBLs. The lower m values of P₄₄₄₄-Ser WBLs compared to pure water mean they have a stronger shear thinning behaviour. Furthermore, the m values from the Cross model parameters in Table 3.4 also reveal an increase in m values with increasing the concentration of P₄₄₄₄-Ser WBLs. The critical shear rate from Table 3.4 indicates that all P₄₄₄₄-Ser WBLs start the shear thinning at shear rates

between $3 \times 10^{10} \text{ s}^{-1}$ to $4 \times 10^{10} \text{ s}^{-1}$, which proves they have very similar shear thinning behaviour. In contrast, the critical shear rate of $1.97 \times 10^{11} \text{ s}^{-1}$ is much higher for pure water than that of P₄₄₄₄-Ser WBLs. At an extremely high shear rate of 10^{12} s^{-1} , shear viscosity is similar for water and WBLs.

The onset shear thinning and power law region behaviours from the Cross model can also be reflected in the Carreau-Yasuda model. The shear thinning parameter, n , in the Carreau-Yasuda model, increases with the concentration of the P₄₄₄₄-Ser. The characteristic time parameter λ for the P₄₄₄₄-Ser WBLs is higher than that for pure water. This means that the transition between the Newtonian and power-law regions becomes more expansive with increasing concentration. Overall, these two models can define the rheological behaviours of the P₄₄₄₄-Ser WBLs.

3.6.2 Effect of AAIL concentration on zero-shear viscosity

The running average of zero-shear viscosity from EMD-GK is plotted against time for 20 ns of the simulation time and shown in Figure 3.4(a) for water and P₄₄₄₄-Ser WBLs with different concentrations.

The results from both the experiment and EMD-GK show that the zero-shear viscosity of P₄₄₄₄-Ser WBLs is higher than water, and there is an increase in viscosity with increasing the concentration of P₄₄₄₄-Ser WBLs. These findings align with the ones from the NEMD simulation.

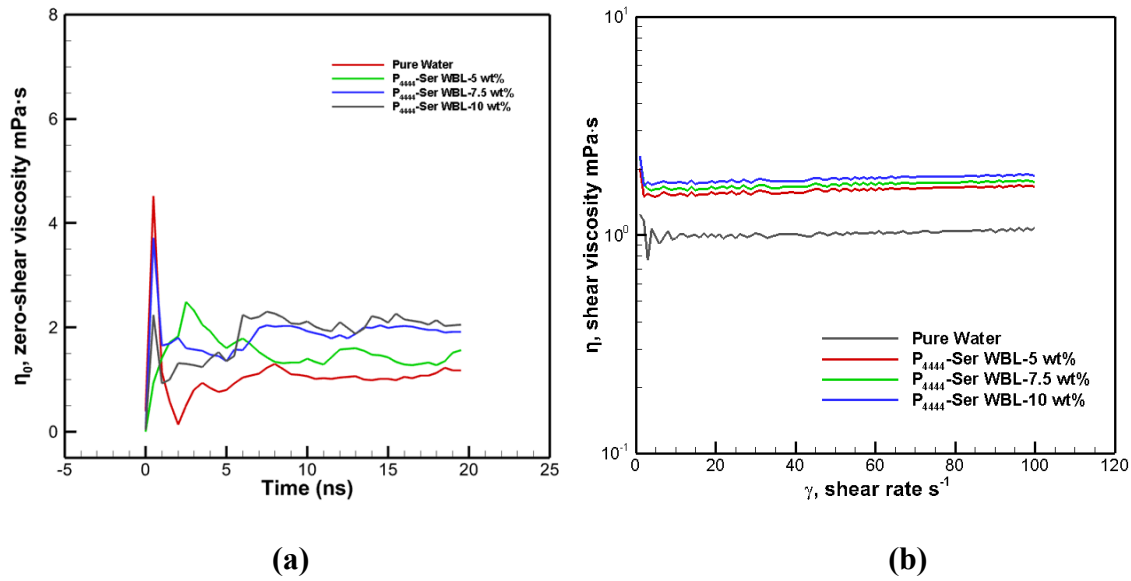


Figure 3.4: (a) Zero-shear viscosity of pure water and 5 wt%, 7.5 wt%, 10 wt% P_{4444} -Ser WBLs versus time obtained from GK-EMD simulation (b) Viscosity versus shear rate of pure water and 5 wt%, 7.5 wt%, 10 wt% P_{4444} -Ser WBLs obtained from experiment.

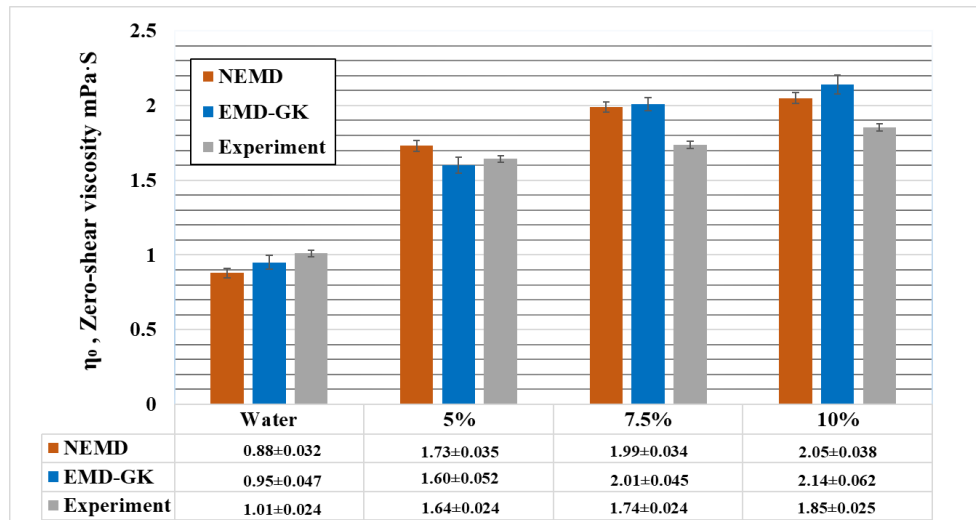


Figure 3.5: Zero-shear viscosity obtained from NEMD, EMD-GK simulations and experimental measurements for pure water and 5 wt%, 7.5 wt%, 10 wt% P_{4444} -Ser WBLs.

Figure 3.5 compares the predicted viscosity from the ensemble average zero-shear viscosity obtained from EMD-GK. The results for the NEMD method are the average of the η_0 values obtained from the Cross, Carreau-Yasuda and Eyring models given in Table 3.4. The results from direct experimental measurements are also shown in Figure 3.6. The two different MD

approaches for predicting the zero shear viscosity (η_0) values between these two methods are consistent and close. The calculated $\eta_{0 \text{ water}}$ is also very close to the experimental value of 1.01 mPa.s from our experiment and 1.002 mPa.s from the literature [204]. This shows that the predicted values are within 5% for EMD-GK and 13% for the NEMD method of the experiments. For P₄₄₄₄-Ser WBLs, the result from the experiment we conducted in this study validates the simulation result. At 5 wt%, the zero-shear viscosity from the experiment is within 8% of the simulation result. At higher concentrations of 7.5 wt% and 10 wt%, the simulation values are within 13-17% of the experimental results. The simulated zero-shear viscosities from EMD-GK for P₄₄₄₄-Ser WBLs show an increase of 68%, 112% and 125%, respectively, for 5, 7.5 and 10 wt% concentrations of P₄₄₄₄-Ser in water. The experimental values also show a viscosity improvement of 60-80% depending on the concentration of P₄₄₄₄-Ser AAIL.

3.6.3 The effect of amino acid Type in AAIL formulation on viscosity

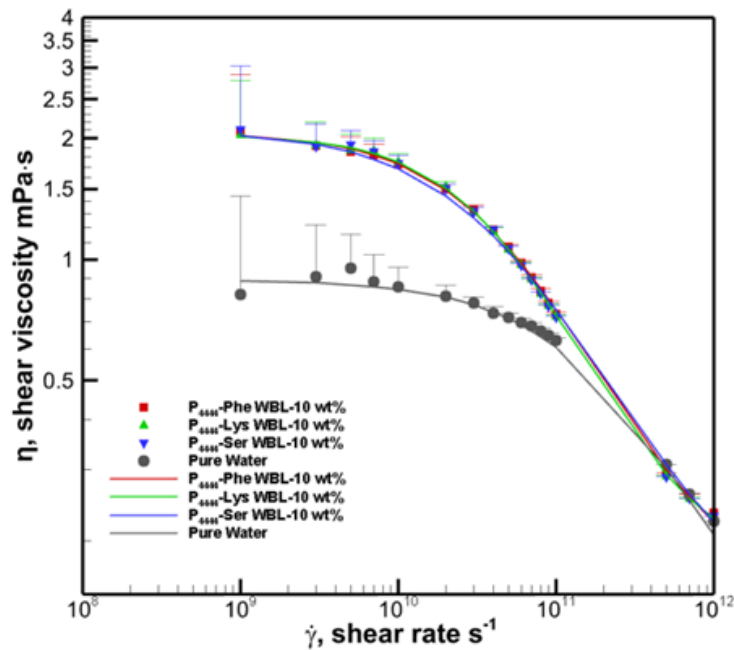


Figure 3.6: Shear viscosity versus shear rate for three different AAIL systems of P₄₄₄₄-Ser, P₄₄₄₄-Phe, P₄₄₄₄-Lys WBLs are compared with water. The solid lines are the Cross model fitting of data points obtained by NEMD simulations.

NEMD simulations were also conducted for AAIL WBLs made from two other types of amino acids, Lysine (Lys) and Phenylalanine (Phe), at 10% concentration over the same range of shear rates. Their shear viscosity is compared with those of P₄₄₄₄-Ser WBL and water in Figure 3.6. We obtained similar shear viscosity values for P₄₄₄₄-Phe and P₄₄₄₄-Lys WBLs, and P₄₄₄₄-Ser. All three types of P₄₄₄₄-AA WBLs show a higher viscosity than pure water. All three AA types showed similar shearing thinning behaviours, and their critical shear rates were higher than water.

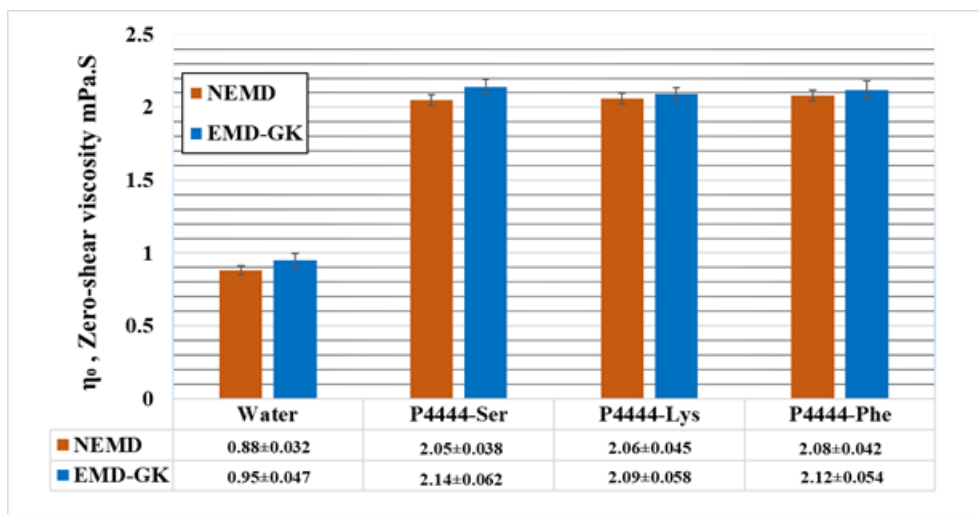


Figure 3.7: Predicted zero-shear viscosity obtained from NEMD and EMD-GK methods for pure water and three different amino acid ionic liquid water-based lubricants P₄₄₄₄-Ser, P₄₄₄₄-Lys and P₄₄₄₄-Phe at a 10 wt% concentration.

Comparing the viscosity among these three P₄₄₄₄-AA WBLs, P₄₄₄₄-Phe has the highest shear viscosity after onset shear thinning, followed by P₄₄₄₄-Lys and P₄₄₄₄-Ser. However, the difference between them is not significant; and the zero-shear viscosity shown in Figure 3.7 are very close for the three AAIL WBLs at the concentration of 10 wt%. Overall, AAIL additives significantly increase water viscosity regardless of the type, which is a promising finding for water-based lubrication applications.

3.6.4 Normal stress difference

The first normal stress difference (N_1) is calculated from Eq.3.10 using the normal stress components obtained from the simulations.

$$N_1 = \sigma_{xx} - \sigma_{yy} \quad (3.10)$$

Figure 3.8 shows the N_1 versus the shear rates for pure water and P₄₄₄₄-Ser WBLs with different concentrations.

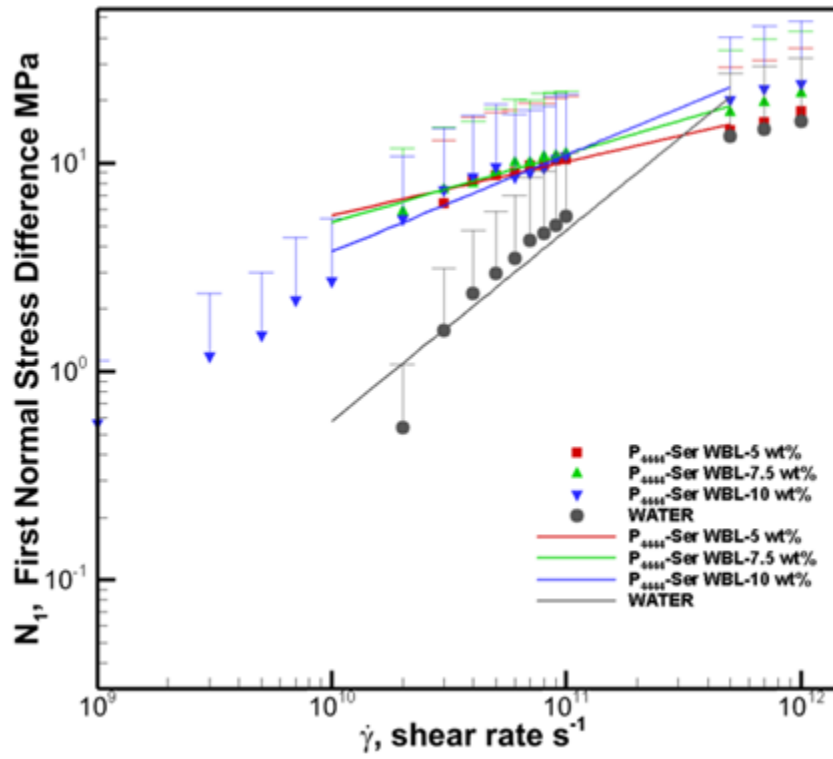


Figure 3.8: First normal stress difference (N_1) versus shear rate (over 10^9 - 10^{12} s^{-1}) for pure water and 5 wt%, 7.5 wt%, 10 wt% P₄₄₄₄-Ser WBLs.

At a lower shear rate, N_1 is very small and has considerable statistical uncertainty. Therefore, the data points between 10^{10} to 10^{11} s^{-1} shear rates are fitted using the power law ($N_1 = A\dot{\gamma}^n$), and The power-law exponent n is tabulated in Table 3.5.

	Pure Water	5 wt% P ₄₄₄₄ -Ser WBL	7.5 wt% P ₄₄₄₄ - Ser WBL	10 wt% P ₄₄₄₄ - Ser WBL
Exponent n	0.916	0.2574	0.3279	0.4642

Table 3.5: Exponent n in power law fitting of normal stress difference, $N_1 = A\dot{\gamma}^n$ for pure water and 5 wt%, 7.5 wt%, and 10 wt% P₄₄₄₄-Ser WBLs.

The results show that all shear rates have a higher N_1 value for P₄₄₄₄-Ser WBLs than pure water. N_1 seems to increase with P₄₄₄₄-Ser concentration, especially at higher shear rates. The statistical uncertainty, however, is considerable, so it is hard to conclude the effect of concentration for the range of concentrations examined here. Higher N_1 of P₄₄₄₄-Ser WBL in all concentrations means the stress in the normal direction is much larger. Higher normal stress differences for P₄₄₄₄-Ser WBL show they can better separate two contacting surfaces in relative motion in tribological applications, and they are promising lubricants. Continuum-based models [205][206] have shown a net increase in the load-carrying capacity due to a finite increase in the normal stress. Our previous works have discussed the molecular origins of normal stress and its impact on load-carrying capacity [114] [207] [208]. The N_1 is a shear rate-dependent property arising from the lubricant's own rheological properties. Normal stress differences can be seen even in parallel plate geometries which is the situation in this study. However, one needs very high shear rates for the lubricants studied here, which is achieved when the thickness of the film is in the order of a few nanometers. At a higher shear rate, the N_1 of water seems to converge toward that of the P₄₄₄₄-Ser WBLs. It suggests a saturation stage in the load capacity of P₄₄₄₄-Ser WBLs. For long polymer solutions, this phenomenon is associated with the polymeric chains' finite extensions effect, whereas for smaller molecules, this is associated with finite molecular alignment, which may limit the further generation of normal stress [114][207][208]. Given the small molecules used in this study, we believe the latter should be the case.

3.6.5 Structural analysis

In order to investigate the mechanism of the rheological behaviour reported in the previous section, the radial distribution function is used to analyse the structure of the P₄₄₄₄-Ser WBLs. The radial distribution function (RDF) between the oxygen atoms of the carboxyl group from AA (O_{AA}) and the hydrogen and oxygen atoms of water (H_w and O_w) for P₄₄₄₄-Ser WBLs with different concentrations is computed and shown in Figure 3.9.

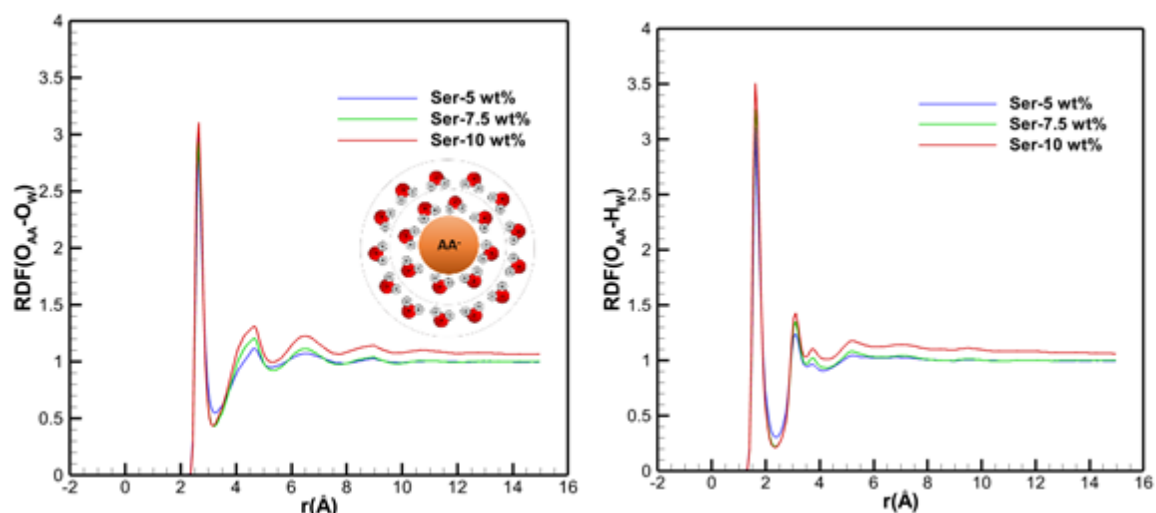


Figure 3.9: RDFs between the oxygen atoms of the carboxyl group from AA (O_{AA}) and the hydrogen atoms of water (H_w) (right), and the oxygen atoms of the carboxyl group from AA (O_{AA}) and the oxygen atoms of water (O_w) (left) for 5 wt%, 7.5 wt%, 10 wt% P₄₄₄₄-Ser WBLs. The inset picture is a schematic of hydration shells surrounding the AA anion, with water, Oxygen and hydrogen atoms shown in red and grey.

The O_{AA} is the central atom in these RDFs, while the H_w and O_w are the distribution surrounding O_{AA} . The left graph of Figure 3.9 clearly shows that two sharp peaks are located at 1.8 Å and 3.2 Å for all concentrations. The high values of the RDF at the first peak indicate a strong interaction between the AA ions and the water molecules in the P₄₄₄₄-Ser WBLs. In the left graph of Figure 3.9, the first high peak of RDF between O_{AA} and O_w is located at a distance of 2.8 Å. The distance difference of the high peak locations between O_{AA} - H_w and O_{AA} - O_w equals the O_w - H_w bond length, which defines a clear hydration shell formed around Ser

ions. The same can be observed at the second peaks from Figure 3.9, which defines a second hydration shell formed with loosely bound water. The absence of a third peak proves the liquidity of P₄₄₄₄-Ser WBLs and the existence of the two well-defined hydration shells [209], and the schematic of these two well-defined hydration shells surrounding the Ser ion is shown in the inset of Figure 3.9.

Figure 3.9 also shows that the 10 wt% P₄₄₄₄-Ser WBL has the highest RDF values on both peaks for O_{AA}-H_w and O_{AA}-O_w, followed by 7.5% and 5%. With increasing the AAIL concentration, the RDF peak value increases, which reveals that higher AAIL content gives hydration shells with more water molecules around the Ser ions. When hydration shells around the Serine anions have formed, the number of free water molecules in P₄₄₄₄-Ser WBLs reduces. The transportation activity of water in the solution that forms the hydration shell around Serine anions will also be slowed down. Overall, the P₄₄₄₄-Ser WBLs mixture flows more complexly than pure water. It explains the phenomenon from the previous discussion that P₄₄₄₄-Ser WBLs have a higher viscosity than pure water. Furthermore, the higher content of the AAILs in the water results in lower water transportation, leading to increased viscosity with increasing AAIL concentration.

In contrast, no well-defined peak can be observed from the RDF between the P₄₄₄₄ cations and water, as shown in Figure 3.10. It reveals that no hydration shell is formed around the P₄₄₄₄ cations. P₄₄₄₄ cation consists of four relatively long hydrophobic butyl (C₄H₉) groups attached to the phosphonium cation. These nonpolar hydrophobic chains tend to repel water molecules, which would not form the hydration shell.

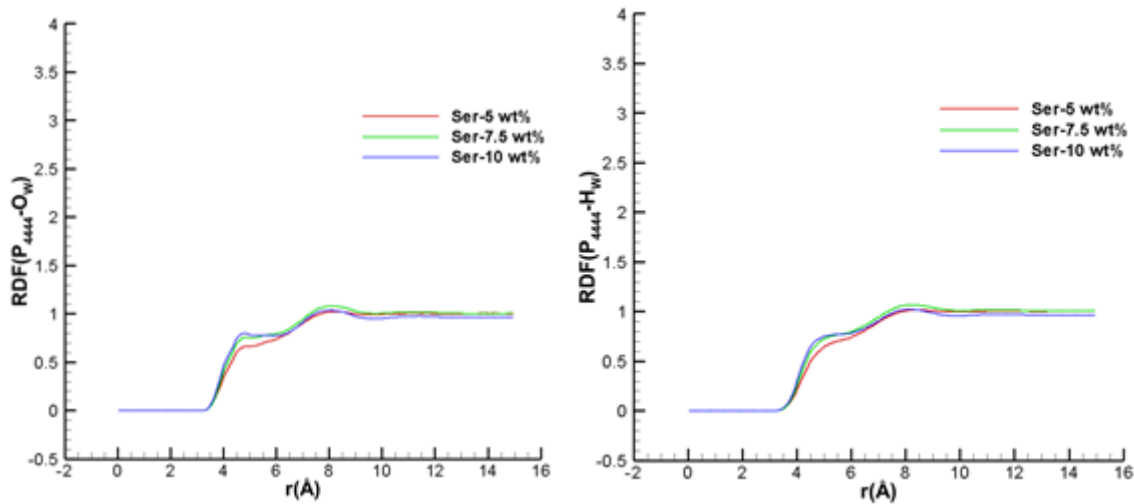


Figure 3.10: RDFs between the phosphorus atoms of P_{4444} and the hydrogen atoms of water(H_w)(right), and the phosphorus atoms of P_{4444} and the oxygen atoms of water(O_w) (left) for 5 wt%, 7.5 wt%, 10 wt% P_{4444} -Ser WBLs.

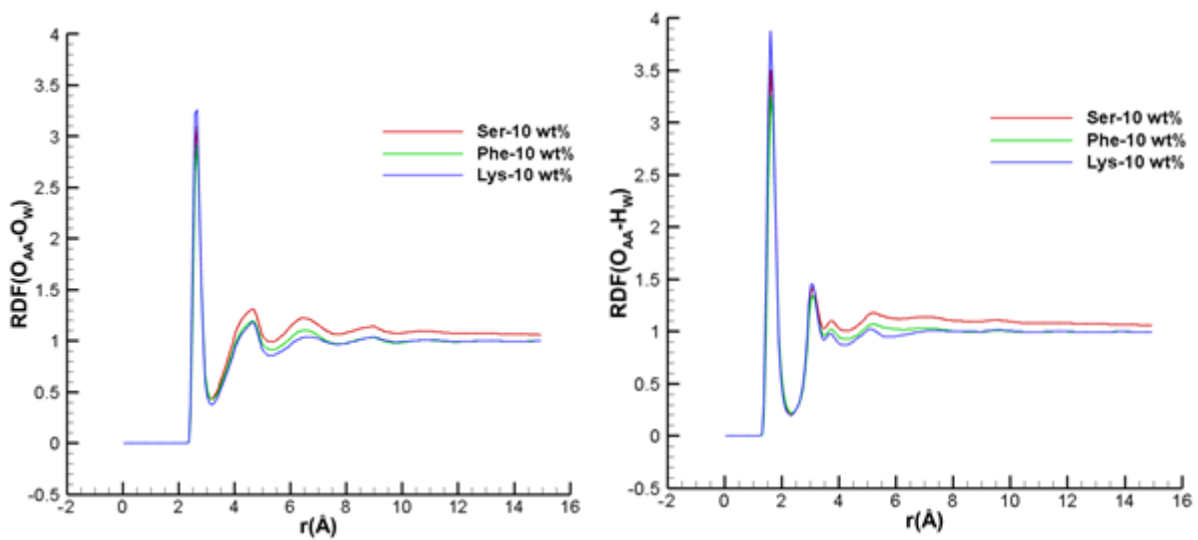


Figure 3.11: RDFs between the oxygen atoms of the carboxyl group from AA (O_{AA}) and the hydrogen atoms of water(H_w)(right), and the oxygen atoms of the carboxyl group from AA (O_{AA}) and the oxygen atoms of water(O_w) (left) for 10 wt% P_{4444} -Ser, P_{4444} -Phe, P_{4444} -Lys WBLs.

Similarly, two clear high peaks of RDF value for 10 wt% P_{4444} -Phe and P_{4444} -Lys WBLs are defined in Figure 3.11, which shows the formation of the hydration shell for them. Even though the difference among these three types of AAIL WBLs is not significant, P_{4444} -Lys and P_{4444} -

Ser have a higher RDF value at the first peak than P₄₄₄₄-Phe; however, P₄₄₄₄-Ser has the highest value at the second peak. This result agrees with what has been reported in the hydration shell study of amino acids by Shen *et al.* [210]. Many factors influence the formation of hydration shells around different amino acid anions. Ideally, the amino acid anions with larger radicals [209] and molecular weight would have much stronger hydration shells due to their increased surface area available for interaction with water molecules [211]. Among the three types of amino acid anions considered, Phe has the largest size, followed by Lys and Ser. However, the RDF result at the first high peak does not indicate a strong hydration shell for Phe. It suggests that size is not the dominant factor in hydration shell formation.

Considering the side-chain effect of these AA anions, Ser anions possess a hydroxyl group (-OH), a polar group with a strong binding ability to water through hydrogen bonding. Among all types of AA, Ser has been shown to have the largest numbers of hydration water, including tightly and loosely bound water [210]. It is reflected in Figure 3.10 that Ser has high values at both peaks despite its small molecular size. The Lys anion features an aliphatic hydrocarbon group side chain with an amine group (-NH₂) at its end, which can participate in hydrogen bonding with water molecules. Hydrogen bonding contributes to the first layer of the hydration shell, which consists of tightly bound water. That explains the higher value at the first peak for Ser and Lys in Figure 3.11. Despite the hydrophilic amine group facilitating hydrogen bonding with water, the long chain of nonpolar methylene groups dilutes the polarity of the side chain. This results in an insignificant difference in the RDF from the others.

In contrast, the side chain of the Phe anion consists of a benzene ring, a nonpolar functional group that influences hydrogen bond formation with water. As a result, it affects the hydration shell formation, which can be observed from the lowest first peak value in RDF. However, Phe does not have the lowest value at the second peak. The hydrophobic benzene ring affects the

first layer of hydration shell formation with the tightly bound water and has the hydrophobic hydration effect on those long-range loosely bound water [210].

Table 3.6 presents the interaction energy between IL ions and the water molecules in the 10 wt% AAIL WBLs with different AA types. The interaction energy is negative for all cases, indicating the affinity between all amino acids and water molecules. The Ser anion has the highest magnitude of interaction energy with water, slightly higher than that of the Lys anion. The magnitude of the interaction energy of Phe with water is lower than that of Ser and Lys anions. A more negative interaction energy indicates a stronger affinity. This means the Ser and Lys anions have a stronger attractive interaction than the Phe anions. This supports the hydration shell formation observed from the RDF in all types of AA anions and also agrees with the discussion on the effect of different structures. The interaction energy of the P₄₄₄₄ cation with water is much smaller than that of AA anions, proving the hydrophobic characteristic observed from the RDF.

	E_{AA-Water} (kcal/mol)	E_{P4444-Water} (kcal/mol)
P₄₄₄₄-Ser WBL	-3780.38	-1051.72
P₄₄₄₄-Lys WBL	-3677.08	-918.19
P₄₄₄₄-Phe WBL	-3159.79	-907.44

Table 3.6: Interaction energy between AA anion and water ($E_{AA-Water}$), P₄₄₄₄ cation and water ($E_{P4444-Water}$) in different types of 10 wt% AAIL WBL

Overall, with all effects acting together, the hydration shell formation between different types did not result in a significant difference for 10 wt% AAIL WBLs. It might explain the consistent viscosity result between different types of AA reported previously.

3.7 Conclusion

This study investigated the rheological behaviour of three different types of AAIL WBLs. The effectiveness of the molecular model was demonstrated by obtaining consistent results for zero-shear viscosity using EMD-GK and NEMD methods. These results were within 5-15% of those obtained from our experiments for P₄₄₄₄-Ser WBLs at different concentrations. The results showed that the zero shear viscosity of all AAIL WBLs was significantly higher than that of water, with improvements ranging from 68-125% depending on the concentration. The shear viscosity of AAIL WBLs was also higher than that of pure water and increased with the concentration of P₄₄₄₄-Ser WBLs. This increased viscosity was maintained over a wide range of shear rates, indicating good performance for lubricating surfaces in contact at various sliding velocities. The more considerable normal stress difference observed for AAIL WBLs indicated their ability to bear higher loads than water. The increased shear viscosity was independent of the amino acid types used in the study, with Serine (Ser), Lysine (Lys), and Phenylalanine (Phe) based lubricants showing similar rheological behaviour. The zero-shear viscosity for all three types of AAIL WBLs was higher than that of water. The first normal stress difference results showed that the P₄₄₄₄-Ser additives significantly increased the normal stress difference, suggesting their potential to separate two contact surfaces in lubrication applications. The formation of hydration shells was observed through RDF analysis. Overall, AAILs show promise as additives for WBLs when higher viscosity is desired in industrial lubrication applications. The methodology used in this study can serve as a guide for computational studies on WBLs, and the results can be valuable for optimising future WBL formulations and designs.

Chapter 4: Tribological Analysis and Lubrication

Mechanism of AAIL WBLs

4.1 Introduction

In Chapter 3, the rheological performance of WBLs with different types of AAIL additives at various concentrations was investigated. Results indicated that P₄₄₄₄-Ser additives increased water viscosity by 68%–125%, depending on concentration. P₄₄₄₄-Ser WBLs also exhibited a significantly higher first normal stress difference than water, suggesting their ability to support greater loads in lubrication. Given the wide range of AA types, Chapter 3 also included a study of the rheological behaviour of AAIL WBLs with different AA types. Analysis of the effect of AA type revealed that the rheological behaviours of AAIL WBLs with different AA types are pretty similar. Both EMD and NEMD simulations demonstrated that AAIL WBLs with different AA types have similar shear and zero-shear viscosities. Additionally, they exhibit similar shear-thinning behaviours in response to changes in shear rates.

In the two respective studies on AAIL lubricants, which have been mentioned in Chapter 1 [65] [87], investigations were conducted on the tribological properties of AAIL-involved lubricants with different AA types. Both studies indicated that the tribological behaviours of AAIL lubricants depend on the AA type in some cases. For example, the tribological studies by Zhu *et al.* [87] showed that Tetrabutylammonium-AA (N₄₄₄₄-AA) lubricants with most AA types exhibited similar tribological behaviour, while N₄₄₄₄-Phe demonstrated superior tribological behaviour in steel-steel contacts. In the study conducted by Yang *et al.* [65], friction tests were performed on AAIL lubricants with seven different AA types, resulting in a wide range of coefficient of friction (COF) values between 0.15 and 0.3. While rheological behaviour can significantly influence tribological properties, Chapter 3 demonstrated that the rheological behaviours of AAIL WBLs are relatively independent of their AA types. Therefore, investigating the underlying lubrication mechanism of AAIL WBLs is essential. The optimised design of AAIL WBLs can only be determined once their lubrication mechanism is fully revealed.

However, existing studies have not yet fully confirmed the lubrication mechanism of AAIL lubricants. While studies from Yang *et al.* [65] and Zhu *et al.* [87] are all experiment-based, providing measurements and tribological analysis of certain bulk-level properties, they both utilised X-ray photoelectron spectroscopy (XPS) to measure the elemental composition on worn metal surfaces. XPS provides information about the types of elements present on the surface after a friction test and offers some insight into the chemical state of those elements. However, as a surface analysis technique, XPS can only provide information about the final state of surfaces. The tribological behaviour is a real-time, dynamic process. Therefore, explaining the lubrication mechanism can be challenging due to the limitations of experimental methods. To gain deeper insights into the lubrication mechanism of AAIL WBLs, it is necessary to employ additional methods.

In general, lubrication performance is determined by atomic-level interactions. As discussed in previous chapters, MD simulations are powerful tools for modelling these interactions at the atomic level. MD simulations can provide a time-resolved, atomistic view of the lubrication process, offering a much more detailed and dynamic perspective on the lubrication mechanism compared to the static, end-point information provided by XPS.

In some lubrication systems, tribological behaviours depend on chemical reactions occurring at the interface between two sliding surfaces [212]. This phenomenon, known as tribochemistry, is fundamental when additives are mixed with the base lubricant, forming protective layers called tribofilms on the surface. In WBLs, interactions involving water molecules, additives, and the contacting surfaces contribute to their lubrication performance. Reactive MD simulations have been employed in this study to investigate tribochemistry and capture the formation and breaking of chemical bonds instead of the classical MD simulations used in Chapter 3. Despite their potential, reactive MD simulations have been limited in tribology research due to their extensive computational demands and the lack of suitable potentials.

However, some studies have successfully employed reactive MD simulations to provide in-depth tribological behaviour analysis [213][214][216]. Chen *et al.* [213] conducted reactive MD simulations to investigate the tribological behaviours of poly α -olefins (PAO) between zinc oxide (ZnO) surfaces. They found that the reduction in the coefficient of friction (COF) could be attributed to the influence of the electric field and the formation of the adsorption film. Similarly, Wang *et al.* [214] found that the formation of C-Fe bonds has a significant impact on the tribological behaviours of monolayer graphene oxide or graphene (GO/Gr) flakes confined between iron oxide surfaces. Ta *et al.* [216] studied the formation of tribofilm on Iron oxide surfaces lubricated by a mixture of hydrocarbon lubricants (decane) and cyclopropane carboxylic acid as additives.

In this chapter, we have employed reactive MD simulations to examine the effect of P₄₄₄₄-AA ionic liquid additives on the tribological properties of WBLs between metallic surfaces. This study explores the mechanism of AAIL WBLs between metallic surfaces. To our knowledge, this class of water-based lubricants has not been previously studied using reactive MD simulations. Here, we aim to understand how these additives lower the friction coefficient of water and why certain amino acids perform better than others.

4.2 Experimental Procedure

4.2.1 AAIL WBLs preparation

The tetrabutylphosphonium amino acid (P₄₄₄₄-AA) WBLs were prepared by using the methodology from Chapter 3, which was adopted from a previous study by Yang *et al.* [65] and Song *et al.* [174]. P₄₄₄₄-Serine (P₄₄₄₄-Ser) and P₄₄₄₄-Tryptophan (P₄₄₄₄-Trp) were chosen as the two different types of AAILs to be investigated. The L-Serine (Sigma-Aldrich, St.Louis, MO, USA, $\geq 99\%$ (HPLC)) or L-Tryptophan (Sigma-Aldrich, St.Louis, MO, USA, $\geq 98\%$ (HPLC)) was added into Tetrabutylphosphonium hydroxide (Sigma-Aldrich, St.Louis, MO, USA, 40

wt %) to achieve the equimolar solution. The AAIL WBLs were prepared by adding different P₄₄₄₄-AA solutions to the distilled water separately to achieve the concentration of 10 wt%. The mixture was stirred for 24 hours. A pure water sample using distilled water was prepared for the reference group. The shelf-life of the AAIL WBLs was demonstrated by conducting multiple tests with the same solution within a week. The consistent results obtained across these tests indicate good long-term stability

4.2.2 Rheological measurements

The methodology of zero-shear viscosity measurement was adapted from Chapter 3 [215]. The Anton Paar MCR-302 rheometer (Anton Paar GmbH, Graz, Austria) with the concentric cylinder (CC) system was employed. The CC system comprises a measuring bob (diameter $D_B = 26.651\text{mm}$) and a measuring cup (diameter $D_C = 28.922\text{mm}$). The measuring cup was loaded with 19 ml of P₄₄₄₄-AA WBL sample, which was then subjected to shear rates ranging from 0 to 100 s^{-1} under a temperature of 20°C (facilitated by a Peltier system integrated with the rheometer). The lubricant is Newtonian at this range of shear rates. The viscosity was recorded during the shearing, and the average viscosity for each test was presented as zero-shear viscosity. The presented value is the average of five tests on each type of P₄₄₄₄-AA WBLs and pure water.

4.3 Molecular Simulation Methodology

To understand the tribological behaviour of AAIL WBLs, it is necessary to investigate the tribochemical properties that classical non-reactive force fields cannot capture. As such, the reactive MD simulations were conducted for both P₄₄₄₄-AA WBLs and pure water. In the reactive MD simulation, atomic interactions depend on the current configurations due to the bond breaking and formation that occur during the movement of atoms [138]. The dynamic nature of bond dissociation and formation in reactive MD simulations provides a powerful

means to study chemical reactions. Such detailed chemical reactions, however, require significant computational power. In this study, the reactive force-field (ReaxFF) interatomic potential [152] was chosen as the force field for all simulations. ReaxFF is a force field based on the concept of bond order, which represents the strength of a bond [217]. The details of ReaxFF methodology have been discussed in Section 2.2.2.

4.4 Molecular Model

All-atom atomistic models for both the lubricant and confining surface are used to capture their detailed behaviour for a tribological model.

4.4.1 Lubricant

In this study, we developed the AAIL WBL model by introducing AA anions and P_{4444} cations as additives to water. Serine (Ser) and Tryptophan (Trp) are the two distinct amino acid types chosen in this study. The molecular structures of AA anions and P_{4444} cation were created using Avogadro [195]. The molecular structures of Ser and Trp anion and P_{4444} cations are presented in Figure 4.1. The molecular information of the AA anions and P_{4444} cation can be found in Table A1 in the Appendix.

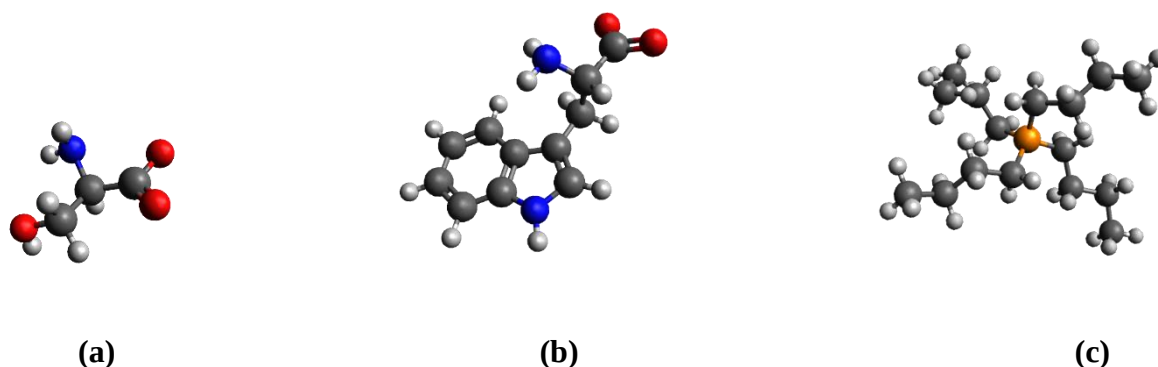


Figure 4.1: Structures of (a) Serine (Ser) (b) Tryptophan (Trp) anion (c) P_{4444} cation

The AAIL WBLs were formulated by packing the water molecules, AA anions and P_{4444} cations together with a concentration of 10 wt%. A model of pure water was also created as the control

for investigating the effect of AAIL additives. The quantity of water molecules, AA anions and P₄₄₄₄ for 10 wt% Ser-P₄₄₄₄, Trp-P₄₄₄₄ WBLs and pure water are presented in Table 4.1.

	Number of lubricant Atoms	Number of Water Molecules	Number of P₄₄₄₄- AA Pairs
Pure water	5220	1740	0
10 wt% P₄₄₄₄-Ser	5370	1790	10
10 wt% P₄₄₄₄-Trp	4830	1610	7

Table 4.1: The number of lubricant atoms and the number of water molecules and P₄₄₄₄-AA pairs for 10 wt% P₄₄₄₄-Ser, P₄₄₄₄-Trp and pure water

4.4.2 Substrate

The WBL film is confined between two molecularly flat iron oxide (α -Fe₂O₃ (0001)) surfaces. These surfaces simulate the oxide layers of bearing steel, which directly interact with the WBLs [218]. The surfaces are composed of rigid, thermostated, and interaction regions. The atoms in the rigid section are frozen to provide rigidity under different loads. The thermostating regions are the middle regions of the surfaces with a thickness of 4.5Å. The interaction regions directly interact with the lubricant and can interact with the confined lubricant to exchange momentum. The simulation box for all simulations is 51Å x 51Å x 46Å, which consists of the upper and lower Fe₂O₃ surfaces, each 13Å thick, and a 20Å confined WBLs. For the 10 wt% P₄₄₄₄-Ser WBLs, the system contains 12030 atoms in the simulation box, comprising 6000 atoms from the wall, 5370 atoms from the water, and 660 atoms from AAIL additives. An example of the configuration of the simulation box is shown in Figure 4.2.

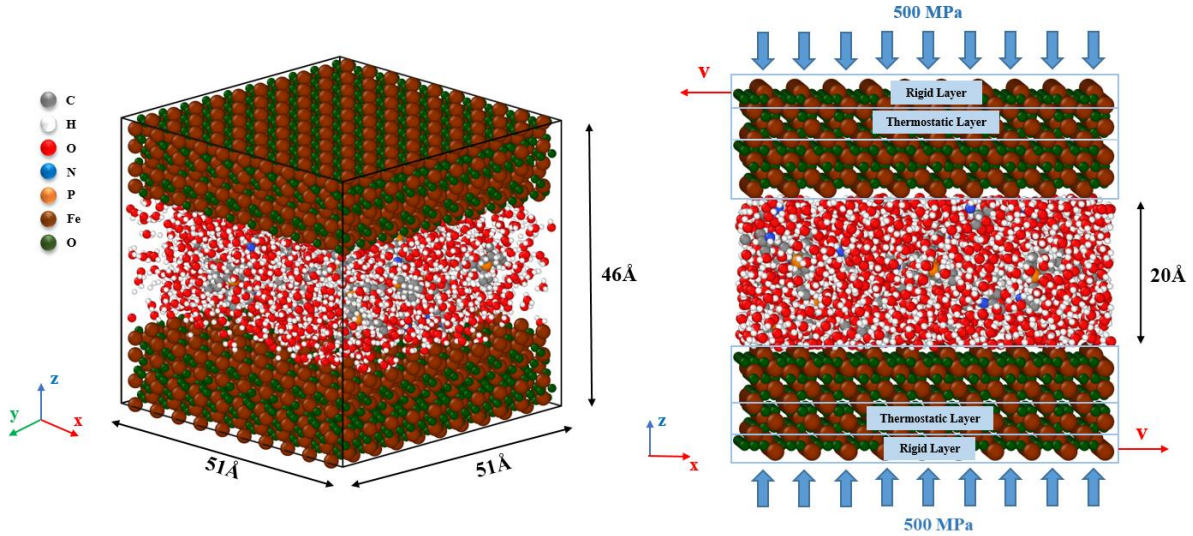


Figure 4.2: The configuration of 10%wt P_{4444} -Ser WBLs confined between the iron oxide surfaces. Atoms are shown in different colours for clarity. The walls comprise three regions to provide rigidity, temperature control, and momentum transfer.

4.5 Simulation Procedure

All simulations were conducted by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The ReaxFF parameters for P/C/H/O/N were adopted from the study by Zhang *et al.* [219], and parameters for interactions with iron oxide were adopted from the study by Khajeh *et al.* [220] and Chia *et al.* [221]. Zhang *et al.* developed the ReaxFF parameters for P_{4444} cation and AA anion and conducted the validation against both experimental data and calculations derived from Density Functional Theory (DFT). These parameters agreed with DFT energies for bond dissociation and angle distortion. Similarly, the parameters for the interaction between P/C/H/O/N and iron oxide surfaces were benchmarked against experiment and DFT calculations [219]. These parameter sets have been used in a previous study to model and investigate the interactions between trihexyltetradecylphosphonium ($P_{6,6,6,14}$) benzoate or salicylate ionic liquid and ferrous surfaces, and the results aligned well with experimental observations [222]. Wu *et al.* [223]

used these parameter sets to model phosphate ionic liquid and investigate its lubrication mechanism. The result was in good agreement with the DFT calculations. The periodic boundary conditions are applied in the x and y directions, and a shrink-wrapped non-periodic boundary condition is used for the z direction. The iron oxide surfaces have been divided into three parts to achieve the desired conditions. This is shown in Figure 4.2. The upper and lower layers are the rigid layers to which load and velocity are applied to keep the system at constant normal load and velocity. A Nosé–Hoover thermostat (NVT) with a damping factor of 30 ps was applied to the thermostat layer to keep the temperature at 293.15K. For this boundary-driven-shear simulation, an NVE ensemble with a Langevin thermostat, as suggested by Yong *et al.* [224] is applied to the inner surface layers and the lubricant. All simulations consisted of three main stages: energy minimisation, compression and shear. The Conjugate Gradient (CG) algorithm was applied in the energy minimisation stage, modifying the lubricant atoms' positions from the initial configuration to minimise the total potential energy and interaction forces. In the compression stage, uniformly distributed loads corresponding to a pressure of 500MPa were applied to the upper and lower rigid layers of surfaces, compressing the lubricant in between for 1ns. This pressure aligns with those experienced in industrial processes such as metal forming and ball-bearing lubrication. [225]. After the compression stage, the upper and lower rigid layers of surfaces slide in opposite directions at a constant velocity of 1 m/s. The friction stage runs for 4 ns. The overall lateral shear stress σ_{xz} and the normal stress σ_{zz} exerted on the atoms of the upper and lower rigid layer were collected once every 5fs and averaged at the end of every 0.01ns to obtain the mean value for that time step. The coefficient of friction (COF) was calculated as the ratio of shear stress and normal stress by Eq.4.1 [225].

$$\mu = \frac{\langle \sigma_{xz} \rangle}{\langle \sigma_{zz} \rangle} \quad (4.1)$$

Besides, the mean squared displacement (MSD) along the x and z directions of AA anions was calculated by Eq.4.2 [226],

$$MSD = \langle (r_t(t) - r_t(0))^2 \rangle \quad (4.2)$$

where $r_t(t)$ is the position of AA anions at time t , and $r_t(0)$ is the initial position. Furthermore, the first normal stress difference (N_1) is calculated from the stress components in x and z directions by Eq.4.3,

$$N_1 = \sigma_{xx} - \sigma_{zz} \quad (4.3)$$

where the stress tensor components are calculated using Irving-Kirkwood [227] formalism given as given by Eq.3.2.

4.6 Results and Discussion

4.6.1 Experimental zero-shear viscosity

Figure 4.3 shows the shear viscosity versus shear rates up to 100 s^{-1} , obtained from experiments for the two types of P₄₄₄₄-AA WBLs and pure water. Table 4.2 shows the average viscosity value obtained from these experiments.

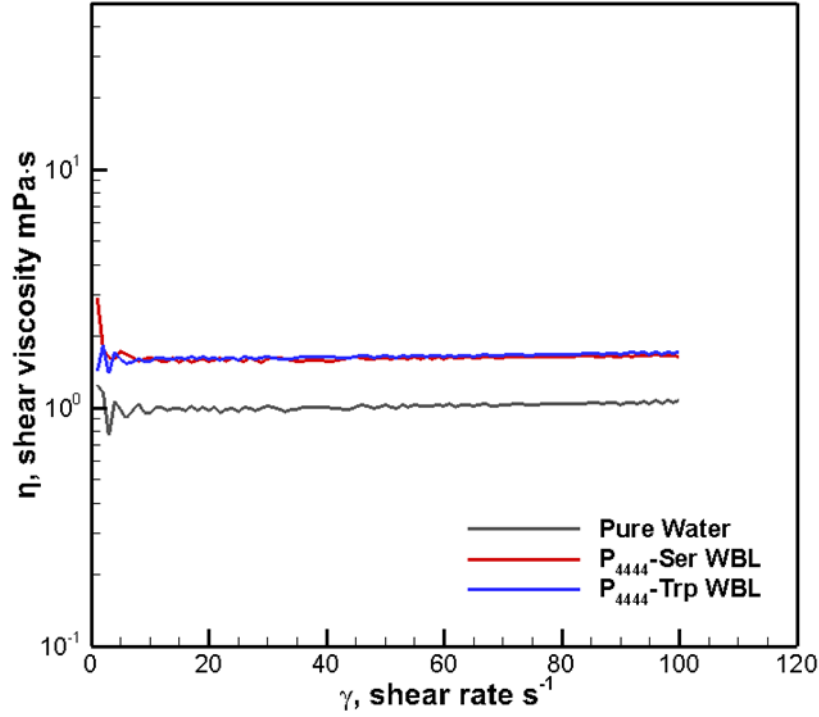


Figure 4.3: Shear viscosity versus shear rate (0 to 100 s^{-1}) for P_{4444} -Ser, P_{4444} -Trp AAIL WBLs and pure water

	Pure water	P_{4444} -Ser WBL	P_{4444} -Trp WBL
η_0 , Zero-shear Viscosity(mPa·s)	1.000±0.034	1.682±0.042	1.623±0.046
COF	0.183±0.011	0.153±0.008	0.121±0.007

Table 4.2: Shear viscosity measured from experiment and COF measured from simulations for P_{4444} -Ser, P_{4444} -Trp AAIL WBLs and pure water

The zero-shear viscosity (η_0) result of water from our experiments is 1 mPa·s, which aligns with the literature result [184]. The η_0 values of the two P_{4444} -AA WBLs are very close, with the P_{4444} -Trp WBL being only 2% lower than the P_{4444} -Ser WBL. The η_0 for both types of P_{4444} -AA WBLs is approximately 68% higher than that of water, suggesting that introducing the P_{4444} -AA additives increases water's viscosity. One of the limitations of using water as a lubricant is its low-viscosity nature. It can be easily squeezed out between two surfaces, making

it challenging to form a lubrication film [228]. Thus, the viscosity enhancement achieved by adding P₄₄₄₄-AA ILs indicates their potential as effective lubricant additives for water.

4.6.2 Coefficient of friction (COF)

The coefficient of friction (COF) was measured during the shear stage and plotted over time in Figure 4.4, and the average COF results are presented in Table 4.2. It shows that adding 10 wt% P₄₄₄₄-Ser and P₄₄₄₄-Trp in water significantly reduces COF by 16% and 34%. This suggests that AAIL additives effectively decrease friction, enhancing water's tribological properties. Interestingly, the COF for P₄₄₄₄-Trp WBL is considerably lower than P₄₄₄₄-Ser WBL. However, the experimental results from the rheological test in this study confirm that both AAIL WBLs have similar rheological behaviour. Our previous simulations have also shown that their rheological behaviour and zero shear viscosity are very similar [215]. Therefore, it is crucial to investigate the mechanism leading to their different tribological behaviour.

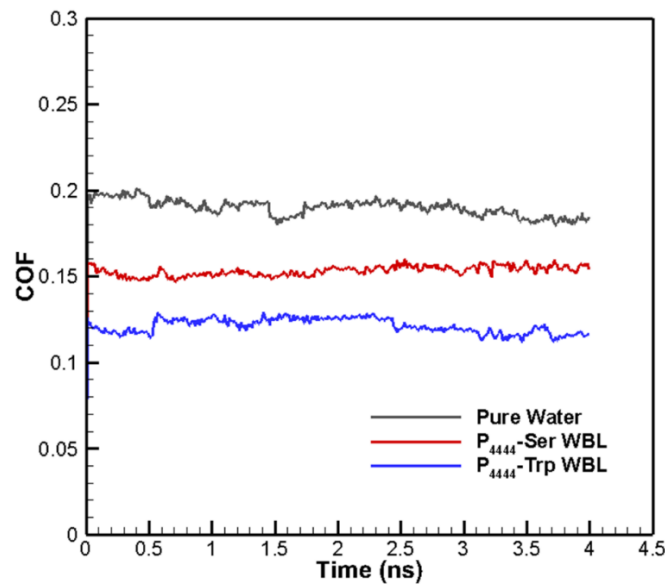


Figure 4.4: Coefficient of friction versus time for P₄₄₄₄-Ser, P₄₄₄₄-Trp AAIL WBLs and pure water

4.6.3 Tribochemistry analysis

The tribological behaviours are significantly influenced by the structure of the boundary film formed by the lubricant [225][229]. As shown from the simulation snapshots of both P_{4444} -Ser and P_{4444} -Trp WBLs in Figure 4.5, AA anions are observed to attach to the iron oxide surfaces. The formation of bonds between AA anions and ferrous atoms on surfaces facilitates this adsorption.

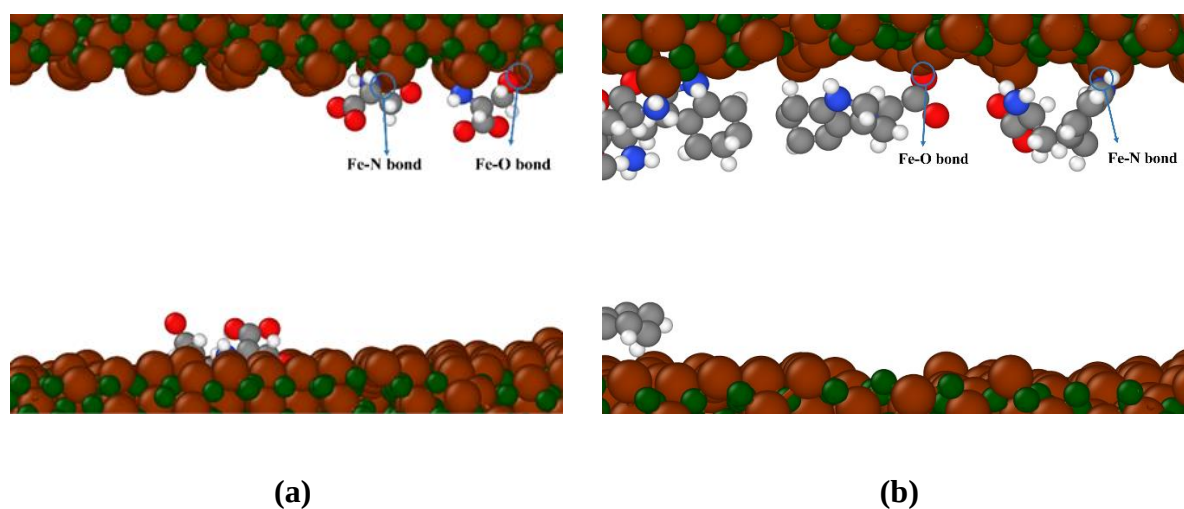


Figure 4.5: Snapshots of AA anions distribution for (a) P_{4444} -Ser and (b) P_{4444} -Trp WBLs. Only AA anions are shown here, and water molecules and P_{4444} cations are not shown for clarity.

The chemical absorption of Ser and Trp anions on the iron oxide surfaces contributes to the Fe-O and Fe-N bond formation, as shown in Figure 4.5. Fe-O bonds are formed between the ferrous atom on the surfaces and oxygen atoms from the carboxyl group of both types of AA anions. In addition, Ser anions contain the hydroxyl group, which includes an oxygen atom that also participates in bond formation with the ferrous atoms on the surfaces. The nitrogen atom of the amino group for both AA types contributes to the Fe-N bond formation. Furthermore, Fe-N bonds also are observed between the nitrogen atom in the imidazole ring and the ferrous atoms.

	Fe-O_{carboxyl}	Fe-O_{hydroxyl}	Fe-N_{amino}	Fe-N_{pyrrole}
Ser	0.5124±0.053	0.5942±0.019	0.7846±0.010	-
Trp	0.5531±0.040	-	0.7851±0.010	0.7948±0.012

Table 4.3: Average bond order of different Fe-O bonds and Fe-N bonds for Ser and Trp anions

Table 4.3 presents the bond order for different Fe-O and Fe-N bonds for both AA anions. It reveals that the bond order of Fe-O_{carboxyl} and Fe-N_{amino} for Trp anions is higher than that for Ser anions. Considering bond formation between the side chain group and surfaces, it is noteworthy that the bond order for Fe-N_{pyrrole} bond is approximately 34% higher than the Fe-O_{hydroxyl} bond order. The higher bond order indicates a higher bond strength, leading to better stability of formed bonds. It has been reported that the lone pair and π electrons of the nitrogen atom in the imidazole ring can coordinate with the d orbital of ferrous atoms to form more stable bonds [230][231][232]. Overall, comparing all Fe-O and Fe-N bond orders for these two types of AA anions, the bonds formed by Trp anions with the surfaces are more stable than those formed by Ser anions. It suggests that Trp anions form stronger chemical bonds with the iron oxide surfaces.

Figure 4.6 (a) illustrates the proportion of surface-adsorbed AA, which is calculated as the number of surface-adsorbed AA anions divided by the total number of AA anions in the lubricant. At the beginning of the shear stage ($t=0$ ns), 10% and 12% of Ser and Trp anions adsorbed with surfaces. This reflects the adsorption in the previous stage when compression was applied to the system. This indicates that compression has a very small effect on AA adsorption. The graph also shows that bond formation increased in the first 0.5 ns after shearing was applied to Trp anions. Then, the number of AA anions adsorbed with the surfaces is saturated and stable. At this stage, AA's stable chemically adsorbed layer on the surface is

formed. In comparison, the P₄₄₄₄-Ser WBL, takes a longer time of 1.2 ns to form a stable chemical adsorption layer.

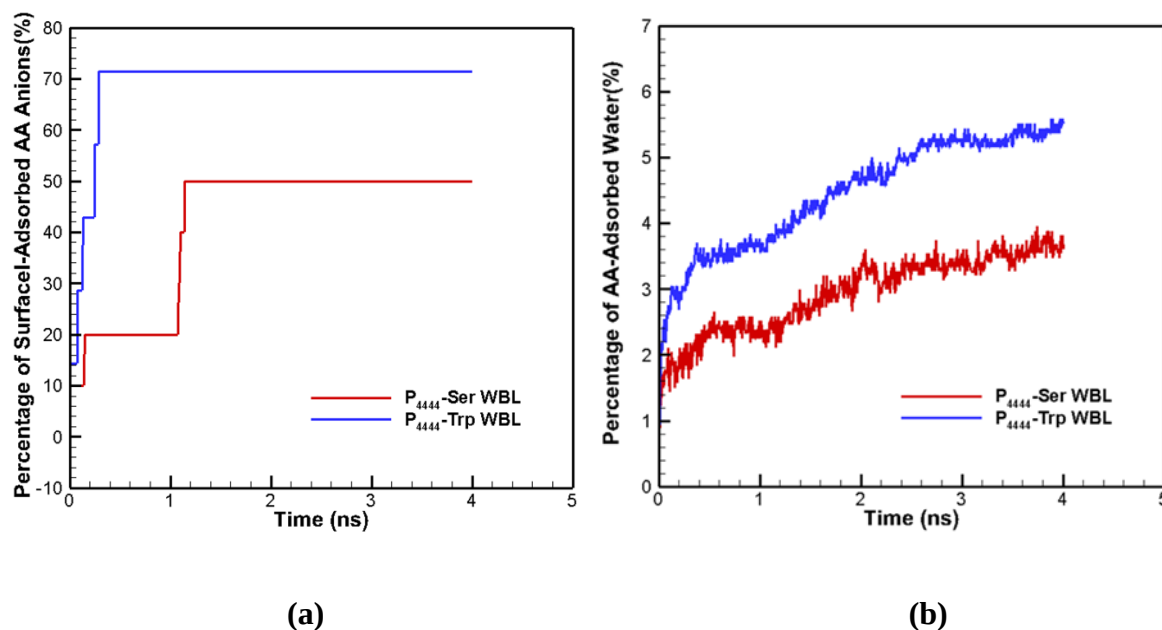


Figure 4.6: Percentage of (a) surface-adsorbed AA anions relative to the total quantity of AA (b) AA-adsorbed water molecules relative to the total quantity of water molecules for Ser and Trp anions

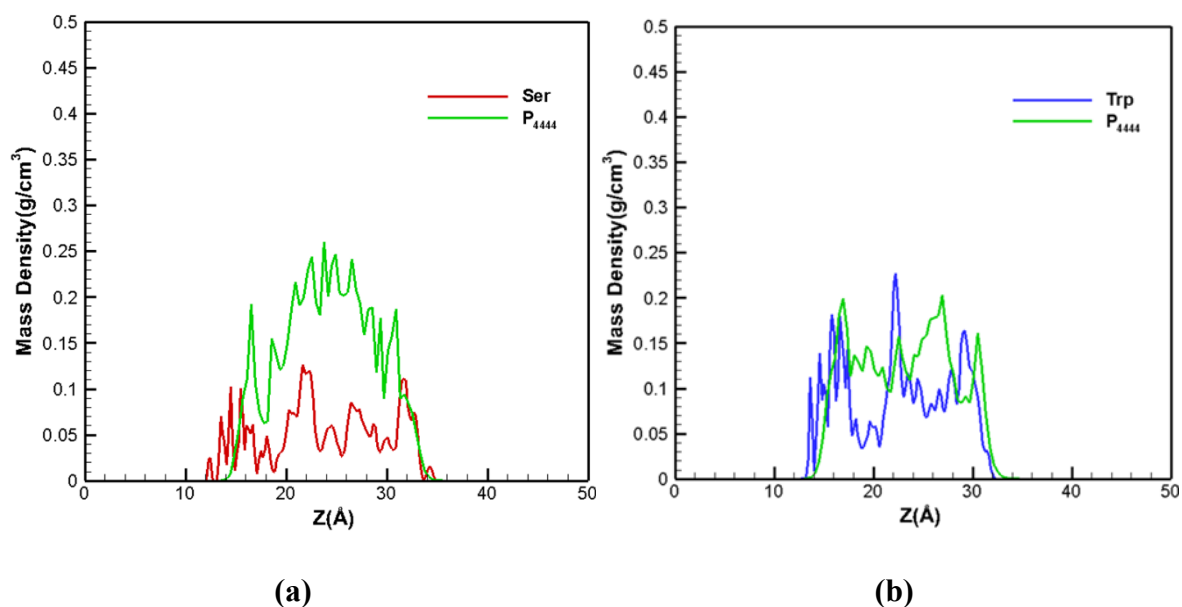
This suggests that the formation of the chemical adsorption layer for Trp anions is faster than that of Ser anions. Figure 4.6 also reveals that 50% of Ser anions and 71% of Trp anions adsorbed on surfaces eventually at the stable stage. The higher percentage for Trp anions indicates that they bond with iron oxide surfaces more readily than Ser anions. Besides the contribution of nitrogen atoms from the pyrrole ring, Trp has a much bigger molecular size due to a more extended side chain group composed of imidazole and benzene rings. This larger size and stronger surface attraction allow the Trp anions to reach the surfaces more quickly and form bonds. In summary, Trp anions can rapidly form more stable and denser chemical adsorption layers with iron oxide surfaces than Ser anions.

4.6.4 Structural analysis

It is essential to understand how all components are distributed within the lubricant and how they contribute to the tribological behaviour. The mass density distribution of AA, P₄₄₄₄ ions and water molecules provides valuable insights into the structure. The distribution of the AA anion and P₄₄₄₄ cation within the lubrication film is illustrated in the mass density profile shown in Figure 4.7.

For both AAIL WBLs, the AA and P₄₄₄₄ ions are initially distributed randomly, as shown in Figure 4.7 (a) and (b). However, the density profiles at the end of the simulation, shown in Figure 4.7 (c) and (d), indicate a significant change in the distribution of AA and P₄₄₄₄ ions. For both Ser and Trp anions, two regions of high local density can be observed, located close to iron oxide surfaces in the density distribution profile. Meanwhile, a lower concentration of AA anions is found in the middle layer of the lubricant film. Compared with the initial density distribution profile, it is evident that AA anions tend to migrate toward the boundary of iron oxide surfaces during the sliding process, forming boundary adsorption layers. As reported earlier, some AA anions have attached to the iron oxide surfaces through chemical bonding. Other AA anions are also drawn to the regions close to the iron oxide surfaces through the physical attraction, eventually forming boundary adsorption layers of AA anions. For P₄₄₄₄-Ser WBL, the upper and lower boundary adsorption layers are approximately 4Å thick. P₄₄₄₄-Trp WBL has a lower boundary adsorption layer of 4Å, which is similar to P₄₄₄₄-Ser, but the thickness of the upper boundary adsorption layer is approximately 10Å, which is much larger than P₄₄₄₄-Ser. A greater thickness of the upper adsorption film indicates a larger number of Trp anions adsorbed on the upper surface than on the lower surface. However, this imbalanced distribution of AA anions is mainly due to the limited quantity of AA anions within the lubricant. As mentioned, due to the significant computational demand of the Reactive MD simulation model, we are limited by the number of molecules in the system. We expect this asymmetry to

vanish for a very large number of molecules. This Trp-P₄₄₄₄ WBL has an overall thicker boundary adsorption layer of AA due to the side chain with pyrrole and benzene rings being much longer than the hydroxyl group of Ser anion. On the contrary, Figure 4.7 (c) and (d) show that most of the P₄₄₄₄ cations tend to move and then remain in the middle region of the lubrication film due to the repulsion from the iron oxide walls. The middle layer of lubricant, which contains P₄₄₄₄ cations for P₄₄₄₄-Ser WBL is approximately 4Å thicker than for P₄₄₄₄-Trp WBL.



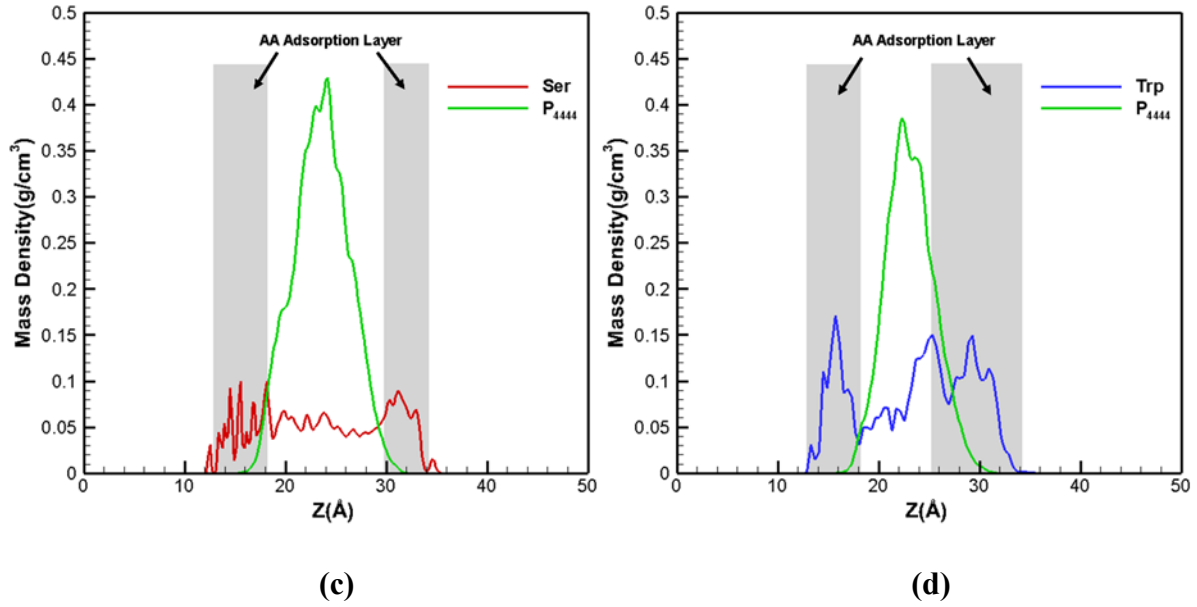


Figure 4.7: Mass Density profiles at $t=0$ before shearing for (a) Ser anion and P_{4444} cation (b) Trp anion and P_{4444} cation These profiles are shown at $t=4\text{ns}$ after shearing for (c) Ser anion and P_{4444} cation (d) Trp anion and P_{4444} cation for comparison. The AA adsorption layers are highlighted in grey.

Ultimately, the P_{4444} -AA lubrication film forms an AA- P_{4444} -AA layered configuration for both types. This layered configuration provides a high load support in the normal direction and prevents direct contact between the iron oxide friction pairs, which reduces friction and wear. In addition to the distribution of IL ions, water distribution in pure water and two AAIL WBLs has also been investigated and presented in Figure 4.8. The figure shows that pure water has a uniform distribution across the thickness.

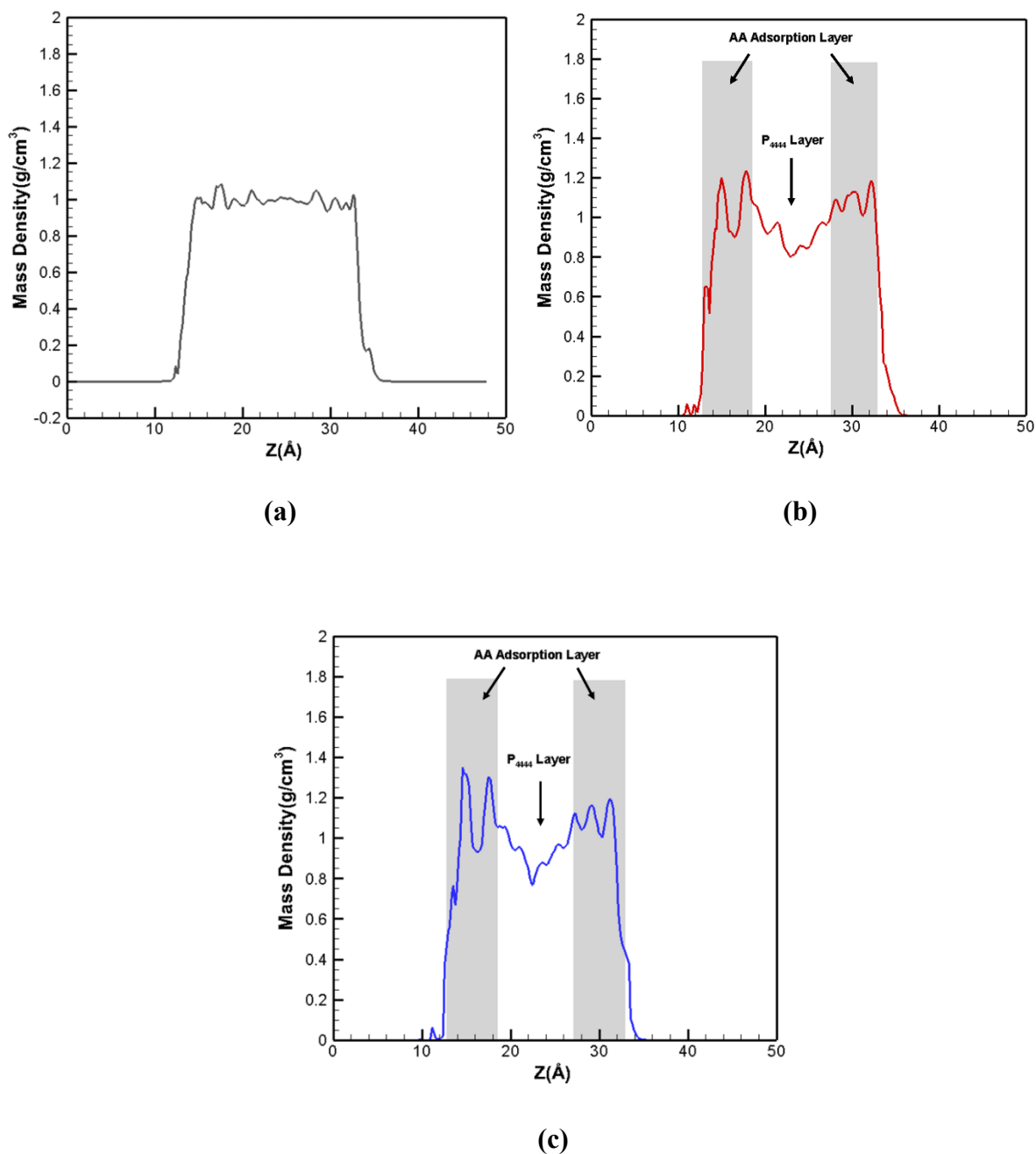


Figure 4.8: Mass density profile of water for (a) Pure water (b) P_{4444} -Ser WBLs (c) P_{4444} -Trp WBLs
(The AA adsorption layers are highlighted in grey)

However, water molecules in the AAIL WBLs exhibit a different distribution, with more water molecules located in the regions close to the surfaces and fewer in the middle region. The finding here, combined with the previously reported AA- P_{4444} -AA layered configuration, suggests that the regions with most AA anions also have a much higher density of water molecules, while the P_{4444} region has a lower density of water molecules.

Our previous study confirmed that AA anions attract surrounding water molecules in the AAIL WBLs and form hydration shells around them [215]. Figure 4.9 (a) shows the radial distribution function (RDF) between the oxygen atom of the carboxyl group from AA (O_{AA}) and the hydrogen atoms of water (H_w) for -Ser and P_{4444} -Trp WBLs. It indicates the distribution of H_w surrounding the central atom O_{AA} .

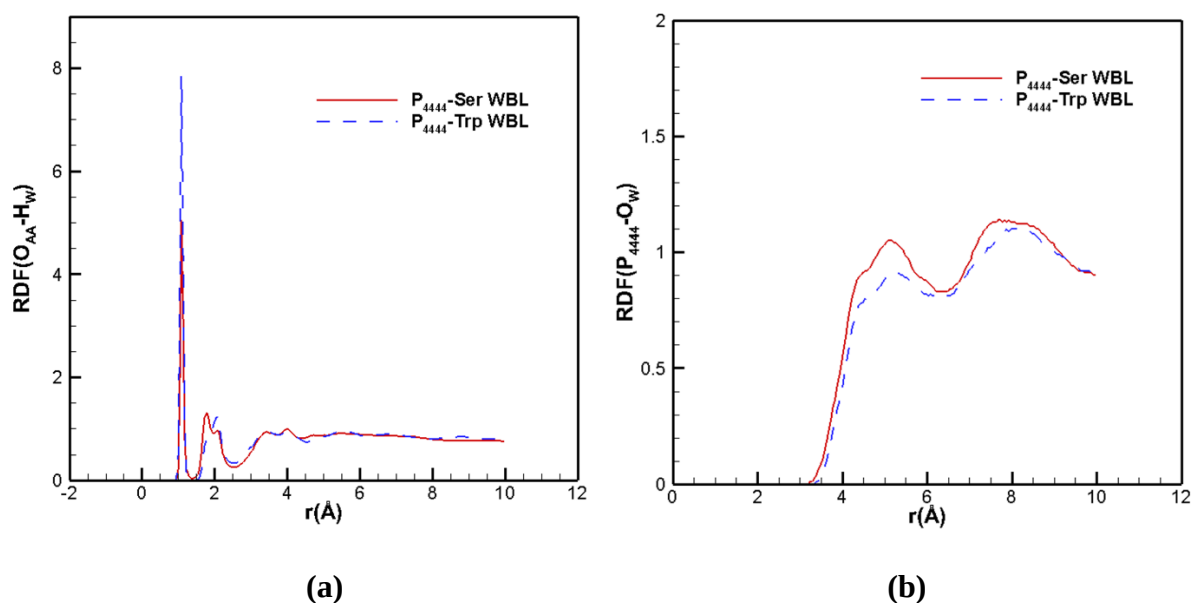


Figure 4.9: RDFs between (a) the oxygen atoms of the carboxyl group from AA (O_{AA}) and the hydrogen atoms of water (H_w), (b) the phosphorus atoms of P_{4444} and the oxygen atoms of water (O_w) (right) for 10 wt% P_{4444} -Ser and P_{4444} -Trp WBLs

For both types of AAIL WBLs, two sharp peaks can be observed at 1 $\text{\AA}$ and 2.2 $\text{\AA}$. These peaks define a two-layer hydration shell formed around AA anions. The absence of a third peak in the RDF evidences the liquidity of the P_{4444} -AA WBLs. The first peak of RDF has very high values, which indicate a strong interaction between AA anions and water molecules. Water molecules in this hydration shell layer are from both chemical bonding seen in Figure 4.6 (b) and the physical attraction that contributes to the second layer of hydration shell formation with the loosely bound water molecules. Figure 4.6 (b) shows that the percentage of AA-adsorbed water for Trp anions is about 33% higher than Ser anions, indicating that more water molecules

are involved from the first layer of the hydration shell for Trp anions. In contrast, Figure 4.9 (b) shows no well-defined peak between P_{4444} and water.

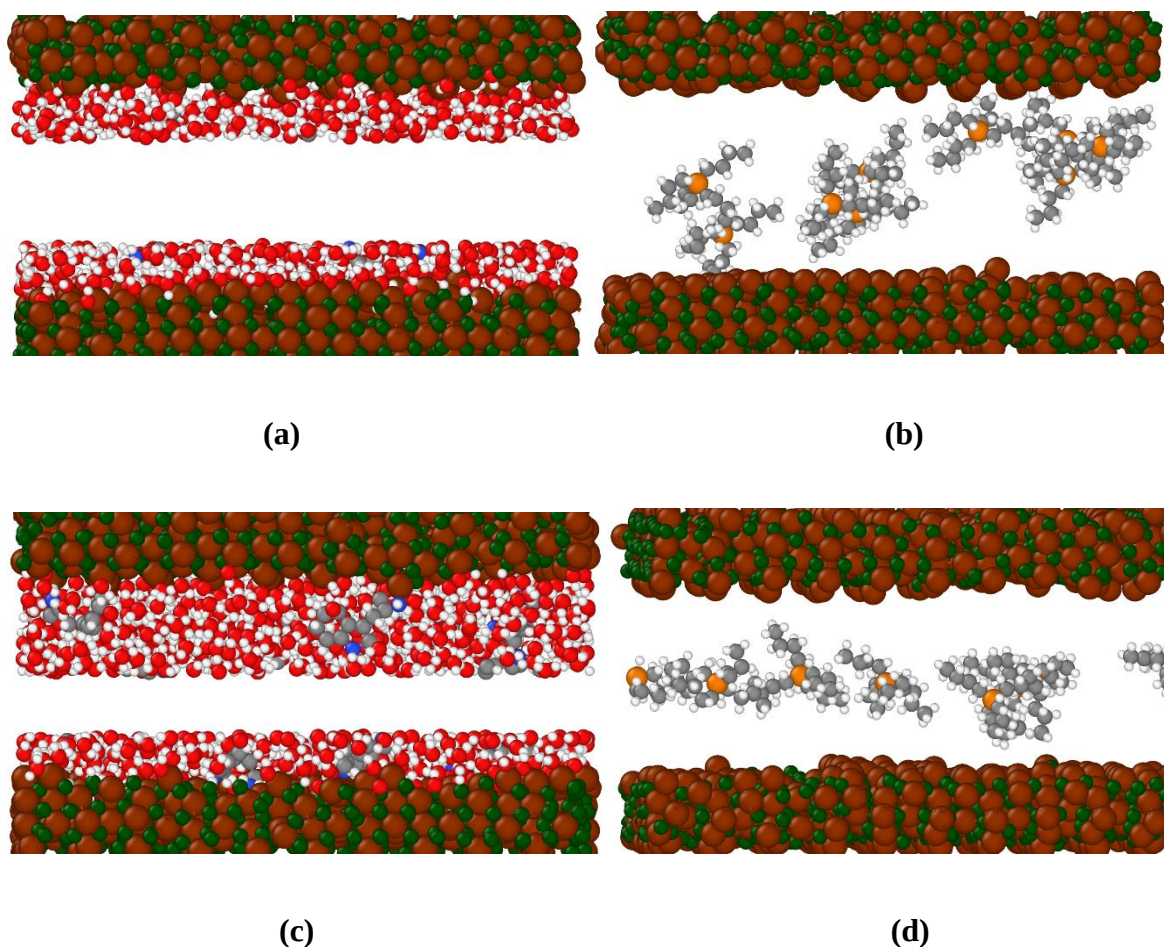


Figure 4.10: Snapshots of (a) hydrated AA adsorption layer, (b) Distribution of P_{4444} cations for P_{4444} -Ser WBL and (c) AA adsorption layer, (d) distribution of P_{4444} cations layer for P_{4444} -Trp WBL

The lack of hydration shell formation around P_{4444} cations aligns with what has been reported in the density profile of P_{4444} cations and water. P_{4444} cations have four long hydrophobic alkyl chains, resulting in fewer water molecules in the middle and a high-viscosity region. This P_{4444} layer acts as a load-supporting layer in the middle of the lubrication film. This ‘hydrated AA- P_{4444} -hydrated AA’ layered configuration can also be seen from the visualisation of the hydrated AA adsorption layers and the distribution of P_{4444} cations in Figure 4.10. This layered configuration that includes water molecules has been reported in a study by Ma *et al.* [233],

contributing to a superlubricity state enabled by hydration lubrication. Unlike most non-associating liquids, including organics and oils, water with higher density suppresses the tendency to solidify, making water maintain fluidity [234]. The adsorption of hydrated AA anions on the surfaces results in a higher density of water in regions near the surfaces, making those regions easy to shear. Furthermore, when AA anions surround water molecules and form hydration shells, the hydration water is reluctant to be squeezed out between sliding surfaces. This allows AAIL WBLs to sustain a large normal loads [234] [235]. The excellent fluidity of AAIL WBLs in response to shear and the ability to sustain large normal loads result in their low-friction behaviour.

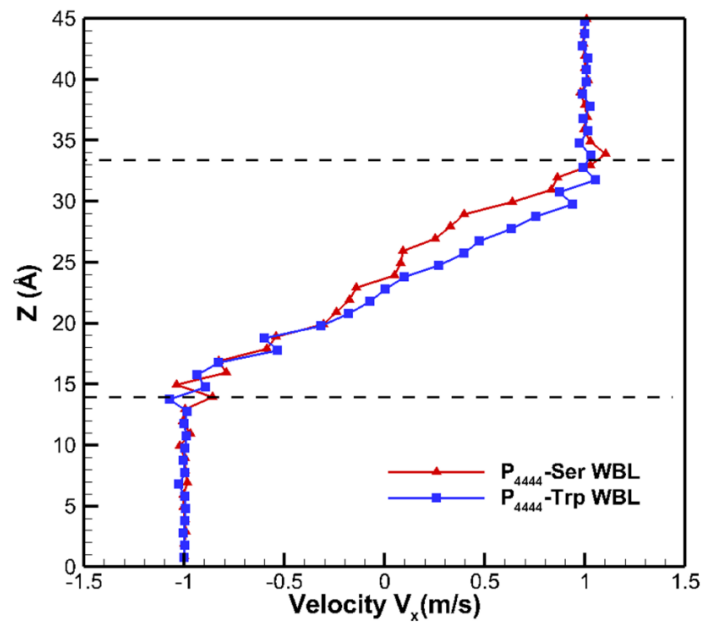


Figure 4.11: Velocity profile for P_{4444} -Ser WBL than P_{4444} -Trp WBLs (The interface between Iron Oxide surfaces and lubricant are marked)

In Figure 4.11, no noticeable velocity slip can be observed from the velocity profile of both WBLs. The chemical adsorption layers of AA on surfaces move with the surfaces, resulting in these no-slip conditions. The velocity profile close to the bottom surface for both WBLs is similar. However, the velocity at the layer close to the upper surface is higher for P_{4444} -Trp

WBL than for P_{4444} -Ser WBL. This observation supports the finding of a thicker upper chemical adsorption layer for P_{4444} -Trp WBL.

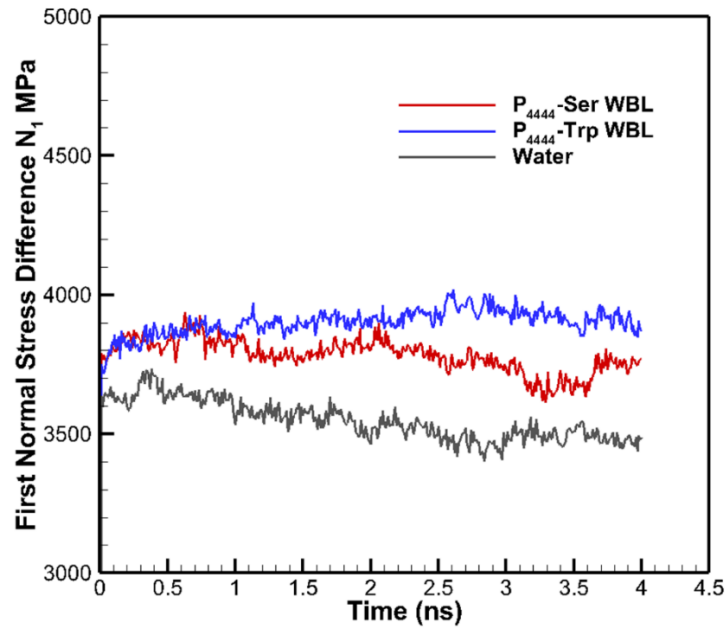


Figure 4.12: First normal stress difference (N_1) versus simulation time for pure water, P_{4444} -Ser and P_{4444} -Trp WBLs

Figure 4.12 shows the first normal stress difference (N_1) for P_{4444} -AA WBLs and pure water. The results reveal that P_{4444} -Trp WBL has the highest N_1 value, followed by P_{4444} -Ser and pure water. A higher N_1 implies more significant stress in the normal direction, indicating a better capability to separate two contacting surfaces. This suggests that P_{4444} -AA WBLs have a significantly better load-carrying capacity than water. Studies employing continuum-based models have discussed the net increase in the load-carrying capacity resulting from the finite increase in the normal stress difference [205] [206]. In our previous works, we also discussed the molecular origins of N_1 and its effect on the load-carrying capacity [114] [207] [208]. The layered configuration of P_{4444} -AA WBLs with a hydration lubrication mechanism is illustrated in Figure 4.13. It contributes to this enhanced load-carrying capacity. The P_{4444} -Trp WBL has a thicker AA adsorption layer and a thinner P_{4444} load-supporting layer, which results in a

stronger repulsive interaction between the AA adsorption layers, thereby sustaining a higher normal load [234] [235].

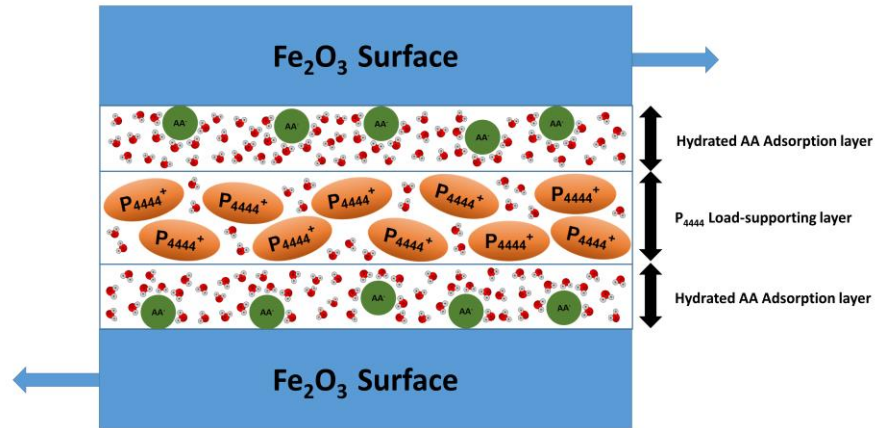
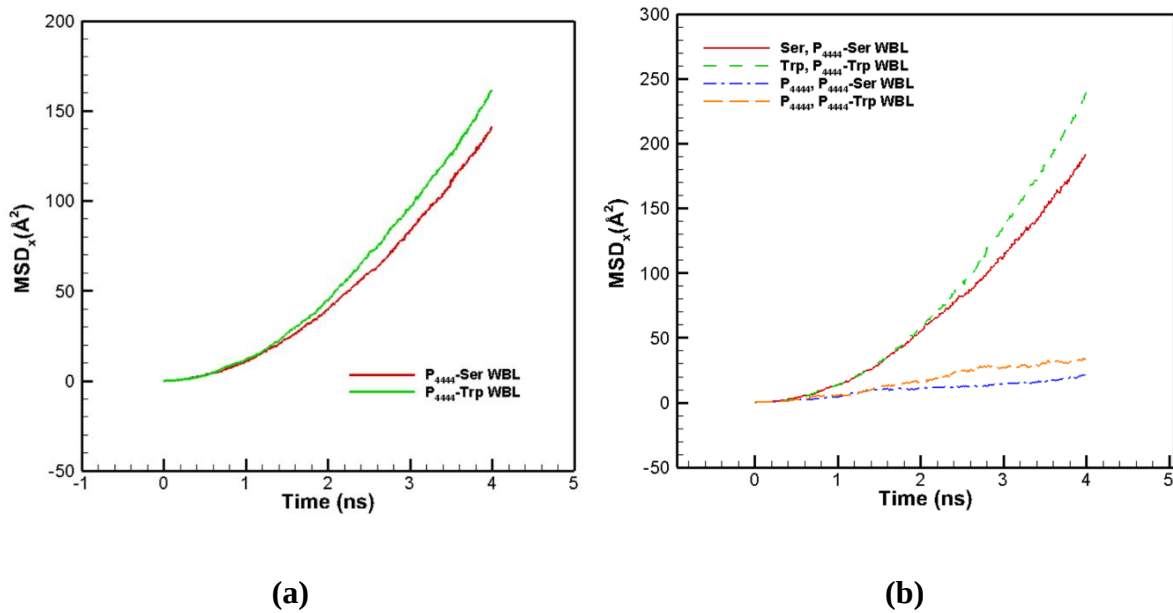
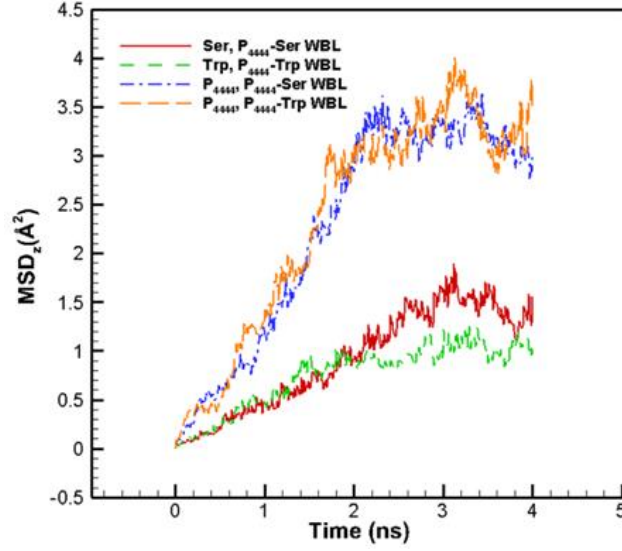


Figure 4.13: The layered configuration of P_{4444} -AA WBLs with a hydration lubrication mechanism

4.6.5 Mobility analysis

In the context of lubricants, investigating the movement of the IL within the lubricant is crucial. The mean square displacement (MSD) is calculated to understand the mobility of ILs.





(c)

Figure 4.14: (a) MSD in x-direction (MSD_x) for P_{4444} -AA WBLs (b) MSD in the x-direction (MSD_x) for AA anions and P_{4444} cations in both P_{4444} -AA WBLs (c) MSD in the z-direction (MSD_z) for AA anions and P_{4444} cations in both P_{4444} -AA WBLs

Figure 4.14 (a) and (b) presents the MSD plots in the x-direction, which describe the mobility of ILs in response to the shear. The MSD plots in the x-direction for the entire lubricant (including water) can be found in Figure 4.14 (a). The trend of increasing slope observed in all MSD plots in Figure 4.14 (a) and (b) indicates they exhibit active, directed motion, which is the shearing in the x-direction. In Figure 4.14 (a), the MSD_x for Trp- P_{4444} WBL increases faster than Ser- P_{4444} WBL, indicating a faster movement in the shear direction. This suggests that Trp- P_{4444} WBL encounters less resistance in response to shearing, leading to a smaller friction force and reduced friction [223]. It is interesting to notice in Figure 4.14 (b) that the MSD_x for Trp anions is higher than that for Ser anions. Despite the expectation that Ser anions, due to their smaller size and molecular weight, should exhibit superior mobility compared to Trp anions, the denser and stronger chemical adsorption films of Trp anions on iron oxide surfaces enhance the motion in the shear direction. Figure 4.14 (b) also shows that the MSD_x for P_{4444}

is significantly lower, proving the limited motion in the shear direction. P_{4444} cations remain in the middle layer of the lubricant, which is the low-velocity region without chemical adsorption on the surfaces. Meanwhile, the large molecular size of P_{4444} also restricts its x-direction motion. This supports the P_{4444} middle layer and serves as the load-supporting layer in the lubricant.

Unlike the x-direction, Figure 4.14 (c) demonstrates that the z-direction MSD for AA and P_{4444} ions initially increases linearly before reaching a plateau. This indicates that both AA anions moved freely until the motion was constrained in the z-direction. The plateaus in the MSD confirm the chemical and physical absorption close to the surfaces, which restrict the movement of AA anions in the z-direction. The plateau height for Trp anions is higher than that of Ser anions, suggesting that the larger molecular size and more substantial capability of surface attraction of Trp anions enable them to reach the surfaces more efficiently, which results in a smaller displacement in the z-direction. The MSD_z of Trp anions reaches the plateaus earlier than the Ser anions, indicating a faster formation of the layered configuration for P_{4444} -Trp WBL than P_{4444} -Ser WBL. For P_{4444} cations, the initial linear part of the MSD_z plot has a higher slope than that of AA anions, and the plateaus reach a much higher value. The absence of bond formation between P_{4444} cations and the surfaces results in a relatively unrestricted motion in the z-direction until the plateaus are reached. Therefore, the plateaus of MSD_z of P_{4444} cations confirm the formation of the layered configuration.

4.7 Conclusion

This study explored the tribological behaviour of two different types of AAIL WBLs. The rheological experiments showed that both AAIL WBLs possess a similar viscosity, which surpasses that of water. This indicates improved rheological properties when introducing AAILs as additives to water. The reactive MD simulation of tribological behaviour results reveal that AAIL additives significantly reduce the coefficient of friction for water. This

reduction also depends on the type of AA, showing much lower COF for P₄₄₄₄-Trp IL. These findings agree with earlier experimental reports [65] that showed P₄₄₄₄-Trp IL show lower COF than other AAILs. This highlights the superior tribological performance of AAIL WBLs. Detailed molecular mechanism analysis indicates that AA anions form a hydration shell with surrounded water molecules and have chemical adsorption with the iron oxide surfaces, while hydrophobic P₄₄₄₄ anions remain in the middle layer of the lubricant. This “hydrated AA-P₄₄₄₄-hydrated AA” layered configuration, in conjunction with the hydration lubrication mechanism, allows AAIL WBLs to sustain a significant normal load as evidenced by the higher first normal stress difference, and maintain the fluidity as demonstrated by better diffusion obtained from the MSD results. The formation of thicker and more stable hydrated AA adsorption layers for P₄₄₄₄-Trp WBL contributes to its superior tribological behaviour compared to P₄₄₄₄-Ser WBL. Overall, AAILs exhibit great potential as additives for WBLs to improve their tribological properties. The molecular mechanisms by which AAIL WBLs function as an exceptional lubricant could benefit future WBL formations and designs. The dependence of COF on the type of AA in the system suggests further work in this area by analysis of results for various AA systems to find suitable formulations for specific applications. We will pursue these studies in our future works.

Chapter 5: Investigation of AA Structure Effects on Tribological Properties of AAIL WBLs

5.1 Introduction

In previous chapters, the rheological behaviours of AAIL WBLs were explored, and the lubrication mechanism was revealed through MD simulations with experimental validation. AA anions tend to form hydration shells with water molecules and bond with metallic surfaces, creating easy-to-shear layers around the surfaces. Meanwhile, hydrophobic P₄₄₄₄ cations move to the middle region of the lubricant, interacting with fewer water molecules and forming a load-supporting layer. The formation of the "hydrated AA-P₄₄₄₄-hydrated AA" layered structure within AAIL WBLs contributes to the excellent tribological behaviours of water with AAIL additives. In Chapter 4, the comparison between water with P₄₄₄₄-Ser and P₄₄₄₄-Trp additives indicates that the type of AA anion significantly affects tribological behaviour. The molecular structure, size, and side chain group of the AA influence the adsorption layer formation, leading to distinct tribological behaviours of AAIL WBLs. There are twenty common types of AA that can potentially be used as AA additives. These AAs are distinguished by their functional groups on the side chain (R group), which impart different properties to them.

Additionally, the molecular sizes of AA have been found to affect the thickness of the adsorption layers, which in turn influences the tribological behaviour of AAIL WBLs. Therefore, investigating the effect of AA types on the tribological performance of AAIL WBLs is crucial. By comparing the performance of AAIL WBLs with different types of AA, the lubrication mechanism of AAIL WBLs can be explored in greater detail. A deep understanding of the influence of AA structure on the lubrication mechanism will provide valuable guidance for developing future high-performance WBL applications.

This chapter uses reactive MD simulations to investigate the tribological behaviour of metallic surfaces lubricated by water and with AAIL additives of different AA types. The mechanism of AAIL WBLs between metallic surfaces discussed in Chapter 4 has been further explored to understand the effect of AA structure on their tribological performance in this chapter.

5.2 Structure and Functions of AAs

As discussed in section 1.5 of Chapter 1, AAs have a basic structure consisting of a central α -carbon atom bonded to four groups: a hydrogen atom, an amino group, a carboxyl group, and an R-group (shown in Figure 1.1). While the hydrogen atom, amino group, and carboxyl groups are common to all AAs, the R-group is unique to each AA, distinguishing the 20 common types as shown in Figure 1.2. Based on the R-group, AAs can be classified into various categories. For example, some simple AAs have no actual functional groups in their side chain, such as glycine (Gly), valine (Val), alanine (Ala), leucine (Leu), and isoleucine (Ile). Other AAs are aromatic, with R-groups containing a benzene ring, such as phenylalanine (Phe), tyrosine (Tyr), and tryptophan (Trp). These R-groups impart characteristic properties to AAs. For instance, AAs with aliphatic and aromatic R-groups tend to exhibit non-polar and hydrophobic behaviours.

Conversely, AAs with R-groups containing an extra amino group demonstrate positively charged behaviour. However, these polar behaviours may change when AA molecules lose a hydrogen atom and become AA anions in ILs. Polarity is one of the most essential properties of ILs [240], especially in lubrication applications, because it plays an essential role in tribofilm formation.

To gain a comprehensive understanding of the effect of AA types on AAIL WBLs, nine different types of AA anions were selected for investigation. In addition to Serine (Ser) and Tryptophan (Trp), which were discussed in Chapter 4, Alanine (Ala), Glutamic (Glu), Histidine (His), Lysine (Lys), Proline (Pro), Phenylalanine (Phe), and Tyrosine (Tyr) were also chosen as AA types for AAIL WBLs.

5.3 Simulation Details

As discussed in previous chapters, classical non-reactive MD simulations are inadequate for accurately capturing the tribological behaviour of lubricants. To address this limitation, reactive MD simulations employing the ReaxFF force field were utilised for P₄₄₄₄-AA WBLs and pure water. The methodology of the ReaxFF force field has been detailed in Section 2.2.2 of Chapter 2. The modelling and simulation methods adopted in this study align with those employed in Chapter 4. The tribological model for all AAIL WBLs comprises two key components: the lubricant and the confining surfaces, which are essential for accurately representing their detailed behaviour.

The molecular structures of all AA anions and the P₄₄₄₄ cation were created using Avogadro [195]. The models for Ser, Trp, and P₄₄₄₄ have been previously prepared and presented in Figure 4.1 of Chapter 4. The remaining six types of AA anions and the P₄₄₄₄ cation are depicted in Figure 5.1. Detailed molecular information for all AA anions and the P₄₄₄₄ cation can be found in Table A1 in the Appendix.

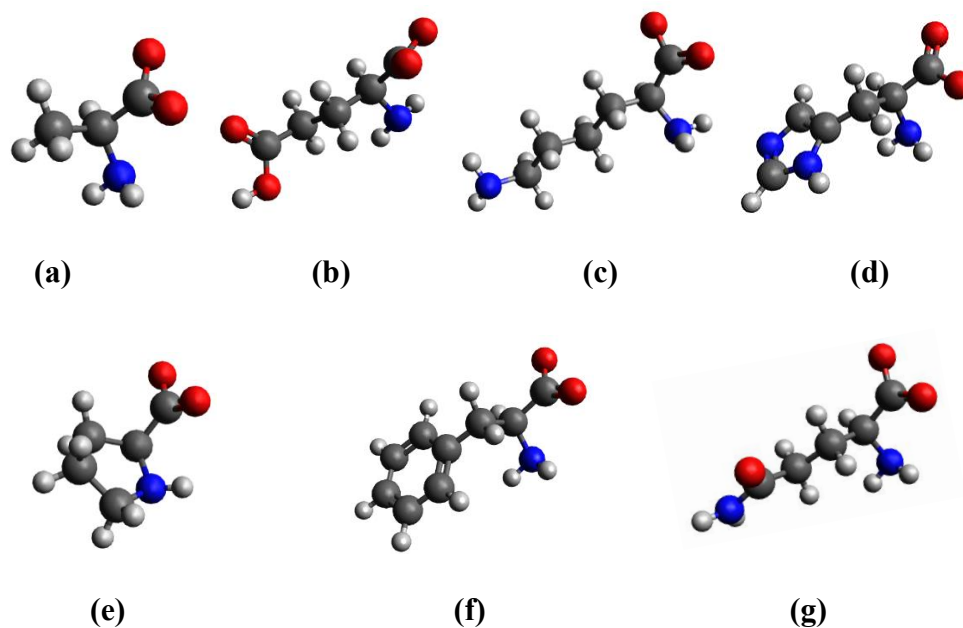


Figure 5.1: Structure of (a) Ala (b) Glu (c) Lys (d) His (e) Pro (f) Phe (g) Gln anion

All AAIL WBLs were formulated by packing water molecules, AA anions, and P₄₄₄₄ cations together at a concentration of 10 wt%. The specific quantities of water molecules, AA anions, and P₄₄₄₄ for 10 wt% P₄₄₄₄-Ser, P₄₄₄₄-Trp WBLs, and pure water are provided in Table 4.1 in Chapter 4. Similarly, the quantities for 10 wt% P₄₄₄₄-Ala, P₄₄₄₄-Glu, P₄₄₄₄-Lys, P₄₄₄₄-His, P₄₄₄₄-Pro, P₄₄₄₄-Phe and P₄₄₄₄-Gln WBLs are presented in Table 5.1.

	Number of Lubricant Atoms	Number of Water Molecules	Number of P ₄₄₄₄ - AA Pairs
10 wt% P₄₄₄₄-Ala	5316	1530	11
10 wt% P₄₄₄₄-Glu	5382	1602	8
10 wt% P₄₄₄₄-Lys	5425	1603	8
10 wt% P₄₄₄₄-His	4786	1425	7
10 wt% P₄₄₄₄-Pro	6145	1815	10
10 wt% P₄₄₄₄-Phe	4960	1476	7
10 wt% P₄₄₄₄-Gln	5390	1602	8

Table 5.1: The number of lubricant atoms and the number of water molecules and P₄₄₄₄-AA pairs for 10 wt% P₄₄₄₄-Ala, P₄₄₄₄-Glu, P₄₄₄₄-Lys, P₄₄₄₄-His, P₄₄₄₄-Pro, P₄₄₄₄-Phe and P₄₄₄₄-Gln WBLs

The WBL film was confined between two molecularly flat iron oxide (α -Fe₂O₃(0001)) surfaces, simulating the oxide layers of bearing steel that directly interact with the AAIL WBLs. The simulation box for all simulations measured 51 Å x 51 Å x 46 Å, consisting of two 13 Å thick Fe₂O₃ surfaces and a 20 Å confined WBL layer. For further details on the surface modelling, please refer to Section 4.4.2 of Chapter 4. The 10 wt% P₄₄₄₄-Ala WBL system contained a total of 11316 atoms within the simulation box, including 6000 atoms from the

wall, 4590 atoms from water, and 726 atoms from AAIL additives. Figure 4.2 in Chapter 4 provides an example of the simulation box configuration.

5.4 Simulation Procedure

All simulations were conducted by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The ReaxFF parameters employed in this chapter align with those used in Chapter 4. The ReaxFF parameters for P/C/H/O/N were adopted from the study by Zhang *et al.* [219], while those for interactions with iron oxide were adopted from the studies by Khajeh *et al.* [220] and Chia *et al.* [221]. A detailed discussion of the validation studies for these parameter sets can be found in Section 4.5 in Chapter 4.

Periodic boundary conditions were applied in the x and y directions, while a shrink-wrapped non-periodic boundary condition was used for the z direction. The desired temperature and pressure conditions were achieved by dividing the iron oxide surfaces into three layers, as presented in section 4.5 and demonstrated in Figure 4.2 in Chapter 4. Velocity and load were applied to the upper and lower rigid layers to maintain constant velocity and normal load. A Nosé–Hoover thermostat with a damping factor of 30 fs was applied to the thermostat layer to keep the temperature at 293.15 K, and an NVE ensemble with a Langevin thermostat was applied to the inner surface layers and lubricant. The simulation started with an energy minimisation stage using the Conjugate Gradient (CG) algorithm to minimise the total potential energy and interaction forces. Subsequently, uniformly distributed loads were applied to the upper and lower rigid layers of surfaces to compress the lubricant for 1 ns with a pressure of 500 MPa. After compression, the upper and lower rigid layers of surfaces slid in opposite directions at a constant velocity of 1m/s. The sampling processes, including collecting stresses, the coefficient of friction (COF), first normal stress difference (N_1), and mean squared displacement (MSD), followed methods that have been described in Section 4.5 in Chapter 4.

5.5 Results and Discussion

5.5.1 Coefficient of friction (COF)

The coefficient of friction (COF) was measured during the shear stage and plotted over time in Figure 5.2. The P_{4444} -Ser, P_{4444} -Trp WBLs and water were measured in Chapter 4. The average COF values for all P_{4444} -AA WBLs and water are presented in Table 5.2.

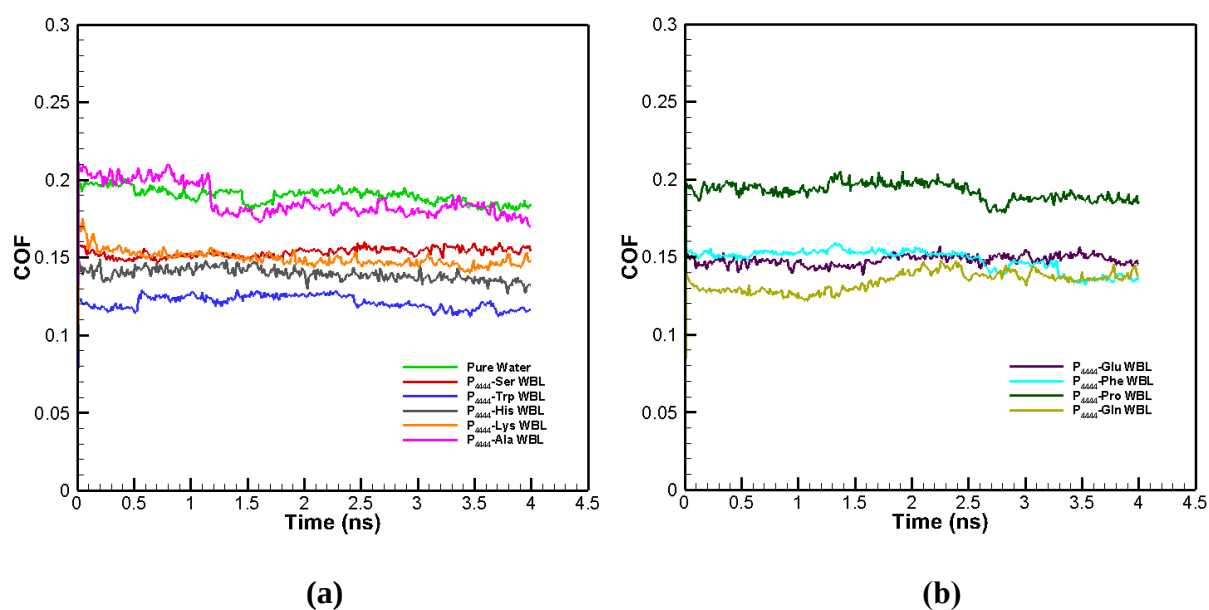


Figure 5.2: Coefficient of friction versus time for (a) pure water and P_{4444} -Ser, P_{4444} -Trp, P_{4444} -His, P_{4444} -Lys WBLs P_{4444} -Ala (b) P_{4444} -Glu, P_{4444} -Phe, P_{4444} -Pro and P_{4444} -Gln AAIL WBLs (P_{4444} -Ser, P_{4444} -Trp and water are from Chapter 4)

	Pure water	P_{4444} -Ser WBL	P_{4444} -Trp WBL	P_{4444} -His WBL	P_{4444} -Lys WBL
COF	0.183 ± 0.011	0.153 ± 0.008	0.121 ± 0.007	0.139 ± 0.008	0.149 ± 0.009
	P_{4444} -Ala WBL	P_{4444} -Glu WBL	P_{4444} -Phe WBL	P_{4444} -Gln WBL	P_{4444} -Pro WBL
COF	0.186 ± 0.014	0.1474 ± 0.008	0.147 ± 0.010	0.138 ± 0.009	0.192 ± 0.010

Table 5.2: Average COF for water and for P_{4444} -Ser, P_{4444} -Trp, P_{4444} -His, P_{4444} -Lys, P_{4444} -Ala, P_{4444} -Glu, P_{4444} -Phe, P_{4444} -Pro, P_{4444} -Gln AAIL WBLs and pure water (Results for P_{4444} -Ser, P_{4444} -Trp and water are from Chapter 4)

From Figure 5.2 and Table 5.2, it indicates that COF results for all P₄₄₄₄-AA WBLs and water, ranked from high to low, are P₄₄₄₄-Pro, P₄₄₄₄-Ala, water, P₄₄₄₄-Ser, P₄₄₄₄-Lys, P₄₄₄₄-Glu, P₄₄₄₄-Phe, P₄₄₄₄-His, P₄₄₄₄-Gln, P₄₄₄₄-Trp WBL. Notably, most types of P₄₄₄₄-AA WBLs exhibit lower COFs than water, with the exception of P₄₄₄₄-Pro and P₄₄₄₄-Ala WBLs, which exhibit COFs similar to those of water. Adding 10 wt% P₄₄₄₄-AA additives to water reduces the COF by 16% to 33% for all P₄₄₄₄-AA WBLs except P₄₄₄₄-Pro and P₄₄₄₄-Ala. Among these P₄₄₄₄-AA WBLs, P₄₄₄₄-Glu, P₄₄₄₄-Lys, P₄₄₄₄-His, P₄₄₄₄-Gln, and P₄₄₄₄-Phe WBLs exhibit COFs within the range of 0.138 to 0.149. Conversely, P₄₄₄₄-Trp WBL demonstrates a much lower COF value than all other types of AAIL WBLs and water, indicating its promising potential as a water additive for improving tribological behaviour. Chapter 4 delves into the superior tribological properties of P₄₄₄₄-Trp WBLs through tribochemistry, structure, and mobility analyses. By comparing P₄₄₄₄-Trp WBLs to P₄₄₄₄-Ser WBLs, the lubrication mechanism of P₄₄₄₄-Trp WBLs was analysed. A comprehensive analysis considering all types of P₄₄₄₄-AA WBLs is necessary for a more complete understanding of their lubrication mechanisms.

5.5.2 Tribochemistry analysis

The tribochemistry analysis presented in Chapter 4 showed clear evidence of chemical adsorption between Ser and Trp anions and iron oxide surfaces. This chemical adsorption indicates the formation of bonds between the AA anions and the iron oxide surfaces. Similar observations were noted for other types of AA anions interacting with iron oxide surfaces.

For all types of P₄₄₄₄-AA WBLs, the Fe-O and Fe-N bond formation contributes to the overall chemical adsorption of AA anions and iron oxide surfaces. The Fe-O bonds form between the ferrous atoms on the surfaces and the oxygen atoms of the carboxyl group (O_{carboxyl}) in all types of AA anions. Similarly, the nitrogen atoms of the amino group (N_{amino}) of all types of AA anions contribute to the Fe-N bond formation. The atoms on different side chains of AA anion

also affect their chemical adsorptions. The Ala anion, which has a methyl group side chain that lacks oxygen and nitrogen atoms, relies solely on O_{carboxyl} and N_{amino} for Fe-O and Fe-N bond formation. Likewise, the Phe and Pro anions have side chains with no oxygen or nitrogen atoms. In contrast, the oxygen atoms on the side chain of Glu and Gln and the nitrogen atoms on the side chains of Trp, His, Lys, and Gln are observed to participate in Fe-O and Fe-N bond formation.

	Fe-O_{carboxyl}	Fe-$O_{\text{R-group}}$	Fe-N_{amino}	Fe-$N_{\text{R-group}}$
Ser	0.5124±0.053	0.5942±0.019	0.7846±0.010	-
Trp	0.5531±0.040	-	0.7851±0.010	0.7948±0.012
His	0.5287±0.025	-	0.7911±0.011	0.7915±0.013
Lys	0.5136±0.032	-	0.7824±0.021	0.7911±0.011
Ala	0.4924±0.038	-	0.7848±0.016	-
Glu	0.5201±0.021	0.5813±0.015	0.7904±0.011	-
Phe	0.5432±0.016	-	0.7891±0.012	-
Pro	0.4901±0.071	-	0.7801±0.018	-
Gln	0.5373±0.024	0.5971±0.023	0.7876±0.018	0.7909±0.018

Table 5.3: Average bond order of different Fe-O bonds and Fe-N bonds for Ser, Trp, His, Lys, Ala, Glu, Phe, Pro, Gln anions (Results for Ser and Trp anions are from Chapter 4)

As presented in Table 5.3, the average bond order for different Fe-O and Fe-N bonds varies among different AA anions. Notably, the bond order for Fe-O bonds is significantly smaller than that for Fe-N bonds, indicating stronger Fe-N bond formation. Furthermore, the bond orders of Fe-O and Fe-N within the side chains are generally higher than that of $Fe-O_{\text{carboxyl}}$ and $Fe-N_{\text{amino}}$, suggesting a crucial role of side chains in forming strong chemical bonds with iron oxide surfaces. Among the AA anions, those with nitrogen atoms on their R-groups, such

as Trp, His, Lys, and Gln, exhibit significantly stronger bonding than others, forming more stable bonds with the surfaces. In contrast, Ala and Pro anions, lacking oxygen and nitrogen atoms on their side chains, which also demonstrate relatively smaller bond orders for the Fe- O_{carboxyl} and Fe- N_{amino} than other types, indicating weaker bonding with surfaces.

Figure 5.3 presents the proportions of surface-adsorbed AA vary between different types of P_{4444} -AA WBLs is calculated as the ratio of surface-adsorbed AA anions to the total number of AA anions in the lubricant. The variations in these proportions among different P_{4444} -AA WBLs are influenced by several factors, including the molecular sizes and structures, as well as the side chains of AA anions. Figure 5.3 reveals Trp and Gln anions exhibit the highest percentages of surface adsorption, reaching 71% at the end of the simulation. Notably, Trp anions quickly reach a saturated and stable state within 0.5 ns after applying shearing. Gln anions, while also reaching a saturated and stable state, require a longer time of 2 ns. In addition, Glu, Phe, Lys, Ser, and His anions have final surface-adsorbed proportions ranging from 50% to 58%. Both Trp and Gln have large molecular sizes with long side chain groups. With the shear applied to the lubricant, Trp and Gln anions easily reach the iron oxide surfaces during their migrations towards surfaces. The molecular size and long side chain groups of Trp and Gln anions facilitate their migration to the iron oxide surfaces during shearing, leading to higher surface adsorption percentages. This molecular size effect is also evident in other AA anions with relatively large molecular sizes and long side chains, such as His, Lys, Glu, Gln, and Phe. Conversely, AA anions with smaller molecular sizes, like Ala and Pro, demonstrate lower surface adsorption percentages of 39% and 26 %, respectively, due to their increased difficulty in reaching the surface despite the attraction forces. Higher percentages of surface adsorbed AA, such as Trp and Gln anions, mean they can form a denser chemical adsorption layer than other AA anions.

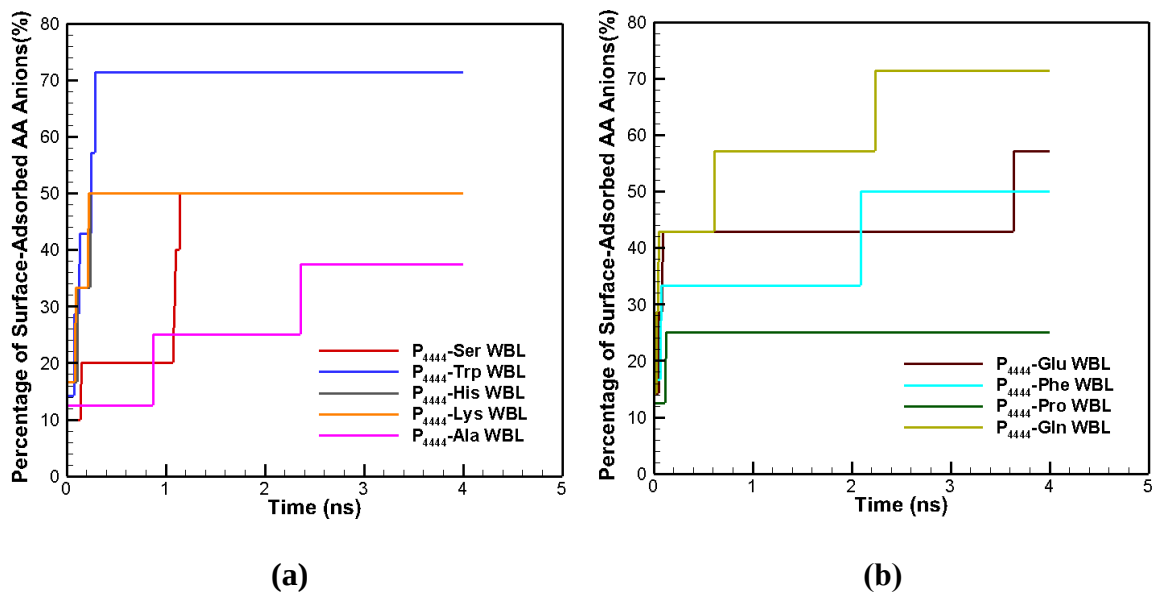


Figure 5.3: Percentage of surface-adsorbed AA anions relative to the total quantity of (a) AA for P_{4444} -Ser, P_{4444} -Trp, P_{4444} -His, P_{4444} -Lys and P_{4444} -Ala WBLs (b) P_{4444} -Glu, P_{4444} -Phe, P_{4444} -Pro and P_{4444} -Gln WBLs (Results for P_{4444} -Ser and P_{4444} -Trp WBLs are from Chapter 4)

In addition to molecular size, side chain components also influence bonding behaviour. As discussed previously, Fe-O and Fe-N bond formation contributes to the chemical adsorption of AA anions on iron oxide surfaces. While the O_{carboxyl} and N_{amino} participate in bond formation for all AA anions, the presence of oxygen or nitrogen atoms on side chains can enhance surface adsorption. For example, Ser anions, with an OH group on the side chain, exhibit relatively high surface adsorption proportions despite their small molecular size. Conversely, Ala and Pro anions, lacking oxygen and nitrogen atoms on their side chains, rely solely on O_{carboxyl} and N_{amino} for bond formation, resulting in lower surface adsorption percentages which can be observed in Figure 5.3. Although lacking oxygen or nitrogen atoms, the Phe anion's benzene ring side chain contains a large π -bond separation region with abundant lone pair electrons. These π electrons can coordinate with the chemical adsorption layer, potentially enhancing the surface adsorption of Phe anions [244]. The Trp anion, with both a benzene ring and an imidazole ring in its side chain, demonstrates even stronger chemical adsorption due to the nitrogen atom on the imidazole ring, as discussed in Section 4.6.3 in Chapter 4 [230][231][232].

The presence of nitrogen atoms on the side chains of AA anions, such as His, Lys, Glu, and Gln, also contributes significantly to their surface adsorption. For instance, Glu and Gln anions have similar structures, differing only by substituting one oxygen atom with an NH_3 group in Gln. The higher surface adsorption proportion of Gln compared to Glu highlights the importance of the nitrogen atom in enhancing chemical adsorption. The combined effects of molecular size and side chain composition determine the overall bond formation ability of AA anions. With their large molecular size and favourable side chain composition, Trp anions exhibit the best bonding characteristics among all AA anions.

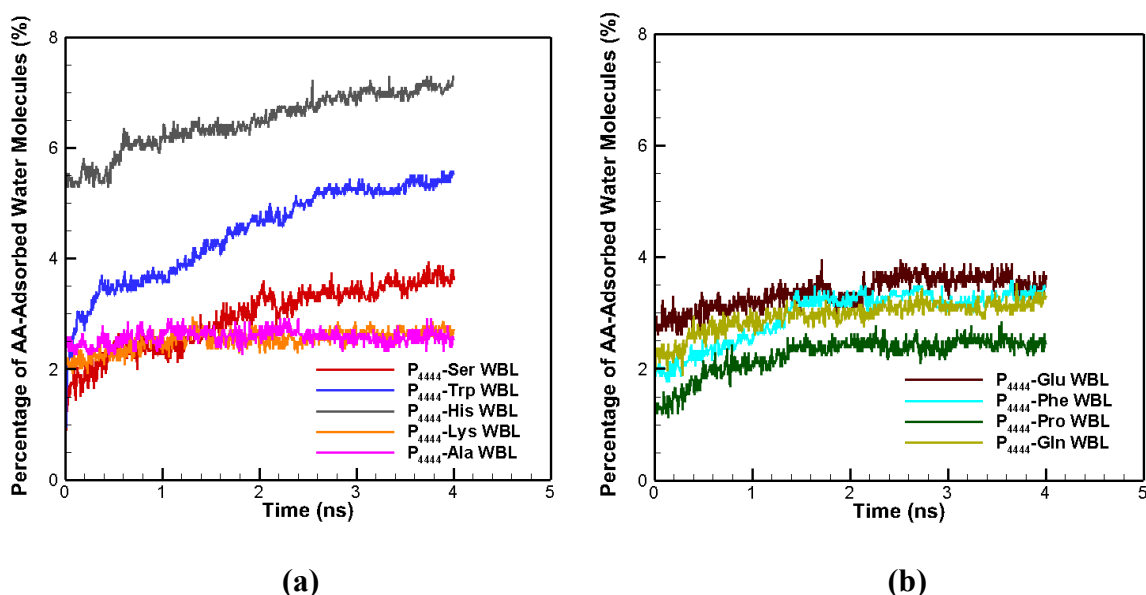


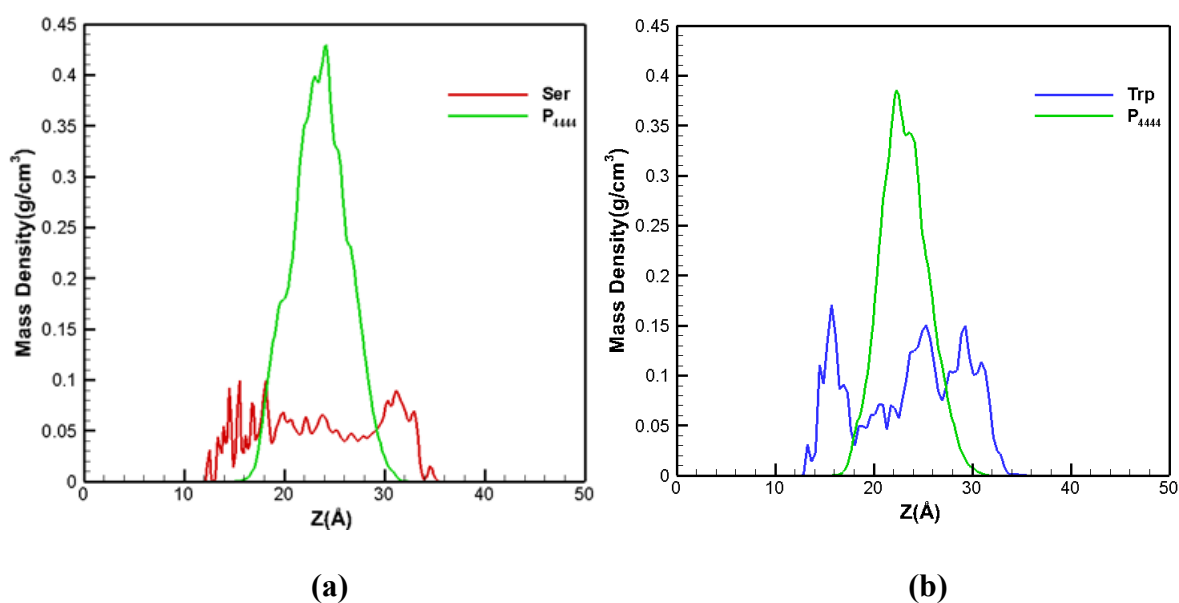
Figure 5.4: AA-adsorbed water molecules relative to the total quantity of water molecules for (a) Ser, Trp, His, Lys and Ala anions and (b) Glu, Phe, Pro and Gln anions (Results for Ser and Trp anions are from Chapter 4)

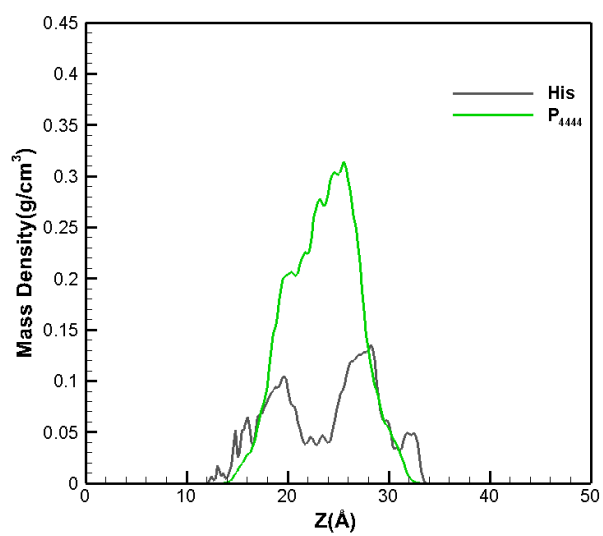
In Chapter 4, the hydration shell formation has been observed around Ser and Trp anions, which contribute to the formation of the low viscosity regions around the iron oxide surface and result in better tribological behaviour. In Figure 5.4, the percentages of AA-adsorbed water molecules for all AA types reflect their hydration shell formation. It shows that His and Trp anions have the highest percentages, significantly higher than the rest. Ser, Lys, Ala, Glu, Gln and Phe have similar percentages, indicating a similar hydration shell size. Pro anions have the lowest value,

which indicates a thin and weak hydration shell around them. For Trp anions, there is a very high proportion of AA adsorbed on surfaces. Combined with the dense hydration shell around Trp anions, lubricant regions close to surfaces have a higher density of water, resulting in low-viscosity regions that are easy to shear. The details of this mechanism, resulting in a low-friction property, have been reported in Chapter 4. On the contrary, the distribution is more random for anions with a small adsorption proportion, such as Ala and Pro. Combining the thin hydration shell observed on Ala and Pro, the AA-water layer in the lubricant structure is not well-defined in this structure, which contributes to the high COF results.

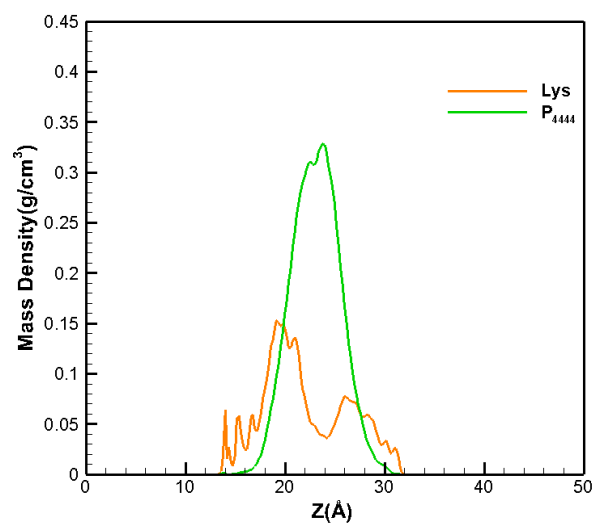
5.5.3 Structure analysis

In Chapter 4, the AA-P₄₄₄₄-AA layered configuration of the AAIL WBLs is identified through the mass density distribution of AA anions and P₄₄₄₄ cations for P₄₄₄₄-Ser and P₄₄₄₄-Trp WBLs. This layered configuration has also been identified for most other types of P₄₄₄₄-AA WBLs, as shown in Figure 5.5.

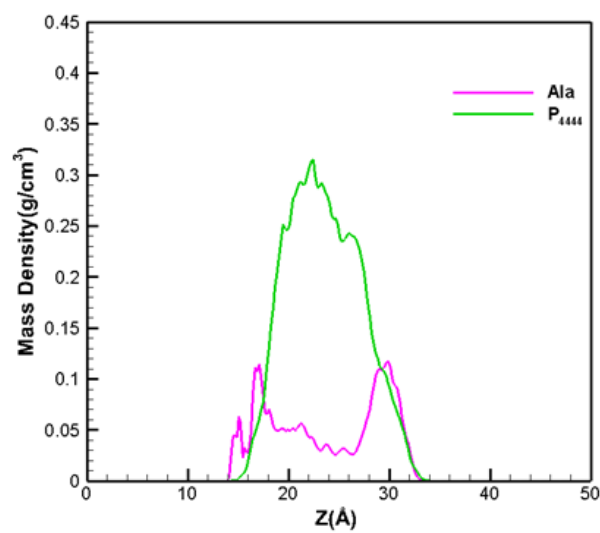




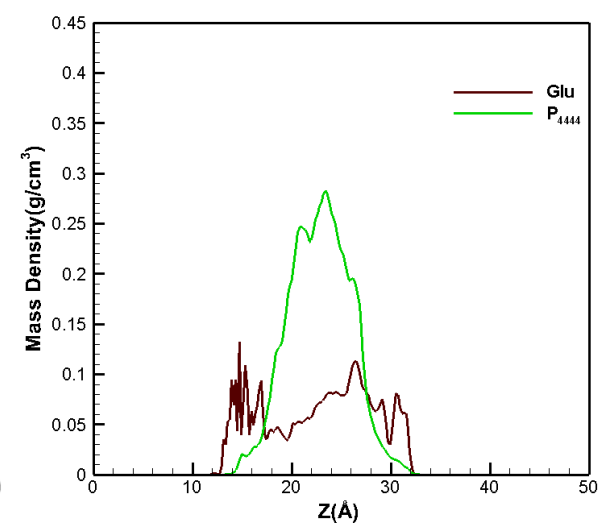
(c)



(d)



(e)



(f)

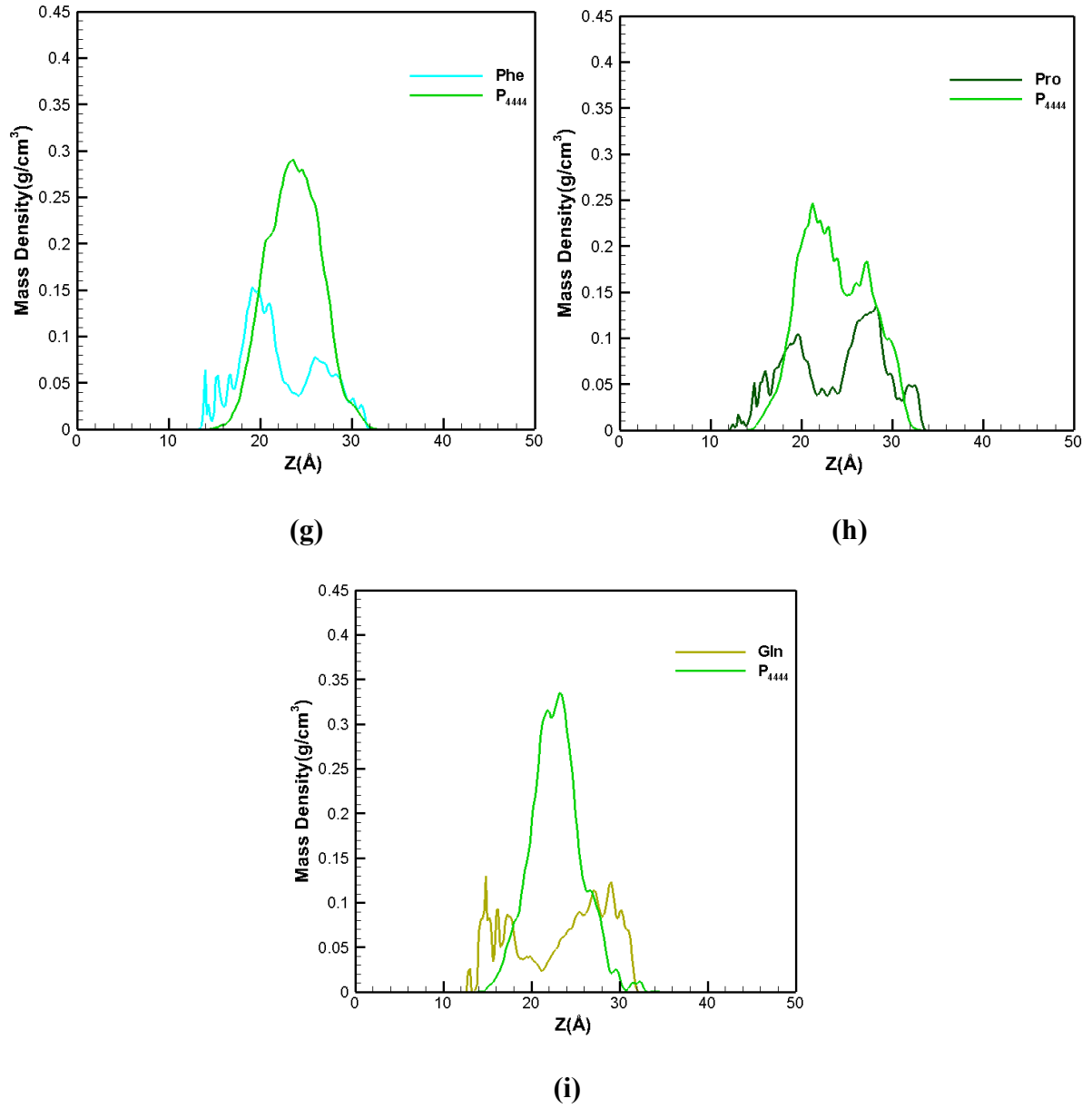


Figure 5.5: Mass density profiles of AA anions and P₄₄₄₄ cations at $t=4\text{ns}$ after shearing for (a)P₄₄₄₄-Ser (b)P₄₄₄₄-Trp (c)P₄₄₄₄-His (d)P₄₄₄₄-Lys (e)P₄₄₄₄-Ala (f)P₄₄₄₄-Glu (g)P₄₄₄₄-Phe (h)P₄₄₄₄-Pro (c)P₄₄₄₄-Gln WBLs anions (Results for Ser and Trp anions are from Chapter 4)

As discussed in Chapter 4, the layered configuration of the P₄₄₄₄-AA WBLs is identified through the high peaks of AA anions at the regions close to surfaces and the high P₄₄₄₄ cations in the middle region. The high peaks of AA anions near surfaces are due to the chemical and physical adsorption, and most of the P₄₄₄₄ cations tend to move and then remain in the middle region of the lubrication film due to the repulsion from the iron oxide surfaces. Figure 5.5

shows a difference in the thickness of AA adsorption layers and P_{4444} middle layers for different types of P_{4444} -AA WBLs. From comparing the thickness of layers, most of the P_{4444} -AA WBLs, for example, P_{4444} -Trp and P_{4444} -Glu, have a thin layer of P_{4444} middle layers, which also reflects thicker AA adsorption layers for them. These P_{4444} -AA WBLs tend to have low COF results. On the contrary, for P_{4444} -Ala WBLs, the AA adsorption layers are very thin, and P_{4444} middle layer is much thicker than the rest. Even the AA adsorption has been observed in the P_{4444} -Ala WBLs. The number of the adsorbed Ala has been reported to be very small previously. The small proportion of the adsorbed Ala on surfaces and the small size of Ala anions itself result in the thin layers of AA adsorption. For P_{4444} -Pro, it is clear that there are no well-defined peaks for either AA anions or P_{4444} cations, which do not form a clear layered configuration. The high COF values for P_{4444} -Ala and P_{4444} -Pro further confirm that the layered configuration contributes to reduced friction. It also indicates that more stable and thicker AA films can reduce friction.

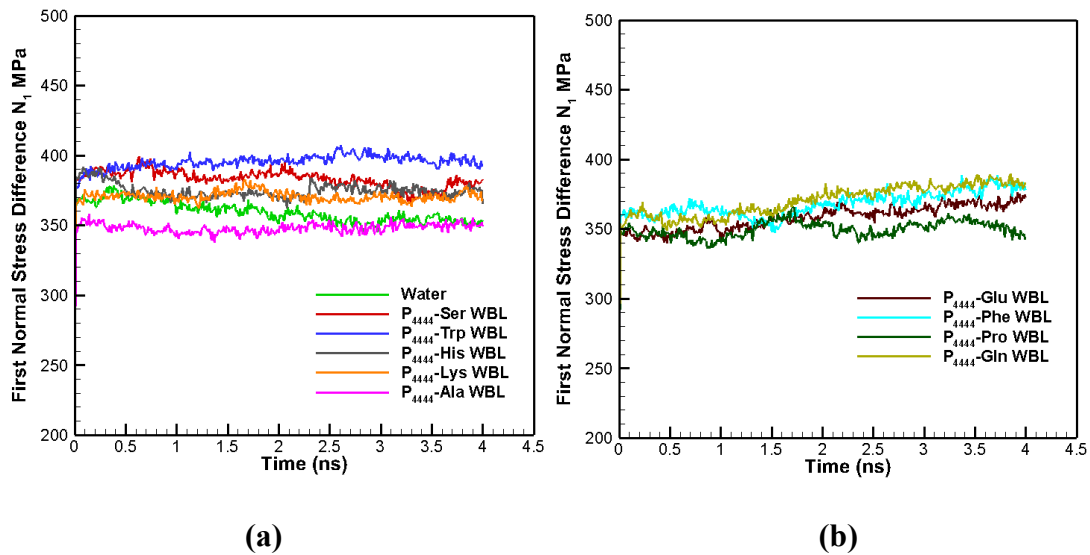


Figure 5.6: First normal stress difference (N_1) versus simulation time for (a) pure water, P_{4444} -Ser and P_{4444} -Trp, P_{4444} -His, P_{4444} -Lys, P_{4444} -Ala (b) P_{4444} -Glu, P_{4444} -Phe, P_{4444} -Pro and P_{4444} -Gln WBLs
(Results for pure water, P_{4444} -Ser and P_{4444} -Trp WBLs are from Chapter 4)

As discussed in Chapters 3 and 4, the first normal stress difference (N_1) can indicate a lubricant's load-carrying capacity. Figure 5.6 compares the N_1 values for AAIL WBLs and pure water. It shows that all types of AAIL WBLs exhibit higher N_1 values than water, except for Ala and Pro. Figure 5.5 illustrates that Pro anions are the only type that did not form a well-defined layered configuration. This further supports the hypothesis that the layered configuration of P₄₄₄₄-AA WBLs and the hydration lubrication mechanism contribute to their excellent load-carrying capacity. Previous chapters have highlighted that higher N_1 values in AAIL WBLs indicate better surface-separation ability, enabling them to sustain higher normal loads. By combining the information from Figure 5.5 and Figure 5.6, it becomes evident that P₄₄₄₄-AA WBLs with well-defined layered structures and thicker AA adsorption layers, such as P₄₄₄₄-Trp, P₄₄₄₄-His, and P₄₄₄₄-Gln, exhibit higher N_1 values compared to those with thin AA adsorption layers, such as P₄₄₄₄-Ala. This configuration allows for stronger repulsive interactions between the AA adsorption layers, enabling them to carry higher loads. Among all types of AAIL WBLs, P₄₄₄₄-Trp demonstrates the highest N_1 value, indicating the best load-carrying capacity.

5.5.4 Mobility analysis

In order to understand the movement of the lubricant, the mean square displacement (MSD) is calculated to understand the mobility of both anions and cations.

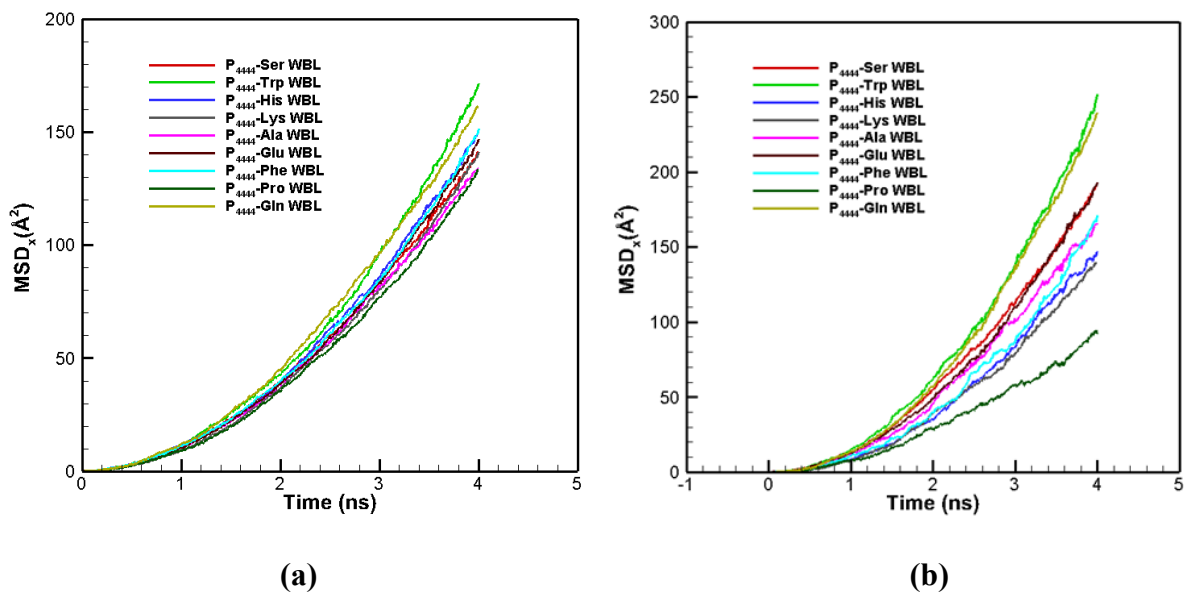


Figure 5.7: MSD in the x -direction (MSD_x) for (a) different types of P_{4444} -AA WBLs and (b) different types of AA anions (Results for P_{4444} -Ser and P_{4444} -Trp WBLs are from Chapter 4)

Figure 5.7 (a) presents the MSD plots versus time in the x -direction. Since the shear is applied in the x -direction, MSD_x represents the mobility of the entire lubricant. In Figure 5.7 (a), all AAIL WBLs exhibit an increasing slope in the MSD_x plots for the entire lubricant (including water). This increasing slope indicates active and directed motion in response to the shearing in the x -direction. Comparing the MSD_x plots for all AAIL WBLs, P_{4444} -Gln and P_{4444} -Trp WBLs exhibit the fastest increase, indicating the fastest movements in the shear direction. The remaining types, P_{4444} -Phe, P_{4444} -His, P_{4444} -Glu, P_{4444} -Ser, and P_{4444} -Lys WBLs, have similar increasing rates of MSD_x , which are slower than P_{4444} -Gln and P_{4444} -Trp WBLs. Finally, P_{4444} -Ala and P_{4444} -Pro WBLs exhibit the slowest increasing rates, reflecting the slowest movements in response to shearing. The fastest movement of P_{4444} -Gln and P_{4444} -Trp WBLs suggests they have the least resistance to shearing, resulting in the lowest friction force and reduced friction. Conversely, the slowest movements of P_{4444} -Ala and P_{4444} -Pro WBLs in the x -direction indicate resistance to shearing, exhibiting higher friction forces. As previously reported, P_{4444} -Trp and P_{4444} -Gln WBLs exhibit the lowest COFs, while P_{4444} -Ala and P_{4444} -Pro WBLs have the highest

COFs among all types. Therefore, the mobility behaviour of AAIL WBLs in the x-direction aligns with the COF results.

From the MSD_x results of AA anions, which are shown in Figure 5.7 (b), it is clear that Gln and Trp anions exhibit the highest increase rate, followed by Ser, Glu, Phe, Ala, His, Lys, and Pro anions. As discussed in section 4.6.5 of Chapter 4, AA anions with smaller size and molecular weight are expected to have superior mobility in the shear direction. However, the primary determinant of AA anion mobility is the chemical adsorption of AA anions on the surfaces. Previous sections have shown that Gln and Trp anions form the densest and strongest chemical adsorption films on iron oxide surfaces compared to other AA anion types. These chemical adsorption films enhance motion in the shear direction. Conversely, Pro anions demonstrate the poorest mobility in the shear direction, reflecting their lowest percentage of surface adsorption and lack of adsorption film formation. The connection between mobility in the shear direction and chemical adsorption film formation can also be observed in other AA anion types. This further confirms that chemical adsorption films reduce friction and improve tribological behaviours.

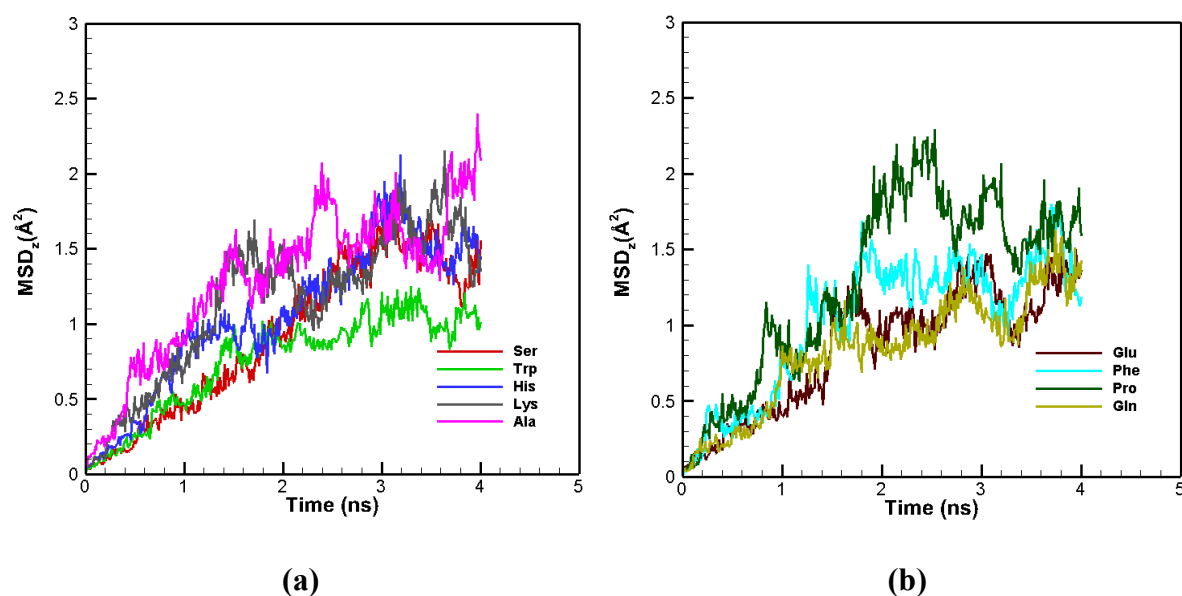


Figure 5.8: MSD in the z-direction for (a) Ser, Trp, His, Lys and Ala anions and (b) Glu, Phe, Pro and Gln anions (Results for Ser and Trp anions are from Chapter 4)

In Figure 5.8 (a) and (b), the z-direction MSD (MSD_z) for AA anions and P_{4444} cations shows distinct behaviour. For all types of AA anions, the MSD_z initially increases before slowly reaching a plateau. This indicates free motion in the z-direction for AA anions until their movement becomes constrained. As discussed in the previous chapter, chemical and physical adsorption on the surfaces restrict the movement of AA anions in the z-direction. In Figure 5.8, the height of the plateaus for AA anions with smaller molecular sizes, such as Pro, Ala, and Ser, is much higher than those with larger molecular sizes, such as Trp, Glu, and Gln. This suggests that AA anions with larger molecular sizes tend to reach the surfaces more easily. Additionally, these larger AA anions may also have stronger surface attraction, resulting in smaller displacements in the z-direction before reaching the surfaces and ultimately leading to lower plateau heights in MSD_z . Furthermore, MSD_z for AA anions with larger molecular sizes reached the plateau earlier, indicating the faster formation of the layered configuration reported in the previous section.

5.6 Conclusion

This chapter examines the tribological behaviour of AAIL WBLs for nine different types of AA anions to determine how the AA structure affects the tribological performance of AAIL WBLs. In the COF results, most types of P_{4444} -AA WBLs exhibit lower COFs than water, except for P_{4444} -Pro and P_{4444} -Ala WBLs, which exhibit COFs similar to those of water. P_{4444} -Trp WBLs demonstrate the best performance among all types of AAIL WBLs, indicating superior friction reduction capabilities. Comparing the AA adsorption from the tribochemistry indicates that the larger size and the presence of oxygen, especially nitrogen atoms, on the side chain group are the main contributors to AA adsorption. This results in AA anions such as Trp, Gln, and Glu having a higher surface-adsorbed percentage, while Ala and Pro anions have a very low value. This AA adsorption then further affects the formation of the "hydrated

AA-P₄₄₄₄-hydrated AA" layered configuration. P₄₄₄₄-Trp and P₄₄₄₄-Gln WBLs have a well-defined "hydrated AA-P₄₄₄₄-hydrated AA" layered configuration with a thicker AA adsorption layer, which results in better load capacity while maintaining good fluidity. Meanwhile, P₄₄₄₄-Pro and P₄₄₄₄-Ala are examples with an undefined layered structure or thin AA adsorption layer, leading to low load capacity. Overall, with the combined effects of larger size and the presence of a nitrogen atom in the side chain group for Trp anions, P₄₄₄₄-Trp WBLs exhibit the best tribological performance. Therefore, a comprehensive study on P₄₄₄₄-Trp WBLs is necessary to assess their feasibility as alternatives to existing oil-based lubricants in industrial applications.

Chapter 6: Investigation on the Optimised WBLs with AAIL Additives for Industrial Applications

6.1 Introduction

Previous chapters have explored the rheological and tribological properties of water-based lubricants containing various types of AAILs. The results consistently demonstrate that tryptophan (Trp) is the most promising AA type for enhancing the tribological properties of water. Trp anions form hydration shells with surrounding water molecules, forming thick adsorption layers near iron oxide surfaces. In contrast, the hydrophobic P₄₄₄₄ cations reside in the middle layer of the lubricant. This "hydrated Trp-P₄₄₄₄-hydrated Trp" configuration, combined with the hydration lubrication mechanism, enables water with P₄₄₄₄-Trp IL additives to sustain significant normal loads while maintaining fluidity.

As discussed in previous chapters, the primary motivation for researching AAIL WBLs is to develop environmentally friendly alternatives to traditional oil-based lubricants for industrial applications. Water-based lubricants containing P₄₄₄₄-Trp additives are fully sustainable and environmentally benign. Furthermore, preparing these WBLs is remarkably straightforward, rendering them suitable for large-scale industrial production. The P₄₄₄₄-Trp IL additives exhibit exceptional potential in reducing friction and enhancing the tribological properties of water-based lubricants. Given these strengths, further analysis of the feasibility of utilising P₄₄₄₄-Trp WBLs as lubricants in various industrial applications is warranted.

Industrial applications of water-based lubricants (WBLs) require careful consideration of various factors. Several industries have successfully implemented WBLs as substitutes for oil-based lubricants, as detailed in Section 1.4.2 of Chapter 1. Cutting fluids, indispensable for machining processes like milling, turning, grinding, and metal forming in the manufacturing industry, primarily serve as lubricants and coolants. [245][246]. Traditionally, cutting fluids have been categorised into two primary types: oil-based and water-based [247][248]. Oil-based lubricants from animal, vegetable, and mineral oils exhibit excellent lubricity [249][250]. However, their limited cooling capacity restricts their use to low-speed machining processes to

prevent fire hazards [251]. Traditional water-based cutting fluids are typically formulated by blending mineral or synthetic oils with water to achieve the desired concentration. [252]. The presence of water not only provides lubrication but also serves as an excellent coolant during machining processes. These combined advantages have led to the widespread adoption of water-based cutting fluids, which accounted for approximately 90% of the global cutting fluid demand in 2018. [253]. The high demand for water-based cutting fluids highlights their substantial potential for research and development.

Although water-based cutting fluids are defined as "water-based," they are not identical to the water-based lubricants (WBLs) studied in this research. Water-based cutting fluids can still have a negative environmental impact similar to oil-based cutting fluids due to their reliance on petroleum or mineral oils. Therefore, investigating the use of environmentally friendly WBLs as a replacement for traditional water-based cutting fluids is a promising avenue.

As a result of the investigation in the previous chapters, the AAIL WBLs, which are environmentally friendly, have shown the potential to improve the rheological and tribological properties. However, the tribological performance of AAIL has not yet been benchmarked with the existing water-based cutting fluids. Therefore, it is essential to identify the necessary modifications and optimisations to ensure that WBLs can achieve the tribological performance of existing industrial water-based cutting fluids.

Furthermore, other properties must be considered. For instance, corrosion is a significant challenge for water-based cutting fluids in practice. However, the corrosion behaviour of AAIL WBLs remains unclear. Therefore, it is crucial to investigate the corrosion properties of AAIL WBLs and explore optimisation strategies to minimise corrosion.

To further enhance the tribological performance of AAIL WBLs, adjusting the concentration of AAIL additives could be a promising strategy. As demonstrated in Chapter 3, increasing the concentration of AAIL led to increased water viscosity. Additionally, some studies have

indicated that higher concentrations of ionic liquids (ILs) can improve the tribological performance of WBLs. Most studies on oil-based lubricants with ionic liquid (IL) additives employ relatively low IL concentrations, typically ranging from 0.5 wt% to 5 wt%. This is primarily because oil-based lubricants often possess excellent tribological performance, requiring only small amounts of additives to enhance their properties [254] [255] [256] [257]. As a relatively new field compared to oil-based lubricants, researchers have followed similar trends and studied the effects of low concentrations of ionic liquid (IL) additives on water-based lubricants (WBLs). These studies have generally shown that even small concentrations of IL additives can significantly improve the tribological behaviour of water [55] [56] [58] [259] [260]. However, these studies rarely address whether the improvement in tribological performance is sufficient to make these WBLs viable replacements for oil-based lubricants in practical applications. In this chapter, AAIL WBLs with a range of different concentrations are investigated to assess their suitability.

Introducing other environmentally friendly additives to the current AAIL WBLs is an alternative approach to further enhance tribological performance. Among the additives studied for WBLs in recent years, glycerol appears to be a promising option.

Glycerol is the simplest triol [261] and belongs to the alcohol family of organic compounds. Figure 6.1 shows that glycerol's structure consists of three hydroxyl groups (-OH) attached to carbon atoms. As a byproduct of biodiesel production, glycerol is abundant and relatively inexpensive [262][263][264]. It has diverse applications in various industries, including food, medical, pharmaceutical, personal care, and cosmetics [265]. Glycerol's nontoxicity, edibility, and biodegradability make it suitable for food and medical applications. In pharmaceuticals, it is used as a solvent, to increase pill humidity, and to thicken liquid drugs [264]. Typical medical applications include cough syrups and ear infection medications [266]. Glycerol's hydrophilic chemical structure provides lubrication and is a humectant in personal care products like skin

and hair care items [266]. Additionally, glycerol possesses properties such as non-flammability, excellent cooling ability, low pressure-viscosity coefficients, and high polarity [267][268]. Given its favourable properties, glycerol has been considered a promising alternative to petroleum-based and mineral oils in many industrial tribological applications, including hydraulic fluids, metalworking fluids, and transport chain lubricants [269][270][271][272].

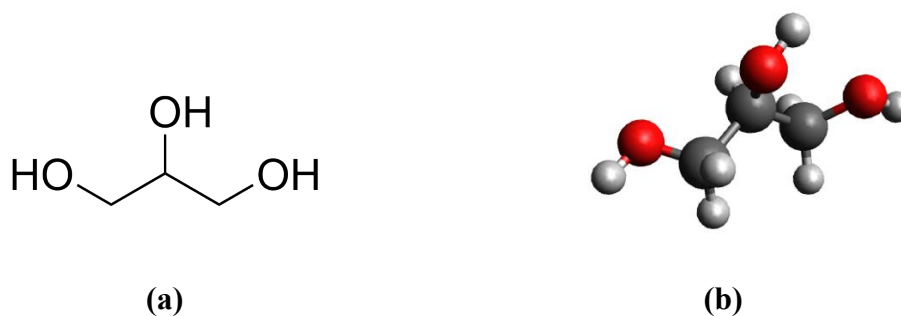


Figure 6.1: (a) The chemical structure of glycerol (b) The 3D structure of glycerol

In a study conducted by Gelinski *et al.*, a biocide-free hydraulic fluid was developed and tested, consisting of a mixture of glycerol, water, and carboxymethyl chitosan (CMC). Long-term tests demonstrated the excellent technical performance of this novel glycerol/water/CMC hydraulic fluid [269]. In the study by Wichmann *et al.*, the focus was on investigating environmentally friendly glycerol-based metalworking fluids (MWFs). The results demonstrated that glycerol/water solutions with a concentration higher than 35% do not require the addition of biocides to achieve optimal performance. Furthermore, glycerol-based MWFs appear economically competitive with traditional petroleum and mineral oil-based lubricants [270]. In their study, Shi *et al.* [271] investigated glycerol aqueous solutions as green lubricants. The tribological performance of these solutions was benchmarked against rapeseed oil. The coefficient of friction (COF) results demonstrated that glycerol aqueous solutions exhibited significantly lower COFs compared to rapeseed oil, highlighting their promising potential as green lubricants [271]. In the study by Le *et al.*, the tribological properties of glycerol were investigated using aluminium nanoparticles as an additive and sodium dodecyl sulphate (SDS)

as the dispersive medium for iron-iron contacts. The results demonstrated a significant reduction in surface roughness due to the introducing of aluminium nanoparticle additives [272].

Given the promising results from existing studies on glycerol's lubrication properties, it is worthwhile to investigate how the introduction of glycerol might affect the tribological performance of AAIL WBLs. Furthermore, it is essential to study the performance of this lubricant under various conditions, including load, velocity, temperature, and different contacts. In industrial-scale applications of WBLs, operations often involve a wide range of velocities and pressures, which play crucial roles in the tribological performance of WBLs. The velocity of the interacting surfaces can affect lubrication performance. For example, high velocities can lead to increased shear viscosity, especially when the gap between the confining slabs approaches nanometer thickness under high pressures and shear rates [217]. Additionally, the sliding velocity of the tribo-pair determines the lubrication regime, significantly affecting lubrication performance [237][238]. Besides sliding velocity, pressure is another critical factor influencing lubrication performance. In some industrial applications, operations are carried out under extreme pressure conditions. High pressures can lead to the ordering of molecules at the solid surface and density oscillations within the oil film [6]. Moreover, water-containing lubricants have been reported to exhibit significantly lower pressure-viscosity coefficients compared to traditional lubricants [239].

In this chapter, the rheological and tribological performances of using both pure water and the glycerol aqueous solution as the based lubricant with AAIL additives are studied under different conditions by experiments. The performances are benchmarked against existing industrial lubricants. Ultimately, optimised AAIL WBLs are suggested for industrial applications.

6.2 Experimental Details

6.2.1 Lubricant preparation

Given the exceptional lubrication performance of P₄₄₄₄-Trp ionic liquid (IL) as an additive for water demonstrated in previous chapters, it was selected as the type of AAIL additive for this study. The lubricant preparation method followed the previous work by Yang *et al.*

[65]. Two base lubricants were used: pure water and glycerol aqueous solutions. Distilled water was used as the pure water source, while glycerol aqueous solutions were prepared by adding glycerol (Sigma-Aldrich, St.Louis, MO, USA, ReagentPlus[®], ≥99.0% (GC)) to distilled water to achieve specific concentrations and then mixing until complete dissolution. AAIL additives were prepared by adding L-Tryptophan (Sigma-Aldrich, St.Louis, MO, USA, ≥ 98% (HPLC)) into Tetrabutylphosphonium hydroxide (Sigma-Aldrich, St.Louis, MO, USA, 40 wt %) to create an equimolar solution. The P₄₄₄₄-Trp IL solution was then added to the base lubricants to achieve the desired final concentration. The final lubricant solution was stirred for 24 hours. Pure water samples and 10 wt% glycerol aqueous solution samples without AAIL additives were prepared as reference groups to investigate the effect of AAIL additives. Additionally, HOCUT[®] 795 MPB, a metal cutting fluid developed by Houghton Australia Pty Ltd, was used as a benchmark for lubrication performance. This cutting fluid is suitable for high-speed CNC machines and high-pressure coolant applications. It is recommended to be mixed with water at a ratio of 20:1 (5%) to 10:1 (10%) for machining applications. Therefore, 5% and 10% HOCUT[®] 795 MPB solutions were prepared. For the final lubricants, a 10 wt% glycerol aqueous solution was selected as the water/glycerol lubricant (WGL) base lubricant. A 50 wt% WGL was prepared as a comparison group for five different concentrations of P₄₄₄₄-Trp IL additives were also prepared: 1 wt%, 3 wt%, 5 wt%, 10 wt%, and 20 wt%. The compositions of 50g of each P₄₄₄₄-Trp WBL are summarised in Table 6.1.

	Trp anion (g)	P₄₄₄₄ cation (g)	Water (g)	Glycerol (g)
Pure water	0	0	50	0
10 wt% WGL	0	0	45	5
1 wt% P₄₄₄₄-Trp in water	0.28	0.22	49.5	0
3 wt% P₄₄₄₄-Trp in water	0.85	0.65	48.5	0
5 wt% P₄₄₄₄-Trp in water	1.42	1.08	47.5	0
10 wt% P₄₄₄₄-Trp in water	2.85	2.15	45	0
10 wt% P₄₄₄₄-Trp in 10 wt% WGL	2.85	2.15	40.5	4.5
10 wt% P₄₄₄₄-Trp in 50 wt% WGL	2.85	2.15	22.5	22.5
20 wt% P₄₄₄₄-Trp in water	5.68	4.32	40	0
20 wt% P₄₄₄₄-Trp in 10 wt% WGL	5.68	4.32	36	4.0

Table 6.1: The composition of different types of P₄₄₄₄-Trp WBLs in 50g

6.2.2 Corrosion test

The corrosion properties of P₄₄₄₄-Trp WBLs were characterised using the cast iron chips test, adapted from the DIN 51360 Part 2 method [275]. The pure water as the base lubricant with 0 wt% (pure water), 1 wt%, 3 wt%, 5 wt%, 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 10 wt% glycerol aqueous solution as base lubricant with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives were chosen to the types of P₄₄₄₄-Trp WBLs to be investigated in regards of the corrosion property. For each test, dry cast iron chips were placed on squared filter paper in individual sections of a cubic container. 10 mL of each P₄₄₄₄-Trp WBL was added to each section, immersing the cast iron chips in the lubricant. The corrosion tests for all P₄₄₄₄-Trp WBLs were conducted simultaneously at room temperature for 24 hours. Afterwards, the cast iron chips and filter paper were removed from the container and dried at room temperature. The rust on the cast chips and filter papers was observed and evaluated as the test result.

6.2.3 Rheological measurements

The methodology of zero-shear viscosity measurement was adapted from Chapters 3 [215] and 4. The Anton Paar MCR-302 rheometer (Anton Paar GmbH, Graz, Austria) with the concentric cylinder (CC) system was employed. The CC system comprises a measuring bob (diameter $D_B = 26.651\text{mm}$) and a measuring cup (diameter $D_C = 28.922\text{mm}$). The measuring cup was loaded with 19 ml of P₄₄₄₄-AA WBL sample, which was then subjected to shear rates ranging from 0 to 100 s^{-1} under a temperature of $25\text{ }^{\circ}\text{C}$ (facilitated by a Peltier system integrated with the rheometer). The lubricant is Newtonian at this range of shear rates. The viscosity was recorded during the shearing, and the average viscosity for each test was presented as zero-shear viscosity. The presented value is the average of five tests on each type of P₄₄₄₄-AA WBLs and pure water.

6.2.4 Tribological measurement

Tribological tests were conducted to measure the coefficient of friction (COF) of P4444-Trp WBLs between steel contacts, validating the MD simulation results. A ball-on-three-plates test using an Anton Paar® MCR-302 machine equipped with a T-PTD 200 tribology measuring cell was employed for COF measurement. The T-PTD 200 tribology measuring cell is designed to measure friction in dry and lubricated contact between various materials [241][242]. In our previous study, this method was proven to be an efficient technique for COF measurement [243]. A Peltier system was used to maintain a constant temperature. Figure 6.2 illustrates the measuring cell and the schematic of the ball-on-three-plates test. Within the the measuring cell, a steel ball was mounted on the end of a shaft, forming three-point contacts with three steel samples ($15.5 \times 6 \times 3$ mm dimensions) arranged in an inclined orientation at equal 120° intervals in the holder cup. Both the steel ball on the shaft and the steel samples in the holder cups were made of 100Cr6 steel with an average surface roughness of $0.1 \mu\text{m}$ for all measurements. P4444-Trp WBLs could be added to the holder cup to perform the tribology test of steel-steel contacts lubricated by these WBLs.

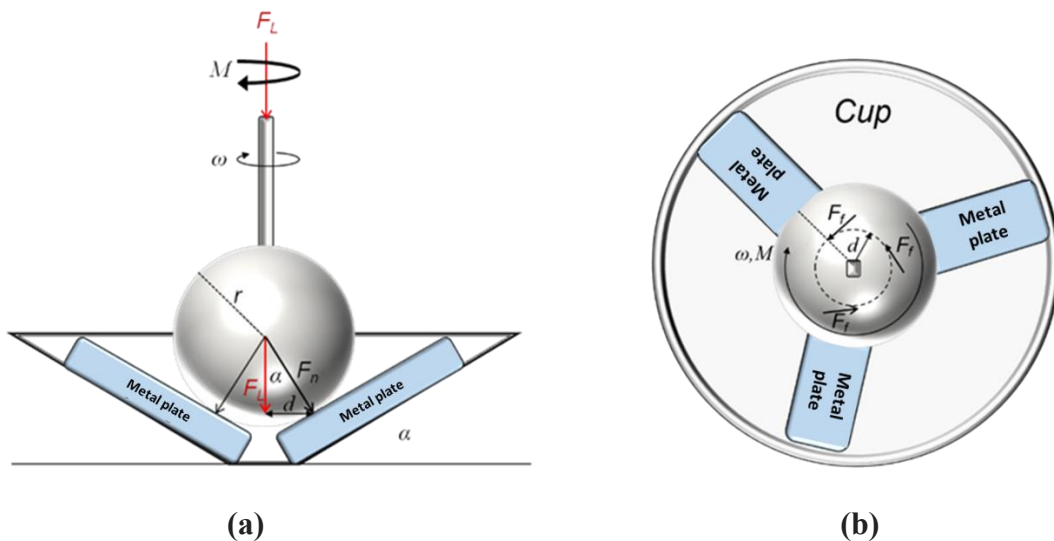


Figure 6.2: (a) Side view and (b) Top view of the ball-on-three-plate tribology test [243]

The shaft applied a load of F_L on the steel, which contacted the three steel samples in the holder cup during the test. The shaft-applied load F_L was transferred as a normal force F_N to each of the three metal plate samples. The normal load F_N on each sample can be described in terms of the shaft applied load F_L and incline angle α by Eq.6.1.

$$F_N = \frac{F_L}{3\cos\alpha} \quad (6.1)$$

The steel ball contact with the metal plate samples in the holder cup at a radial distance given by Eq.6.2,

$$d = r\sin\alpha \quad (6.2)$$

where r is the radius of the steel ball, which is 6.35mm. The shaft with the mounted steel ball has a rotational velocity ω , provided by the machine. Therefore, the linear velocity of the steel ball could be calculated by Eq.6.3.

$$V_s = rd = r\omega\sin\alpha \quad (6.3)$$

Then, the average friction force can be calculated by Eq.6.4,

$$F_f = \frac{M}{3d} \quad (6.4)$$

where M is the measured torque and d is the sliding distance, calculated from the rotational velocity and time. Finally, the COF μ can be calculated using Eq. 6.5.

$$\mu = \frac{F_f}{F_N} \quad (6.5)$$

The reported COF was obtained by averaging the COF of three metal plate samples used in each test. The average COF of three samples used in each test was measured and recorded.

In the friction tests, each test was conducted for 1800 seconds. Steel and copper were selected as the plate materials to create steel-steel, steel-copper contacts. To investigate the effect of temperature, the tests were performed at 25°C, 50°C, and 70°C, representing room temperature and potentially high temperatures encountered in industrial applications. To study the effect of load, the tribological tests were conducted under three different loads: 5N, 10N, and 15N, corresponding to pressures between 700 MPa and 1000 MPa. The tribological tests were conducted under three different rotational velocities: 319 rpm, 957 rpm, and 1914 rpm, resulting in sliding velocities of 0.15 m/s, 0.45 m/s, and 0.9 m/s, respectively. The chosen loads and velocities align with similar studies on WBLs [271][272].

6.2.5 Minimum film thickness and lubrication regimes determination

Load and velocity play crucial roles in determining the lubrication regime during the friction process. To investigate the effects of load and velocity on the tribological behaviours of P₄₄₄₄-Trp WBLs, it is essential to identify the lubrication regime.

The minimum film thickness, h_0 , can be calculated using the Hamrock and Dowson equation as shown in Eq.6.6 [283]:

$$h_0 = 3.63R' \left(\frac{U\eta_0}{E'R'} \right)^{0.68} (\alpha E')^{0.49} \left(\frac{W}{E'R'^2} \right)^{-0.073} (1 - e^{-0.68k}) \quad (6.6)$$

where the R' is the reduced radius of curvature, η_0 is the dynamic viscosity of the lubricant, U is the velocity of entraining surfaces, E' is the reduced young's modulus, α is the pressure viscosity index, W is the normal load and k is the ellipticity parameter ($k=1$ in this case because of the point contact). In addition, the lambda ratio λ is calculated in Eq.6.7 to determine the lubrication regimes [284].

$$\lambda = \frac{h_0}{R_q} \quad (6.7)$$

It is the ratio between the h_0 and R_q which is the root-mean-square roughness of two surfaces.

The R_q can be calculated by Eq.6.8.

$$R_q = \sqrt{R_{q1}^2 + R_{q2}^2} \quad (6.8)$$

Where R_1 and R_2 represent the root-mean-square roughnesses for the ball and plate surfaces, respectively. Generally, λ is expected to be smaller than 1 in the boundary lubrication regime. If $1 \leq \lambda \leq 3$, the lubrication regime is considered as mixed lubrication. When λ is greater than 3, hydrodynamic lubrication is anticipated [285].

6.2.6 Wear characterisations

In the pin-on-three-plates friction test, the load is applied through the shaft, causing the ball at the end of the shaft to contact the plates in the holder. The shaft rotation creates angular sliding between the ball and plates, resulting in spherical wear marks at the contact points. A Leica DFC420 microscope was used to investigate the wear marks and to quantify wear. A 5x lens captured the wear marks on steel and copper plates. The diameters of the wear marks were measured, representing the wear of each plate. The average diameter of the wear marks on three plates in each test represents the average wear for that test.

6.3 Results and Discussion

6.3.1 Anticorrosion properties

Figure 6.3 illustrates the dried cast iron chips and filter papers after corrosion tests conducted on various types of P₄₄₄₄-Trp WBLs. Given the yellow colour of P₄₄₄₄-Trp WBLs and the

darkening of lubricants with increasing P₄₄₄₄-Trp IL additive concentrations, the base colour of the filter paper was disregarded when evaluating corrosion levels. Instead, the rust present on the cast iron chips and filter papers was used as an indicator of corrosion.

A significant amount of rust was observed on the cast iron chips and filter papers when using pure water, indicating severe corrosion. Adding 1 wt% P₄₄₄₄-Trp IL additives did not noticeably reduce the amount of rust compared to pure water, suggesting that this concentration does not improve anticorrosion properties. However, increasing the concentration to 3 wt% resulted in a significant reduction in rust compared to pure water and water with 1 wt% P₄₄₄₄-Trp IL additives. Further increases in P₄₄₄₄-Trp IL additive concentration led to a continued decrease in rust, with no observable corrosion at 20 wt%. These results demonstrate the excellent anticorrosion properties of P₄₄₄₄-Trp IL additives. Previous studies on the anticorrosion properties of IL lubricants have attributed their effectiveness to the formation of adsorption films of ILs on metallic surfaces, which hinder water contact [276] [277]. As discussed in the previous section on lubrication mechanism analysis using MD simulation, AA adsorption layers form on the surfaces. Higher concentrations of P₄₄₄₄-Trp IL additives lead to denser and thicker Trp adsorption layers, enhancing corrosion prevention.

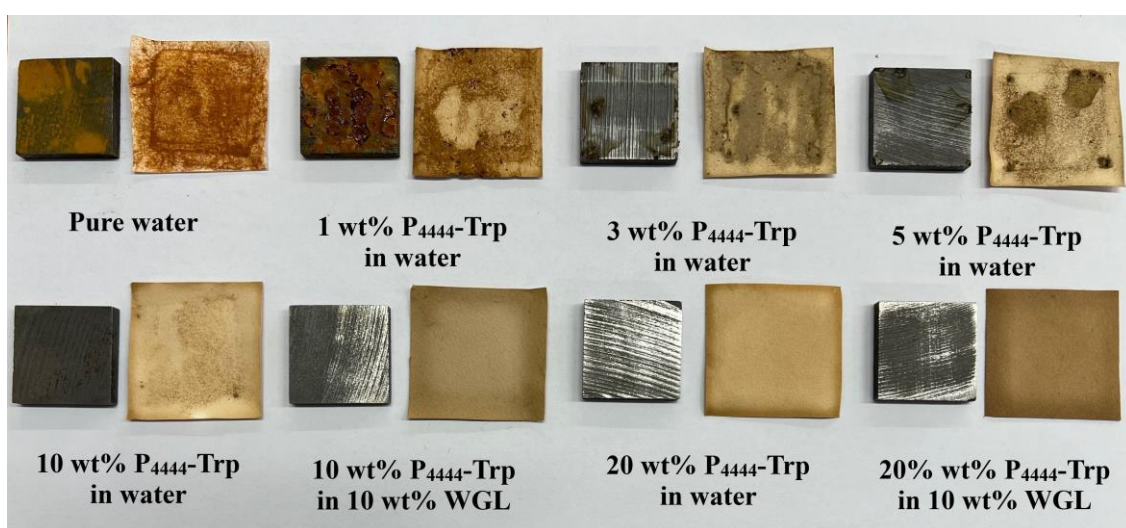


Figure 6.3: Cast iron chips and the corresponding filter papers from corrosion tests of different types of P₄₄₄₄-Trp WBLs and pure water

When comparing the base lubricants of pure water and 10 wt% glycerol aqueous solution at a P₄₄₄₄-Trp concentration of 10 wt%, it was observed that the amount of rust was significantly less with the 10 wt% glycerol aqueous solution. This result indicates that the presence of glycerol in the lubricant can contribute to corrosion reduction. Previous studies on glycerol aqueous solutions as lubricants have demonstrated the tendency of glycerol to form adsorption layers on metallic surfaces [59]. Adding glycerol to P₄₄₄₄-Trp WBLs likely further increases the density and thickness of these adsorption layers, providing enhanced surface protection against corrosion. However, confirming the role of glycerol in improving anticorrosion properties becomes challenging when the P₄₄₄₄-Trp IL additive concentration reaches 20 wt%, as no corrosion is observed even with pure water. This suggests that the adsorption protection layer has reached saturation, reinforcing the hypothesis that forming thicker adsorption films is the primary mechanism behind the excellent anticorrosion properties of P₄₄₄₄-Trp WBLs.

6.3.2 Rheological properties

Figure 6.4 (a) presents the shear viscosity versus shear rates up to 100 s⁻¹ for P₄₄₄₄-Trp WBLs at various concentrations. The plot also includes pure water and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids as references for comparison. The averaged viscosity values are summarised in Figure 6.4 (b).

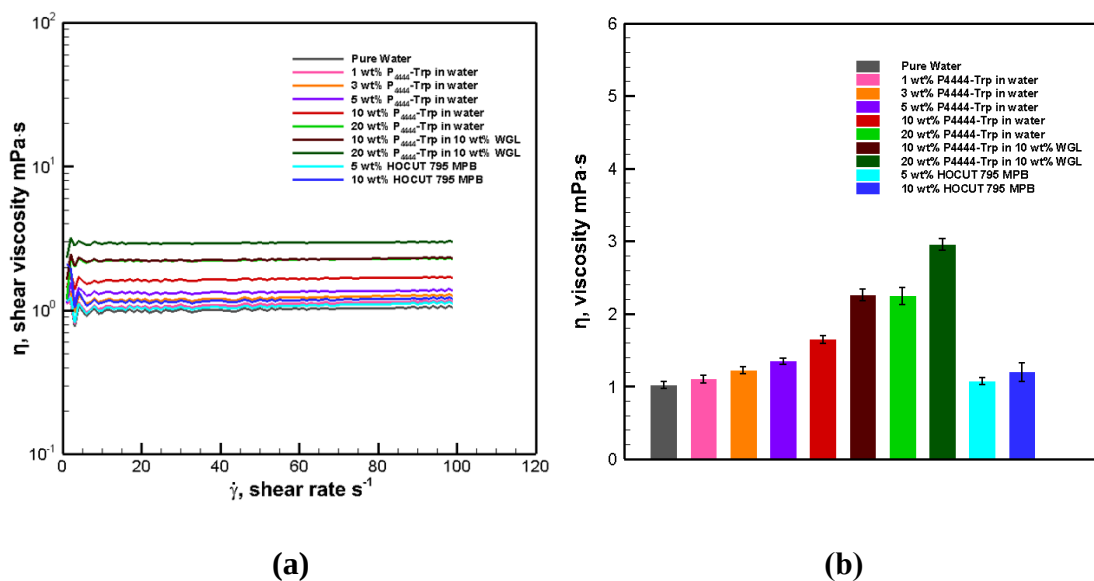


Figure 6.4: (a) Shear viscosity versus shear rate (0 to 100 s⁻¹) (b) zero-shear viscosity averaged from experiment for water with 1 wt%, 3 wt%, 5 wt%, 10 wt% and 20 wt% P₄₄₄₄-Trp additives, 10 wt% WGL with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, pure water, and 5 wt% and 10 wt% HOCUT® 795 MPB cutting fluids at 25°C

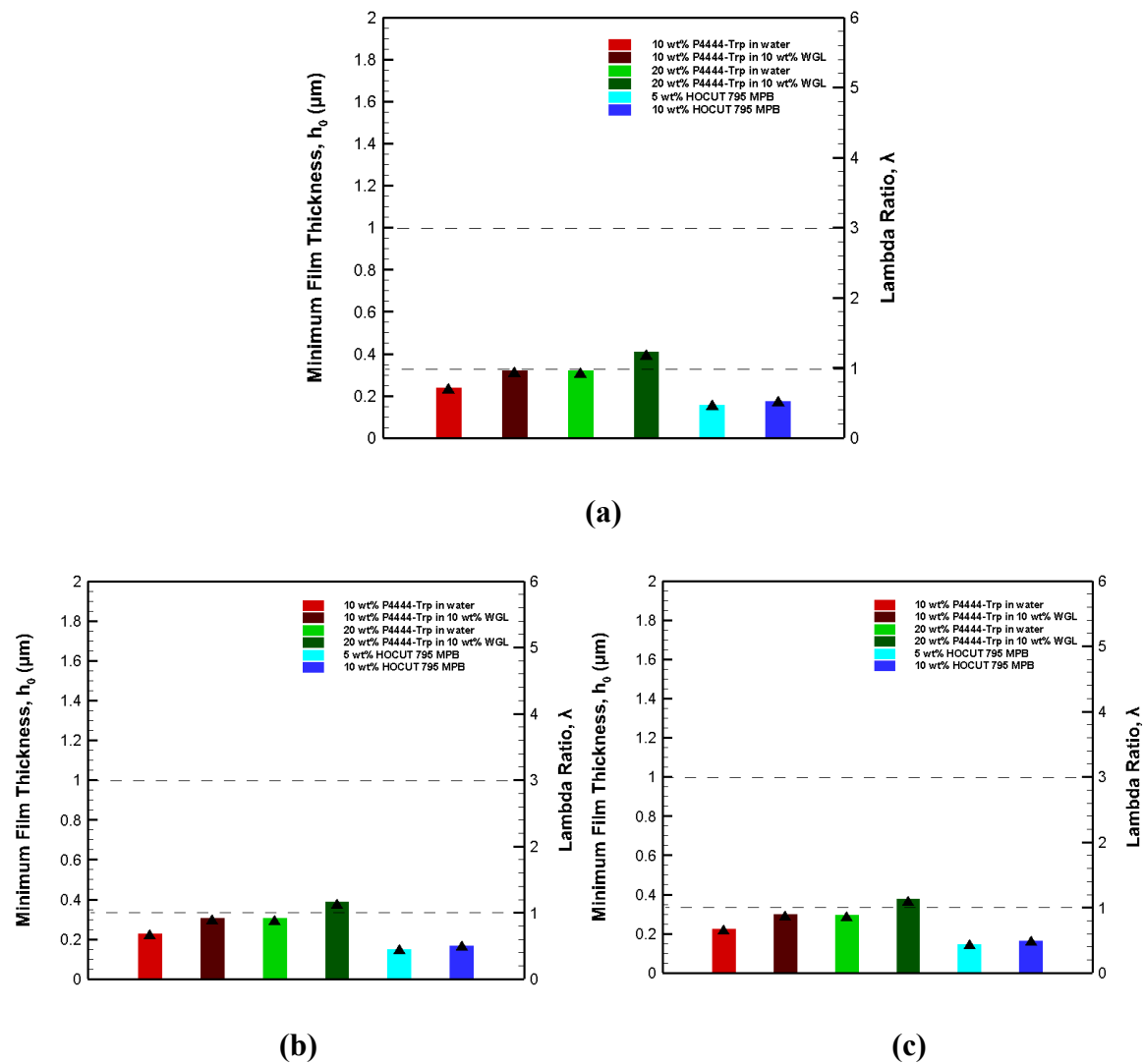
The results demonstrate that adding P₄₄₄₄-Trp IL additives increases the viscosity of pure water. As the concentration of P₄₄₄₄-Trp IL additives increases from 1 wt% to 20 wt%, the viscosity of pure water increases by 8% to 189%. When using a 10 wt% WGL base lubricant, the viscosity of the lubricant is 37% higher than that of pure water at a P₄₄₄₄-Trp IL additive concentration of 10 wt%. This trend of increased viscosity with higher P₄₄₄₄-Trp IL additive concentrations persists when using the 20 wt% WBL. These findings indicate that the viscosity of P₄₄₄₄-Trp WBLs can be flexibly adjusted by varying both P₄₄₄₄-Trp IL additive and glycerol contents.

Moreover, the viscosity values of 5 wt% and 10 wt% HOCUT® 795 MPB fall between those of pure water and water with 3 wt% P₄₄₄₄-Trp additives. Conversely, P₄₄₄₄-Trp WBLs with higher concentrations exhibit significantly higher viscosity values than HOCUT® 795 MPB. The enhanced viscosity achieved by adding P₄₄₄₄-Trp IL additives and glycerol highlights their

potential as effective lubricant additives for water, offering a promising alternative to traditional oil-based lubricants.

6.3.3 Film thickness and lubrication regimes

Figure 6.5 shows the minimum film thickness (h_0) and the lambda ratio (λ) for different P₄₄₄₄-Trp WBLs under different loads and velocities. The tribological behaviours will be discussed in detail in subsequent sections.



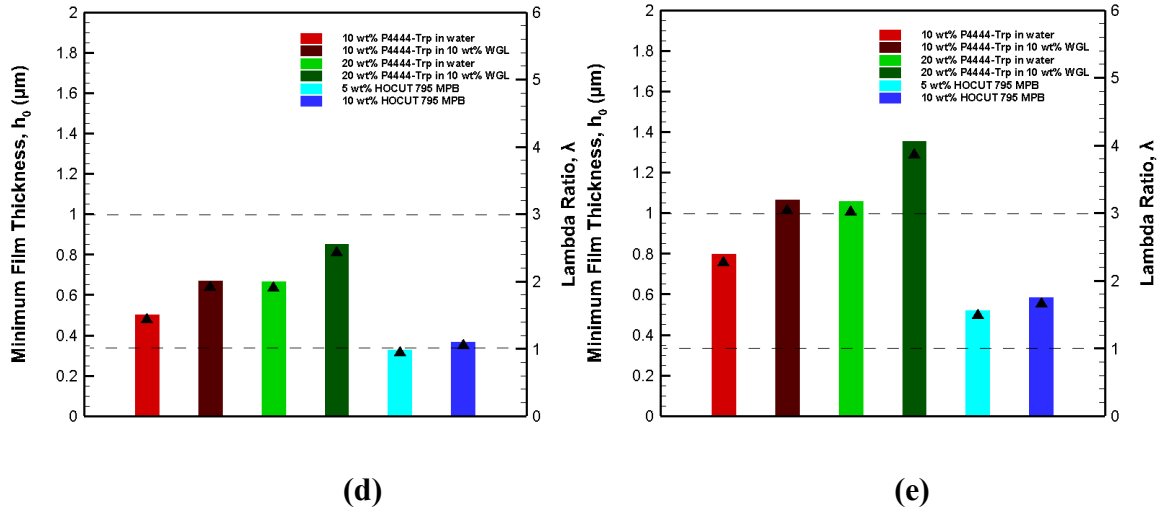


Figure 6.5: Minimum film thickness (bars) and the lambda ratio (triangle marks) for different P_{4444} -Trp WBLs between the steel-steel contact at 25°C under (a) load: 5N, velocity: 0.15 m/s (b) load: 10N, velocity: 0.15 m/s (c) load: 15N, velocity: 0.15 m/s (d) load: 5N, velocity: 0.45 m/s (e) load: 5N, velocity: 0.9 m/s (The dashed lines indicate $\lambda=1$ and $\lambda=3$, which show different lubrication regimes)

Figure 6.5 shows that increasing the concentrations of both P_{4444} -Trp additives and glycerol leads to a thicker minimum film thickness. This increase is primarily attributed to the enhanced viscosity resulting from higher concentrations of P_{4444} -Trp additives and glycerol.

Furthermore, it can be observed from Figure 6.5 (a) that all lambda ratios (λ) are below 1, except for the 10 wt% glycerol aqueous solution with 20 wt% P_{4444} -Trp additives under a load of 5N and a velocity of 0.15 m/s. This indicates that the lubrication regime for these conditions is predominantly boundary lubrication. Even in the latter case, where λ is slightly higher than 1 which represents a mixed lubrication regime, the lubrication regime remains predominantly boundary lubrication.

Comparing Figure 6.5 (b) and (c) with Figure 6.5 (a) demonstrates that increasing the normal load reduces both the minimum film thickness and λ values. The lubrication regime for all P_{4444} -Trp WBLs remains boundary lubrication at higher loads. In contrast, comparing Figure 6.5 (d) and (e) with Figure 6.5 (a) reveals a significant increase in both minimum film thickness and λ values at higher velocities (0.45 m/s and 0.9 m/s). At 0.45 m/s, the lubrication regimes

shifted to the mixed lubrication for all P₄₄₄₄-Trp WBLs. When the velocity is 0.9 m/s, all P₄₄₄₄-Trp WBLs except for pure water with 10 wt% P₄₄₄₄-Trp, exhibit λ values greater than 3, indicating a transition to the hydrodynamic lubrication regime.

6.3.4 Tribological properties

6.3.4.1 Concentration effect (pure water as a base lubricant)

Figure 6.6 (a) presents the coefficient of friction (COF) results over time for steel/steel contacts lubricated with water with different concentrations of P₄₄₄₄-Trp additives. The averaged COFs are presented in Figure 6.6 (b). For reference, the COFs for pure water, 5 wt%, and 10 wt% HOCUT[®] 795 MPB cutting fluids are also included in Figure 6.6. The results indicate that using pure water as a lubricant for steel/steel contacts results in a COF of approximately 0.29. However, adding 1 wt% P₄₄₄₄-Trp IL additives to water significantly reduces the COF by 17% compared to pure water. As the concentration of P₄₄₄₄-Trp IL additives increases, the COF continues to decrease substantially. At a concentration of 20 wt%, the COF of the lubricant drops to 0.113, which is 60% lower than that of pure water. This promising result highlights the excellent potential of P₄₄₄₄-Trp IL additives to improve the tribological behaviour of water as a lubricant in steel/steel contacts.

In addition, as illustrated in Figure 6.6, the COF for water exhibits significant fluctuations during the test, indicative of severe wear on the plates. While adding 1 wt% P₄₄₄₄-Trp IL additive to water reduces the COF, it does not substantially mitigate the COF fluctuations, suggesting that wear on the plates remains severe. However, when the concentration of P₄₄₄₄-Trp IL additives reaches 3 wt% or higher, the COF fluctuations become minimal. This observation demonstrates that increasing the concentration of P₄₄₄₄-Trp IL additives reduces wear on the plates.

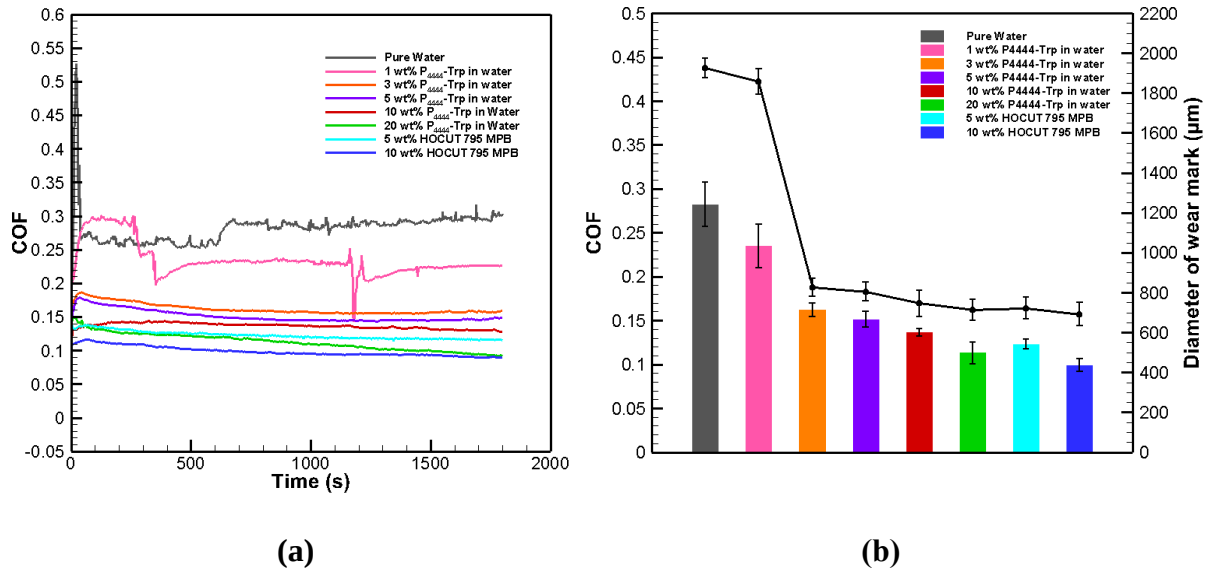
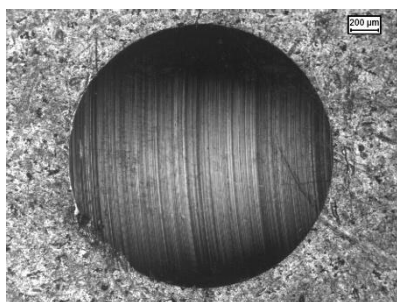
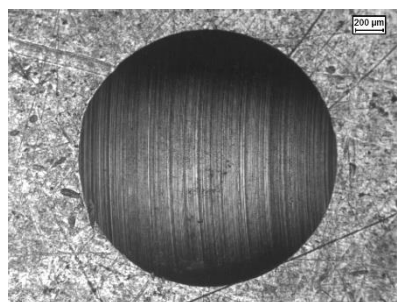


Figure 6.6: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for pure water, water with P₄₄₄₄-Trp additives with concentrations of 1 wt%, 3 wt%, 5 wt%, 10 wt% and 20 wt%, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.15 m/s Temperature: 25°C)

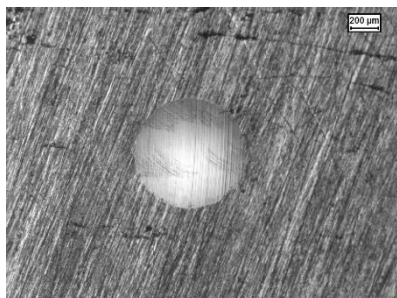
Figure 6.7 presents the microscopy images of wear marks on steel plates lubricated by P₄₄₄₄-Trp WBLs at various concentrations. The average diameters of these wear marks are quantified in Figure 6.6 (b). It can be observed that as the concentration of P₄₄₄₄-Trp additives increases, the size of the wear marks decreases, indicating a reduction in wear. Notably, at a concentration of 3 wt%, the diameter of the wear marks decreases significantly by 57% compared to those observed with pure water. Furthermore, when the concentration reaches to 20 wt%, the average diameter of the wear marks is comparable with the result using 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids.



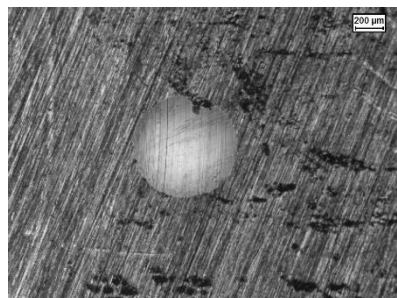
(a) Pure water



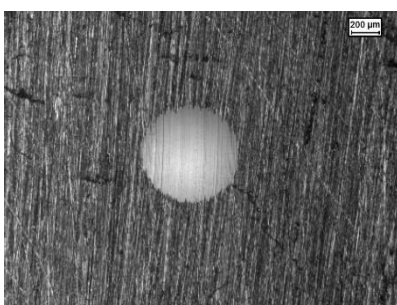
(b) 1 wt% P₄₄₄₄-Trp in water



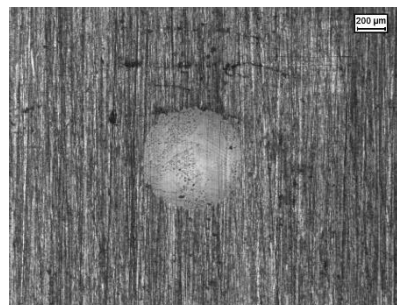
(c) 3 wt% P₄₄₄₄-Trp in water



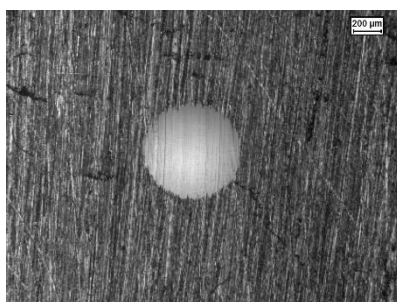
(d) 5 wt% P₄₄₄₄-Trp in water



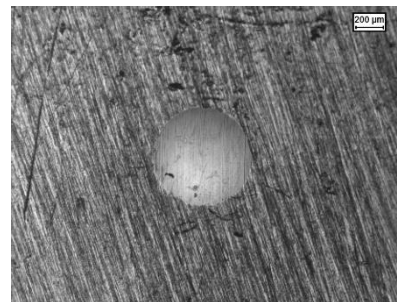
(e) 10 wt% P₄₄₄₄-Trp in water



(f) 10 wt% P₄₄₄₄-Trp in 10 wt% WGL



(g) 20 wt% P₄₄₄₄-Trp in water



(h) 20 wt% P₄₄₄₄-Trp in 10 wt% WGL

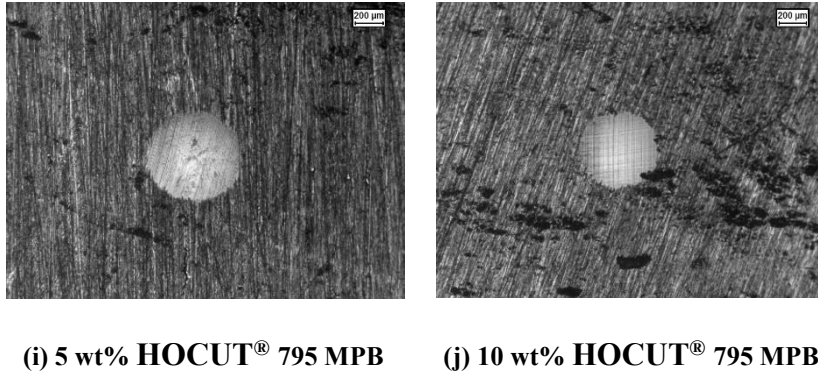


Figure 6.7: microscopy images of wear marks on steel plates lubricated by (a) pure water, (b) 1 wt% P_{4444} -Trp in water, (c) 3 wt% P_{4444} -Trp in water, (d) 5 wt% P_{4444} -Trp in water (e) 10 wt% P_{4444} -Trp in water (f) 10 wt% P_{4444} -Trp in 10 wt% WGL (g) 20 wt% P_{4444} -Trp in water (h) 20 wt% P_{4444} -Trp in 10 wt% WGL (i) 5 wt% HOCUT® 795 MPB (j) 10 wt% HOCUT® 795 MPB cutting fluids (Load: 5N, Velocity: 0.15 m/s, Temperature: 25°C)

Although Figure 6.6 shows that while adding even small amounts of P_{4444} -Trp IL additives (1 wt% to 5 wt%) to water significantly improves friction and wear compared to pure water, the COFs of these AAIL WBLs at lower concentrations remain higher than those of 5 wt% and 10 wt% HOCUT® 795 MPB cutting fluids. This suggests that the tribological performance of AAIL WBLs at lower concentrations may not be sufficient for industrial cutting fluid applications. Figure 6.6 also illustrates that even when the concentration of P_{4444} -Trp additives reaches 10 wt% the COF is still 5% and 31% higher than 5 wt% and 10 wt% HOCUT® 795 MPB, respectively. However, as the concentration of P_{4444} -Trp IL additives increases to 20 wt%, the COF and average diameter of wear marks fall within the range observed for 5 wt% and 10 wt% HOCUT® 795 MPB cutting fluids. This promising result demonstrates that water-based lubricants containing P_{4444} -Trp IL additives at higher concentrations possess comparable tribological performance to traditional oil-based cutting fluids.

The reduction in COF with increasing P_{4444} -Trp additive concentration observed for steel/steel contacts is also evident in steel/copper contacts, as shown in Figure 6.8. Adding P_{4444} -Trp IL

additives to pure water at concentrations ranging from 1 wt% to 20 wt% reduces the COF by 43% to 63%. Pure water exhibits significant COF fluctuations, indicating severe wear on the copper plates. While adding 1 wt% P₄₄₄₄-Trp IL additives reduces the COF, fluctuations persist. However, increasing the concentration to 3 wt% or higher significantly diminishes COF fluctuations, suggesting a reduction in wear. Microscope images presented in Figure 6.9 reveal the wear marks on copper plates lubricated by water and P₄₄₄₄-Trp WBLs at various concentrations, and the diameter of the wear mark is presented in Figure 6.8 (b). Pure water results in a significantly large wear mark diameter of 2369 μm . Adding P₄₄₄₄-Trp IL additives reduces the wear mark diameter by 18% to 69%, demonstrating the formation of protective adsorption layers on the copper surfaces. Meanwhile, The MD simulation results from the previous section indicate that Trp anions can form adsorption layers on surfaces, providing a protective barrier that reduces both friction and wear. Higher concentrations of Trp IL anions lead to thicker and more stable adsorption layers, further enhancing surface protection and reducing wear.

As shown in Figure 6.8, the COF evaluation also includes HOCUT[®] 795 MPB cutting fluids for benchmarking. At P₄₄₄₄-Trp IL additive concentrations of 1 wt% and 3 wt%, the COFs are 20% and 17% higher, respectively, compared to 5 wt% HOCUT[®] 795 MPB. However, as the P₄₄₄₄-Trp IL additive concentration increases to 5 wt% and 10 wt%, the COF decreases to 0.225 and 0.218, respectively, falling within the COF range of 0.243 and 0.179 for 5 wt% and 10 wt% HOCUT[®] 795 MPB. Notably, at a P₄₄₄₄-Trp IL additive concentration of 20 wt%, the COF of the P₄₄₄₄-Trp WBL becomes comparable to that of 10 wt% HOCUT[®] 795 MPB, indicating its potential as a viable replacement for traditional oil-based cutting fluids.

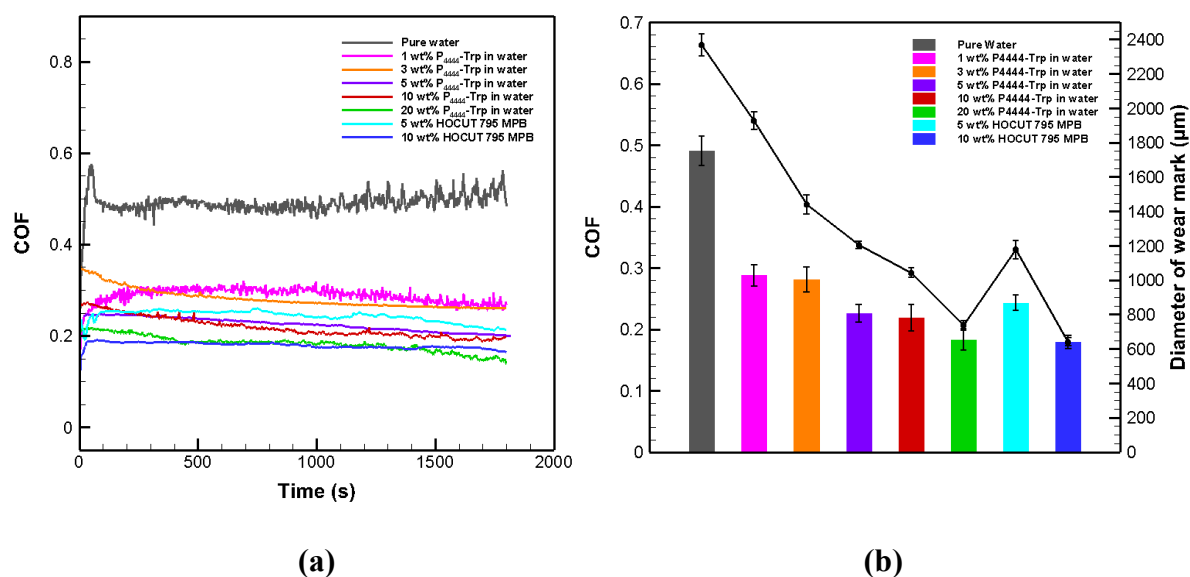
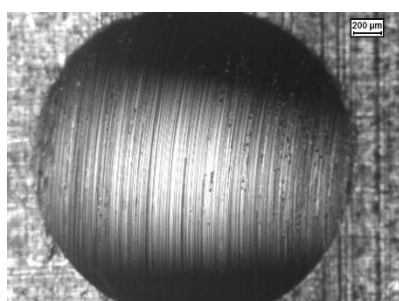
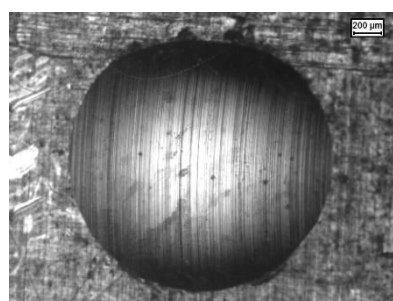


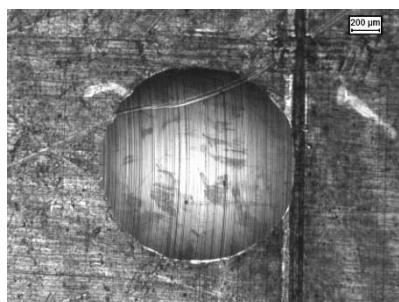
Figure 6.8: (a) Coefficient of friction (COF) versus time (b)) averaged COF (Bars) and diameter of wear marks (Lines) for water with P₄₄₄₄-Trp additives with concentrations of 1 wt%, 3 wt%, 5wt%, 10 wt% and 20 wt%, and pure water and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/copper contacts (Load: 5N, Velocity: 0.15 m/s, Temperature: 25°C)



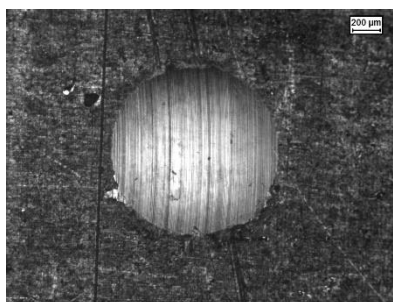
(a) Pure water



(b) 1 wt% P₄₄₄₄-Trp in water



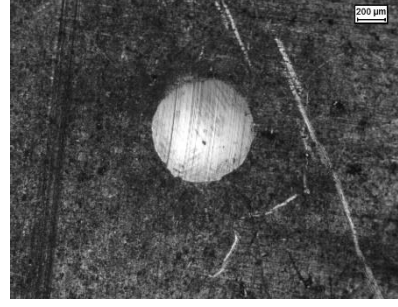
(c) 3 wt% P₄₄₄₄-Trp in water



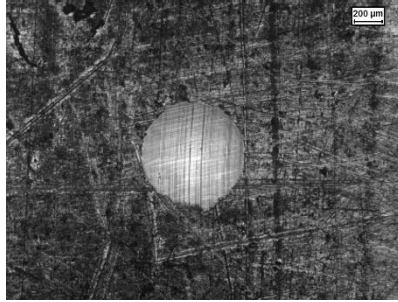
(d) 5 wt% P₄₄₄₄-Trp in water



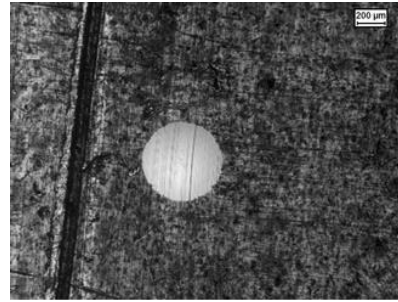
(e) 10 wt% P₄₄₄₄-Trp in water



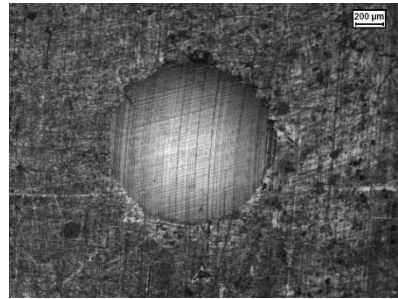
(f) 10 wt% P₄₄₄₄-Trp in 10 wt% WGL



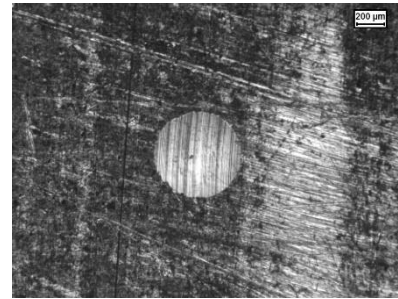
(g) 20 wt% P₄₄₄₄-Trp in water



(h) 20 wt% P₄₄₄₄-Trp in 10 wt% WGL



(i) 5 wt% HOCUT[®] 795 MPB



(j) 10 wt% HOCUT[®] 795 MPB

Figure 6.9: microscopy images of wear marks on copper plates lubricated by (a) pure water, (b) 1 wt% P₄₄₄₄-Trp in water, (c) 3 wt% P₄₄₄₄-Trp in water, (d) 5 wt% P₄₄₄₄-Trp in water (e) 10 wt% P₄₄₄₄-Trp in water (f) 10 wt% P₄₄₄₄-Trp in 10 wt% WGL (g) 20 wt% P₄₄₄₄-Trp in water (h) 20 wt% P₄₄₄₄-Trp in 10 wt% WGL (i) 5 wt% HOCUT[®] 795 MPB (j) 10 wt% HOCUT[®] 795 MPB cutting fluids (Load: 5N, Velocity: 0.15 m/s, Temperature: 25°C)

As illustrated in Figure 6.9, the microscopy images reveal that the average diameters of wear marks on copper plates lubricated by water with 1 wt% to 5 wt% P₄₄₄₄-Trp additives are consistently larger than those lubricated by 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids. However, increasing the P₄₄₄₄-Trp additive concentration to 10 wt% results in a 11%

reduction in wear mark diameter compared to 5 wt% HOCUT[®] 795 MPB. Further increasing the concentration to 20 wt% leads to a 37% reduction in wear mark diameter compared to 5 wt% HOCUT[®] 795 MPB, although it remains 15% higher than 10 wt% HOCUT[®] 795 MPB. These findings, combined with the steel/steel contact analysis results, suggest that while introducing small concentrations of P₄₄₄₄-Trp additives to water can significantly reduce friction and wear, achieving levels comparable to industrial applications may require higher concentrations.

6.3.4.2 Concentration effect (glycerol aqueous solution as a base lubricant)

To further improve the tribological performance of the pure water with P₄₄₄₄-Trp IL additives, the glycerol aqueous solution as the base lubricant is considered. Figure 6.10 shows the comparison between pure water with P₄₄₄₄-Trp IL additives and glycerol aqueous solution in concentrations of 10 wt%, 20 wt% and 50% with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives in steel/steel contacts. For the WBLs with 10 wt% P₄₄₄₄-Trp IL additives, Figure 6.10 shows that 10 wt% glycerol aqueous solution has a COF of 0.13, which is 5% lower than pure water. The results indicate that introducing 10 wt% glycerol in the water further reduces the friction of pure water with 10 wt% P₄₄₄₄-Trp IL additives. The same behaviour has been observed for the WBLs with 20 wt% P₄₄₄₄-Trp IL additives. The COF of 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives is 8% lower than using pure water as the base lubricant. In addition, the COF of 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives also reaches a level that is very close to 10 wt% HOCUT[®] 795 MPB and 15% lower than 5 wt% HOCUT[®] 795 MPB. The reduction of the wear by using glycerol aqueous solution as a base lubricant can also be found in Figure 6.10 (b). For using the 10 wt% glycerol aqueous solution as a base lubricant, the diameter of the wear reduces 4% and 2% for WBLs 10wt% and 20 wt% P₄₄₄₄-Trp additives compared to pure water as a base lubricant. Significantly, the diameter of the wear for steel plates lubricated by the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-

Trp is at the same level as 10 wt% HOCUT[®] 795 MPB. This indicates an outstanding potential to be the replacement of the industrial cutting fluid regarding its tribological behaviours.

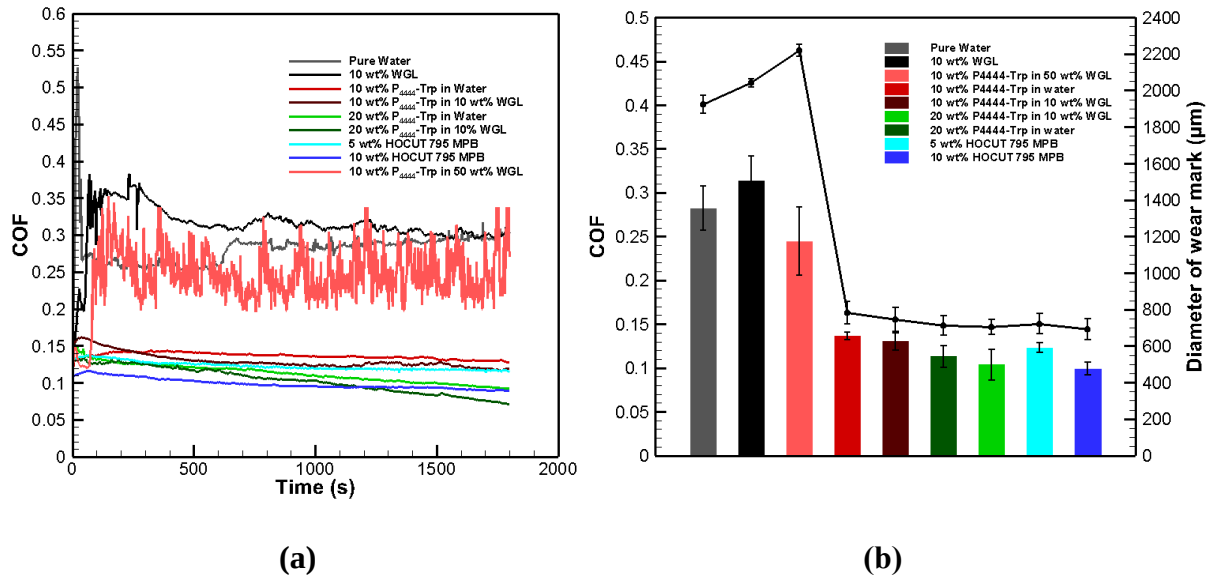


Figure 6.10: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 0 wt%, 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 50 wt% glycerol aqueous solution with 10 wt% P₄₄₄₄-Trp IL additives, pure water, 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.15 m/s, Temperature: 25°C)

To further explore the effect of glycerol in P₄₄₄₄-Trp WBLs, friction tests were conducted using 10 wt% glycerol aqueous solutions without 10 wt% P₄₄₄₄-Trp additives. The results in Figure 6.10 indicate that the 10 wt% glycerol aqueous solution exhibits a slightly higher COF and wear mark diameter than pure water, suggesting that glycerol alone may not significantly improve tribological properties. While previous rheological studies showed that glycerol increases the viscosity of P₄₄₄₄-Trp WBLs, these results suggest that viscosity alone is not the primary factor influencing friction reduction in this system.

To further investigate the impact of glycerol on P₄₄₄₄-Trp WBLs, a friction test was conducted using a 50 wt% glycerol aqueous solution containing 10 wt% P₄₄₄₄-Trp additives. The results presented in Figure 6.10 demonstrate a significantly higher COF compared to the 10 wt%

glycerol aqueous solution. This indicates that while glycerol can enhance some properties, excessive concentrations may adversely affect tribological performance.

Previous rheological studies revealed that increasing glycerol concentration in P₄₄₄₄-Trp WBLs significantly increases viscosity. However, these friction test results suggest that viscosity alone is not this system's primary determinant of friction reduction. While higher viscosity generally correlates with reduced friction, other factors, such as the formation of adsorption layers, play a more significant role in AAIL WBLs. As discussed in Chapters 4 and 5, the excellent friction reduction ability of P₄₄₄₄-Trp WBLs is primarily attributed to forming AA adsorption layers on the surfaces and the 'hydrated AA-P₄₄₄₄-hydrated AA' layered configurations. High glycerol concentrations may hinder the formation of these structures by competing with Trp anions for adsorption sites, leading to a less effective lubricant.

Therefore, based on these findings, an optimal glycerol concentration of 10 wt% is recommended for P₄₄₄₄-Trp WBLs to achieve the desired tribological performance while minimising potential adverse effects. This glycerol concentration was chosen for the rest of the study.

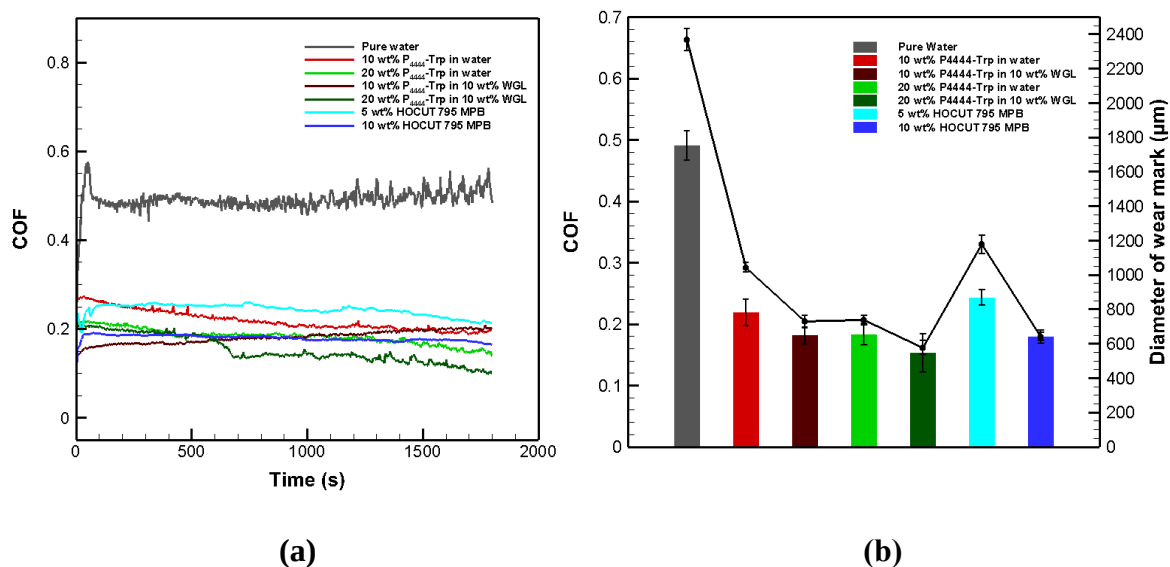


Figure 6.11: (a) Coefficient of friction (COF) versus time (b)) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, pure water, 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/copper contacts (Load: 5N, Velocity: 0.15 m/s, Temperature: 25°C)

As shown in Figure 6.11, the same COF reduction trend observed for steel/steel contacts is evident in steel/copper contacts when using P₄₄₄₄-Trp IL additives. At a given P₄₄₄₄-Trp IL additive concentration, WBLs with 10 wt% glycerol aqueous solution as the base lubricant exhibit lower COFs than those with pure water. Notably, a 10 wt% glycerol aqueous solution containing 20 wt% P₄₄₄₄-Trp IL additives demonstrates a COF 16% lower than that of 10 wt% HOCUT[®] 795 MPB, highlighting its superior tribological performance.

Additionally, the significantly reduced wear observed in steel/copper contacts using P₄₄₄₄-Trp WBLs is evident in the smaller wear mark diameters in Figure 6.11 (b). Compared to 10 wt% HOCUT[®] 795 MPB, the wear mark diameter is 15% lower when using the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives. These findings collectively suggest that P₄₄₄₄-Trp WBLs with 10 wt% glycerol aqueous solution as the base lubricant offer excellent

tribological performance, comparable to or even surpassing that of traditional oil-based cutting fluids like HOCUT[®] 795 MPB.

6.3.4.3 Temperature effect

To investigate the effect of temperature on the tribological behaviour of P₄₄₄₄-Trp IL WBLs, friction tests for steel/steel contacts were conducted at 50°C and 70°C. The COF and wear mark diameter results for these temperatures were compared to those for 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids 50°C and 70°C, as presented in Figure 6.12 and Figure 6.13, respectively. The results indicate an apparent decrease in COF over time for all tests conducted at 50°C and 70°C, a behaviour not observed in previous tests at 25°C. This decrease is likely attributed to increased water evaporation at higher temperatures, leading to a higher concentration of P₄₄₄₄-Trp IL additives in the lubricant and, consequently, a higher viscosity. Comparing the tests at 50°C and 70°C, the COF decreases more rapidly at 70°C. This is likely due to the accelerated rate of water evaporation at higher temperatures.

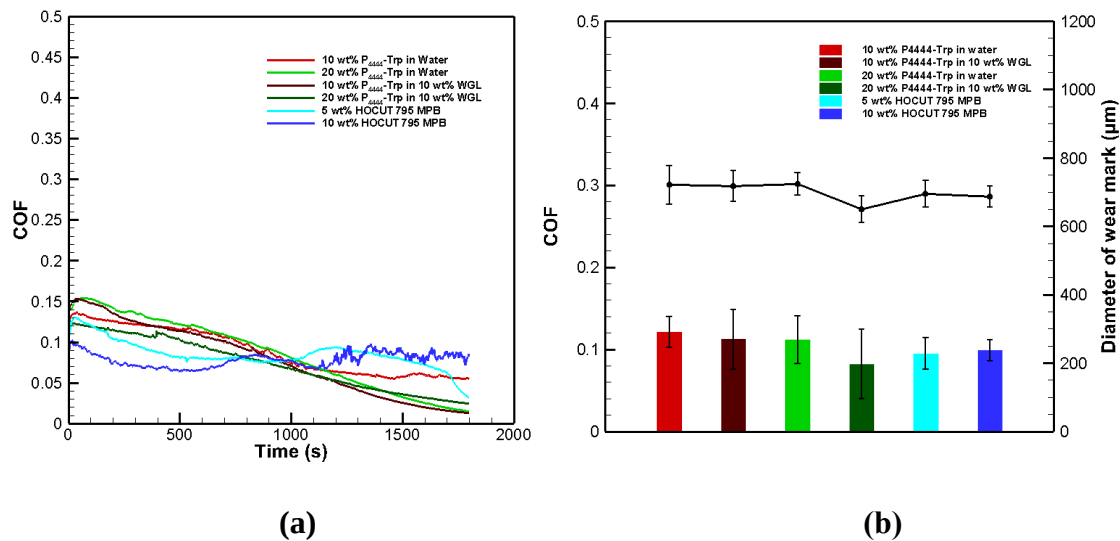


Figure 6.12: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.15 m/s, Temperature: 50°C)

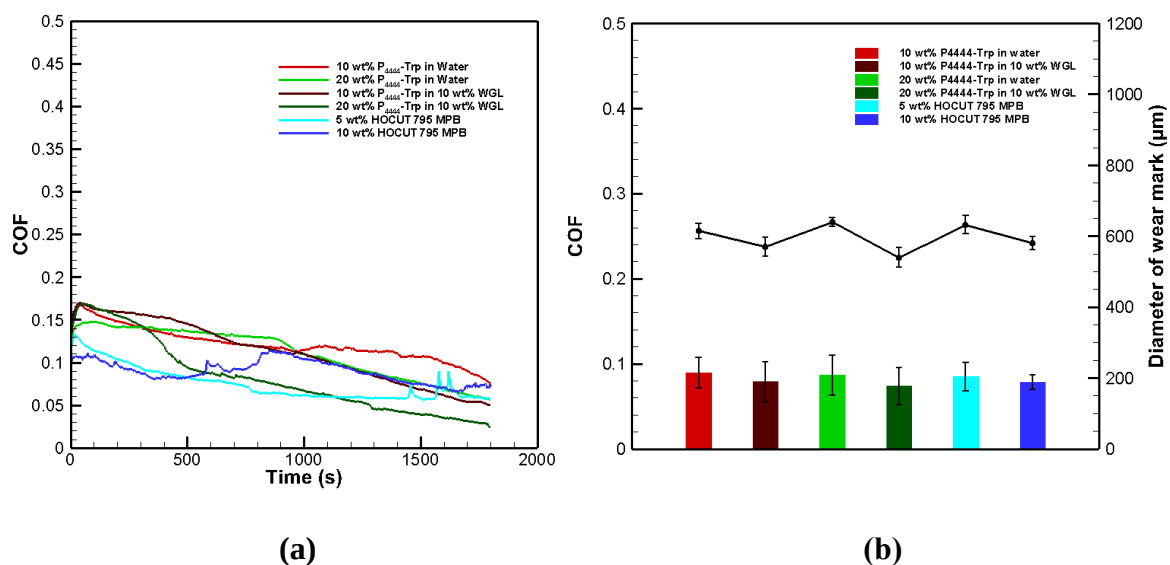


Figure 6.13: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.15 m/s, Temperature: 70°C)

As observed in previous sections, increasing the concentration of P₄₄₄₄-Trp IL additives reduces COF at 25°C. This trend persists at 50°C and 70°C, as illustrated in Figure 6.12 (a). While increasing the P₄₄₄₄-Trp IL additive concentration from 10 wt% to 20 wt% in pure water results in a 4% increase in COF at 50°C, using a 10 wt% glycerol aqueous solution as the base lubricant leads to a 27% reduction in COF compared to the 10 wt% P₄₄₄₄-Trp IL additive concentration. Compared to HOCUT[®] 795 MPB cutting fluids, the COFs of P₄₄₄₄-Trp WBLs with lower concentrations are generally higher. However, at a P₄₄₄₄-Trp IL additive concentration of 20 wt% in 10 wt% glycerol aqueous solution, the COF reaches a level that is 17% lower than that of 10 wt% HOCUT[®] 795 MPB. This indicates comparable tribological performance to industrial cutting fluids. As shown in Figure 6.12 (b), the average diameter of wear marks on steel plates lubricated by 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp additives is 10% lower than that of 10 wt% HOCUT[®] 795 MPB cutting fluid. This reduction in wear marks further emphasises the superior tribological performance of the P₄₄₄₄-Trp WBLs. The outstanding

friction and wear reduction capabilities of the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives are evident at room temperature and elevated temperatures, as demonstrated in Figure 6.12 and Figure 6.13. This suggests that the lubricant maintains its effectiveness under a wide range of operating conditions, making it a promising candidate for industrial cutting fluid applications.

6.3.4.4 Load effect

To further investigate the effect of load on tribological behaviour, friction tests were conducted at loads of 10N and 15N, in addition to the normal load of 5N. Figure 6.13 (a) and Figure 6.14 (a) show the COF evolution over time for these loads. As observed in previous sections, P₄₄₄₄-Trp WBLs with 10 wt% glycerol aqueous solution as the base lubricant consistently exhibit lower COFs compared to those with pure water at all loads. Furthermore, increasing the P₄₄₄₄-Trp IL additive concentration to 20 wt% results in even lower COFs, demonstrating superior tribological performance at both 10N and 15N. While the COFs for 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids remain within the range of 0.08 to 0.12 across all loads, the COFs of P₄₄₄₄-Trp WBLs with 10 wt% glycerol aqueous solution and 20 wt% P₄₄₄₄-Trp IL additives exhibit a slight decrease with increasing load. This suggests that the load has a more pronounced effect on the tribological behaviour of P₄₄₄₄-Trp WBLs compared to HOCUT[®] 795 MPB cutting fluids. The wear reduction is observed in Figure 6.14(b) and Figure 6.15 by reduced wear mark diameters. This correlates well with the observed reduction in friction coefficient. At higher loads, the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives consistently demonstrates excellent tribological performance, comparable to or even surpassing that of 10 wt% HOCUT[®] 795 MPB cutting fluids.

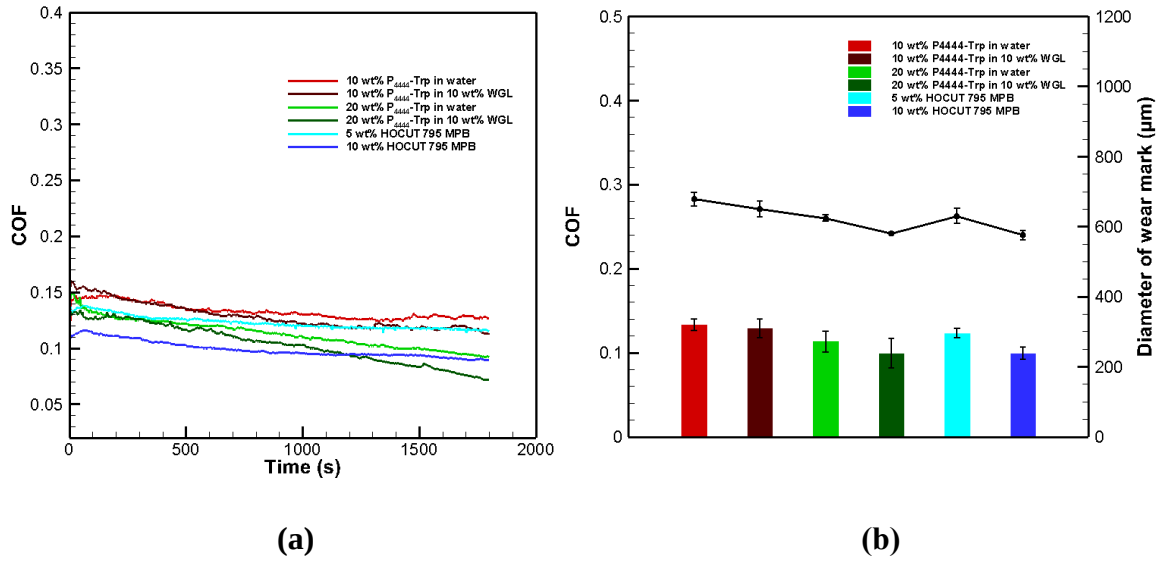


Figure 6.14: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 10N, Velocity: 0.15 m/s, Temperature: 25°C)

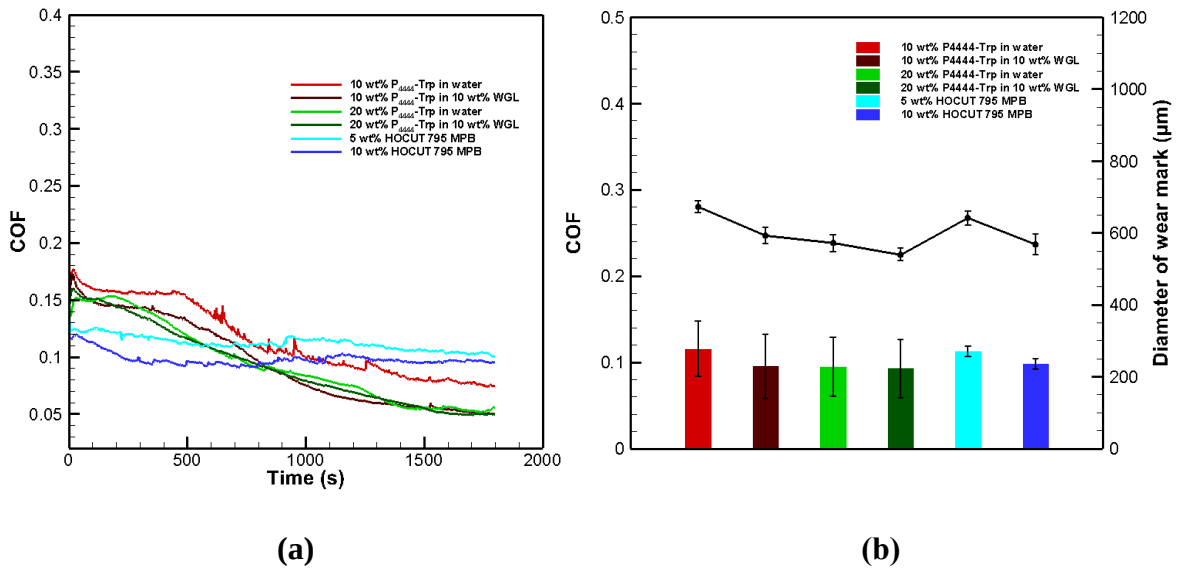


Figure 6.15: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 15N, Velocity: 0.15 m/s, Temperature: 25°C)

The distinct behaviours of HOCUT[®] 795 MPB cutting fluids and P₄₄₄₄-Trp WBLs suggest underlying differences in their lubrication mechanisms. As an oil-based cutting fluid, HOCUT[®] 795 MPB relies primarily on viscosity to establish a thick dynamic pressure lubricating film, providing load support and reducing friction [274]. However, Figure 6.5 demonstrates that P₄₄₄₄-Trp WBLs and HOCUT[®] 795 MPB stayed at the boundary lubrication regime at higher loads, where the boundary lubrication protective layer becomes more critical for effective lubrication. Traditional lubrication oils often lack the necessary polarity and boundary film formation ability to provide adequate load-carrying capacity [273]. In contrast, P₄₄₄₄-Trp WBLs exhibit an exceptional ability to form adsorption layers on surfaces, as demonstrated in previous chapters. These tribofilms, formed by Trp anions, are highly robust, particularly under high loads, and offer excellent load-carrying capacity. The improved tribological performance of P₄₄₄₄-Trp WBLs at high loads further confirms the effectiveness of these adsorption layers. The combination of enhanced viscosity and the formation of robust adsorption layers in P₄₄₄₄-Trp WBLs contributes to their superior tribological performance, making them competitive with traditional oil-based cutting fluids.

6.3.4.5 Velocity effect

To investigate the effect of velocity on tribological performance, friction tests were conducted at sliding velocities of 0.45 m/s and 0.9 m/s. The resulting COF and wear mark diameter data are presented in Figure 6.16 and Figure 6.17, respectively.

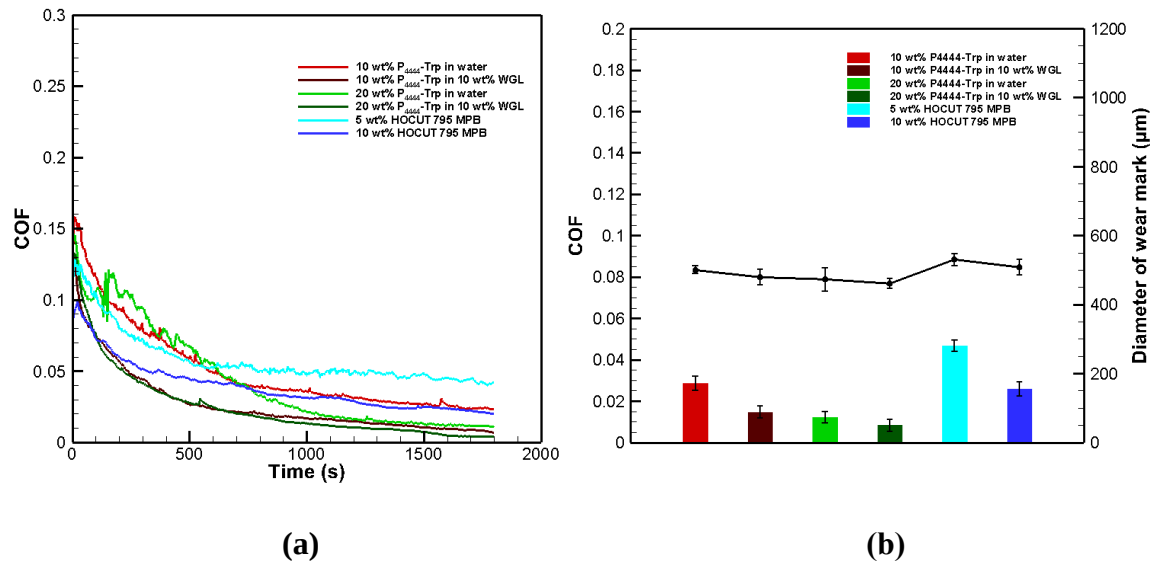


Figure 6.16: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.45 m/s, Temperature: 25°C)

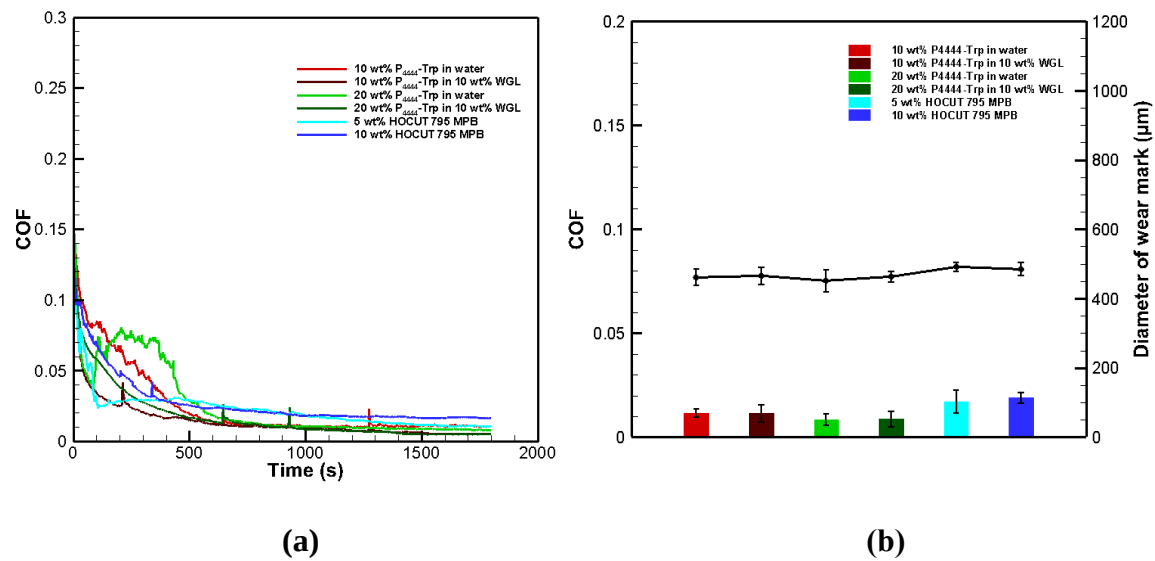


Figure 6.17: (a) Coefficient of friction (COF) versus time (b) averaged COF (Bars) and diameter of wear marks (Lines) for water with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, 10wt% glycerol aqueous solution with 10 wt% and 20 wt% P₄₄₄₄-Trp IL additives, and 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids for steel/steel contacts (Load: 5N, Velocity: 0.9 m/s, Temperature: 25°C)

As shown in Figure 6.16(a), the COFs for all P₄₄₄₄-Trp WBLs and HOCUT[®] 795 MPB exhibit a significant decrease until they reach a stable state with very low COF values ranging from 0.015 to 0.047 at a velocity of 0.45 m/s. A similar trend is observed at a velocity of 0.9 m/s. Considering the findings from Figure 6.5, this behaviour can be attributed to the transition from boundary lubrication to mixed and hydrodynamic lubrication. At high velocities, the lubricant is a mixed or boundary lubrication regime with a thin and incomplete lubrication film. As the velocity increases, the lubricant starts to develop a thicker film between the surfaces due to the increasing shear forces that spread the lubricant across the contact area. This film formation is essential for transitioning to hydrodynamic lubrication. Once a full hydrodynamic film is established, the lubricant completely separates the surfaces, resulting in minimal friction and a stable and low COF.

As illustrated in Figure 6.16 (a) and (b), the stable COF state is reached more rapidly at a velocity of 0.9 m/s compared to 0.45 m/s. At higher velocities, corresponding to higher shear rates, the lubricant is more swiftly drawn into the contact zone, facilitating the quicker formation of a full hydrodynamic film. This accelerated film formation reduces the time spent in the mixed lubrication regime, resulting in a more rapid transition to hydrodynamic lubrication and a more stable COF. To account for the unsteady COF results during the transition phase, the average COF was calculated based on the data points starting at 1000 seconds for tests conducted at 0.45 m/s and 500 seconds for tests conducted at 0.9 m/s, respectively.

Comparing different types of P₄₄₄₄-Trp WBLs in Figure 6.16 reveals that higher concentrations of P₄₄₄₄-Trp IL additives generally result in lower COFs. Furthermore, the superior tribological performance of AAILs with 10 wt% glycerol aqueous solution as the base lubricant is evident even at these higher velocities. Specifically, the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives exhibits exceptionally low COF values at both 0.45 m/s and 0.9 m/s. This

combination also demonstrates a significant reduction in wear, as evidenced by the smaller wear mark diameters in Figure 6.16 (b) and Figure 6.17(b).

When comparing the COF results of P₄₄₄₄-Trp WBLs with HOCUT[®] 795 MPB at the stable state under these high-velocity conditions, only pure water with 10 wt% P₄₄₄₄-Trp IL additives exhibits a slightly higher COF than 10 wt% HOCUT[®] 795 MPB at a velocity of 0.45 m/s. All other P₄₄₄₄-Trp WBLs demonstrate significantly lower COF values than 10 wt% HOCUT[®] 795 MPB at the stable state. Notably, the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives exhibits COF values that are 68% and 54% lower than 10 wt% HOCUT[®] 795 MPB at velocities of 0.45 m/s and 0.9 m/s, respectively.

As discussed in the section effect, P₄₄₄₄-Trp WBLs exhibit a superior friction and wear reduction performance compared to the cutting fluids at a high load condition, which refers to the boundary lubrication regime. The AA anion adsorption layer formation is the mechanism that reduces the direct contact between two metallic surfaces. However, the surface adsorption layers of AA anions do not play the most crucial role in low friction and wear observed at these high-velocity conditions, which refers to mixed or hydrodynamic lubrication. In fact, the lubricant's viscosity is crucial in the hydrodynamic regime because it determines the thickness of the lubricant film formed between the surfaces. A lubricant with a relatively high viscosity will create a film thick enough to separate the surfaces fully, preventing direct contact and thus reducing friction and wear. As illustrated in Figure 6.4, increasing both P₄₄₄₄-Trp IL and glycerol concentrations significantly enhances the viscosity of P₄₄₄₄-Trp WBLs. Additionally, the viscosity of 5 wt% and 10 wt% HOCUT[®] 795 MPB cutting fluids is comparable to that of water with 1 wt% and 3 wt% P₄₄₄₄-Trp WBLs, respectively. However, P₄₄₄₄-Trp WBLs with higher concentrations exhibit substantially higher viscosities. Even in hydrodynamic conditions, where surfaces are ideally separated by a lubricant film, transient boundary lubrication can occur, particularly during start-up. In such scenarios, AA adsorption layers

provide a secondary protective layer on the surfaces, contributing to friction and wear reduction. The combination of enhanced viscosity and the formation of adsorption layers in P₄₄₄₄-Trp WBLs results in excellent tribological performance across various lubrication regimes. This suggests that P₄₄₄₄-Trp WBLs have promising potential for applications under diverse operating conditions.

6.4 Conclusion

This chapter presents a comprehensive experimental investigation of the tribological and rheological properties of P₄₄₄₄-Trp WBLs, exploring their potential as future green industrial lubricants. P₄₄₄₄-Trp WBLs were prepared using both pure water and glycerol aqueous solutions as base lubricants. The corrosion analysis revealed that the presence of both P₄₄₄₄-Trp IL additives and glycerol enhances the anticorrosion properties of P₄₄₄₄-Trp WBLs. No corrosion was observed at a P₄₄₄₄-Trp IL additive concentration of 20 wt%, indicating excellent anticorrosion performance. The formation of thick Trp adsorption films, combined with the enhanced density provided by glycerol adsorption on the metallic surfaces, contributes significantly to the anticorrosion mechanism of P₄₄₄₄-Trp WBLs. Rheological studies demonstrated that the viscosity of P₄₄₄₄-Trp WBLs can be easily adjusted by varying the concentrations of P₄₄₄₄-Trp IL additives and glycerol. The viscosity of 20 wt% P₄₄₄₄-Trp WBLs is significantly higher than that of industrial cutting fluids. The friction tests demonstrated that P₄₄₄₄-Trp additives significantly reduce COF and wear compared to pure water when used as lubricants in both Fe-Fe and Fe-Cu contacts. Increasing the concentration of P₄₄₄₄-Trp additives further enhances tribological performance. For the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp additives, the friction and wear levels are comparable to or even lower than those of industrial oil-based cutting fluids. The synergistic effect of adsorption film formation and enhanced viscosity contributes to the exceptional tribological performance of P₄₄₄₄-Trp WBLs across various lubrication regimes. This highlights their promising potential as

environmentally friendly alternatives to traditional oil-based lubricants for industrial applications.

Chapter 7: Conclusion and Future Works

This thesis presents a comprehensive study on AAIL WBLs as a novel, green industrial lubricant. A detailed literature review discusses the background of WBLs, current research progress in the industry, and the future prospects of this new lubricant in industrial applications. AAILs were selected as specific additives for WBLs to investigate their rheological and tribological properties using both classical and reactive MD simulations, as well as experiments. Ultimately, optimised AAIL WBLs are suggested as potential alternatives to current petroleum-based lubricants in cutting fluid applications.

The key findings and conclusions from this study can be summarised as follows:

- With growing awareness of sustainability and the limited availability of petroleum-based oils, finding potential environmentally friendly WBLs to replace traditional oil-based lubricants in various industrial applications has become urgent and necessary. To enhance the lubrication performance of water, one research area involves introducing additives, such as solid particles, bio-based polymers, and ionic liquids (ILs), to modify its properties. Previous studies have reported that ILs containing AA anions and P₄₄₄₄ cations are promising green additives with extremely low environmental toxicity.
- This study investigated the rheological properties and zero-shear viscosity of WBLs containing AAILs using EMD and NEMD simulations. Experimental measurements also validated the results. The simulations demonstrated that adding AAIL additives to water increased both the shear viscosity and zero-shear viscosity. NEMD simulations on P₄₄₄₄-Ser WBLs indicated that water viscosity increased by 68% to 125% when 5 to 10 wt% P₄₄₄₄-Ser IL additives were added to pure water. These rheological results demonstrate that the viscosity of AAIL WBLs can be adjusted by varying the AAIL content. For P₄₄₄₄-Ser WBLs, the rheological behaviours could be described using Cross, Carreau-Yusuda, and Eyring models, and the improved rheology persisted over a wide range of shear rates up to $\sim 10^{11} \text{ s}^{-1}$. EMD and NEMD simulations on 10 wt% P₄₄₄₄-Ser,

P₄₄₄₄-Lys, and P₄₄₄₄-Phe WBLs revealed that different AAIL WBLs exhibited very similar viscosity and rheological behaviours. This finding was also observed in viscosity measurements using experimental methods on 10 wt% P₄₄₄₄-Ser and P₄₄₄₄-Trp WBLs.

- Despite their similar rheological behaviours, investigations of the tribological behaviours of AAIL WBLs using reactive MD simulations have shown that the introduction of 10 wt% P₄₄₄₄-Ser and P₄₄₄₄-Trp into water significantly reduces COF by 16% and 34%, respectively. The reactive MD simulations used in this study have also revealed the underlying lubrication mechanism. This reduction is attributed to the formation of hydration shells around the amino acid anions, creating a chemically adsorbed tribofilm on iron oxide surfaces. Additionally, P₄₄₄₄ cations establish a load-bearing layer in the middle regions of the lubricant. This dual-layer structure, supported by hydration lubrication, effectively maintains lubricant fluidity while bearing substantial loads.
- Among the AAIL WBLs tested, those with thicker, more stable hydrated amino acid tribofilms demonstrated more significant friction reduction. The size and side chain groups of the AA anions influence tribofilm formation. Generally, AA anions with larger sizes tend to form thicker hydrated amino acid tribofilms on the surfaces. Additionally, side chains containing oxygen or nitrogen atoms contribute to forming more stable bonds with the surfaces. Overall, P₄₄₄₄-Trp WBLs exhibited the best tribological performance among all AAIL WBLs.
- To further enhance lubrication properties and achieve industrial-level performance while maintaining environmental friendliness, P₄₄₄₄-Trp IL additives were introduced not only to pure water-based lubricants but also to glycerol aqueous solutions. The viscosity of WBLs formulated with glycerol aqueous solutions as the base lubricant

was significantly higher than those using pure water as the base lubricant. These results further demonstrate that the viscosity of AAIL WBLs can be adjusted by varying both AAIL and glycerol content.

- Corrosion analysis revealed that P₄₄₄₄-Trp IL additives and glycerol enhance the anticorrosion properties of P₄₄₄₄-Trp WBLs. No corrosion was observed at a P₄₄₄₄-Trp IL additive concentration of 20 wt%, indicating excellent anticorrosion performance.
- Friction tests demonstrated that the tribological performance of AAIL WBLs using a 10 wt% glycerol aqueous solution as the base lubricant improved compared to using pure water as the base lubricant under various test conditions spanning different lubrication regimes. When benchmarked against industrial oil-based cutting fluids, the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives achieved a comparable tribological performance in terms of friction wear reduction and performance under various conditions. The combined effects of improved viscosity and layered configuration from the AAIL contributed to this superior tribological performance under different lubrication regimes. These promising results highlight the potential of AAIL WBLs as viable replacements for industrial oil-based cutting fluids.

While this study has provided a comprehensive investigation of AAIL WBLs, several areas offer opportunities for future research:

- Due to the relatively new nature of this research area, particularly when using MD simulations, the availability of current force field parameters for AAILs in MD simulations is limited. For example, the LJ parameters for Trp have not been developed in previous studies, preventing the investigation of the rheological performance of P₄₄₄₄-Trp WBLs using EMD and NEMD simulations. Additionally, ReaxFF parameter sets suitable for describing the interaction of P₄₄₄₄-AA WBLs with copper surfaces are currently unavailable, hindering the study of the lubrication mechanism for these WBLs

between these metal surfaces using ReaxFF. With the future development of new MD force field parameters, these limitations can be addressed in future research.

- While the 10 wt% glycerol aqueous solution with 20 wt% P₄₄₄₄-Trp IL additives was identified as the AAIL WBL with the best tribological performance in this study, industrial metal cutting applications involve a wide range of conditions and materials with varying requirements for tribological performance. Therefore, further research is needed to optimise the concentrations of both AAIL and glycerol to suit specific applications. This will require additional testing under various conditions and with different materials.
- While this study focused on metal-cutting applications, a potential area for using WBLs, there are numerous other industrial applications discussed in Chapter 1 where WBLs could replace traditional oil-based lubricants. These include metalworking, metal deformation, and machinery applications. Research on WBLs for these applications might require investigations under different conditions or consideration of additional lubricant properties. For example, specific properties or conditions relevant to metalworking, metal deformation, or machinery applications may need to be evaluated to assess the suitability of WBLs in these contexts.
- The ultimate goal of this study is to commercialise AAIL WBLs. A future research direction could involve a feasibility analysis of commercialisation, including considerations such as production process development, market demand analysis, and cost estimation.

Overall, this study demonstrates the promising potential of AAIL WBLs as alternatives to traditional oil-based lubricants, contributing to a more sustainable mechanical manufacturing industry. In addition, the methodology employed in MD simulations and experiments in this study also provides a valuable guideline for future green lubrication research.

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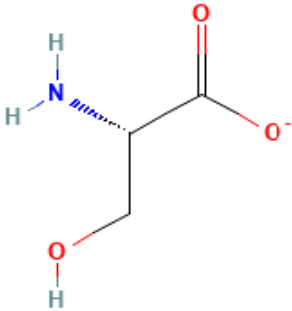
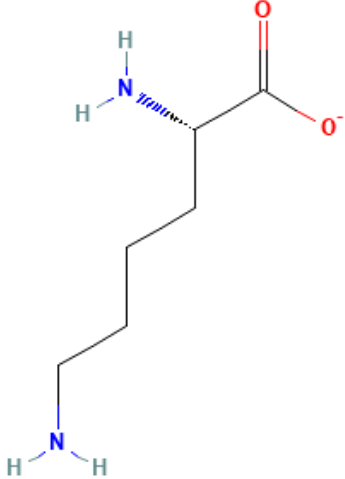
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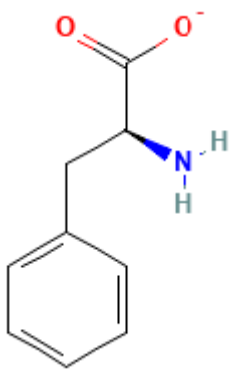
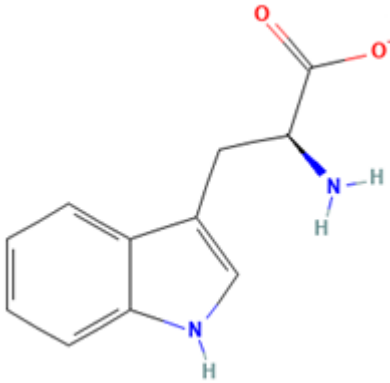
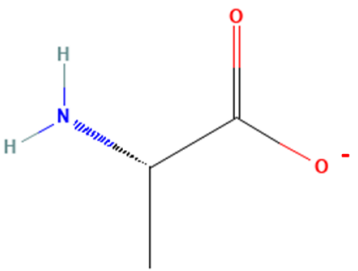
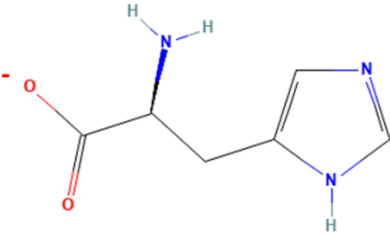
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Appendix

Table A1: The chemical name, formula, structure and molar mass of the cation and anions used for creating AAILs in this work.

		Molecular Formula	Structural Formula [278]	Molar Mass (g/mol)
Cation	Tetrabutylphosphonium (P ₄₄₄₄)	C ₁₆ H ₃₆ P ⁺		259.43
	Serine (Ser)	C ₃ H ₆ NO ₃ ⁻		104.08
	Lysine (Lys)	C ₆ H ₁₃ N ₂ O ₂ ⁻		145.1

Anion	Phenylalanine (Phe)	$C_9H_{10}NO_2^-$		164.2
	Tryptophan (Trp)	$C_{11}H_{11}N_2O_2^-$		203.2
	Alanine (Ala)	$C_3H_6NO_2^-$		88.1
	Histidine (His)	$C_6H_8N_3O_2^-$		154.2

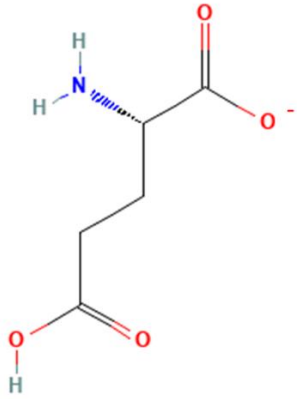
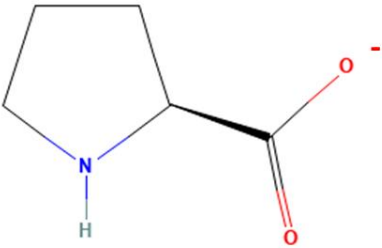
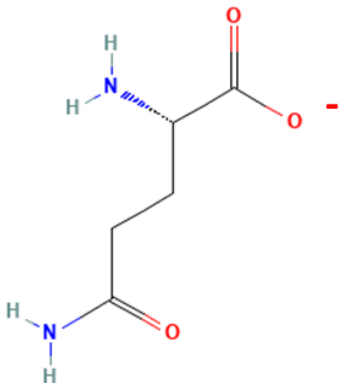
	Glutamic (Glu)	$C_5H_8NO_4^-$		146.1
	Proline (Pro)	$C_5H_8NO_2^-$		114.1
	Glnamine (Gln)	$C_5H_{10}N_2O_3^-$		145.2

Table A2: The bond and angle potential parameters for P_{4444} cation AA anions [197]

Bond Parameters					
	$K_r(\text{kcal/mol}/\text{\AA}^2)$	$r_0(\text{\AA})$			
		P_{4444}	Ser	Lys	Phe
CT-CT	310	1.5334	1.5279	1.5295	1.5375
CT-C	317		1.5549	1.5539	1.5607

CT-CA	317				1.5181
CT-N3	367		1.4573	1.4647	1.4647
CT-N3*	367			1.4627	
CT-P	210	1.8273			
CT-HC	331	1.0860		1.0884	1.0884
CT-H1	325		1.0849	1.0875	1.0894
CT-HP	336.5	1.0862			
C-O2	500		1.2360	1.2379	1.2367
CA-CA	400				1.3903
CA-HA	258.76				1.0765
N3-H	450		1.0038	1.0045	1.0039
N3*-H	450			1.0025	
OH-HO	545		0.9515		
Bond Angle Parameters					
	K_r(kcal/mol/ Å²)	θ₀ (Å)			
		P₄₄₄₄	Ser	Lys	Phe
CT-CT-CT	41	111.88		113.39	
CT-CT-C	60		109.87	110.95	113.85
CT-CT-CA	63				115.69
CT-CT-N3	60		108.10	108.13	110.17
CT-CT-N3*	70			111.24	
CT-CT-OH	55		111.29		
CT-CT-P	75	116.24			
CT-CT-HC	42.5	109.96		109.08	107.78

CT-CT-H1	47		109.11	109.11	105.53
CT-CT-HP	31	110.07			
C-CT-N3	90		114.21	108.13	114.71
C-CT-H1	58		108.47	108.31	104.50
N3-CT-H1	60		108.46	107.89	106.67
N3*-CT-H1	60			109.96	
P-CT-HP	32.5	106.74			
HC-CT-HC	38.3	106.47		106.34	108.05
H1-CT-H1	38.5		107.82	106.85	
HP-CT-HP	36.7	107.36			
CT-C-O2	80		115.30	115.57	115.57
O2-C-O2	85		129.38	128.84	128.80
CT-CA-CA	70				121.00
CA-CA-CA	63				120.00
CA-CA-HA	38				119.80
CT-N3-H	50		107.63	107.29	107.43
CT-N3*-H	50			110.68	
H-N3-H	50		104.63	104.51	103.66
H-N3*-H	50			107.00	
CT-OH-HO	51		105.50		
CT-P-CT	50	109.46			

Table A3: Dihedral potential parameters for P_{4444} cation AA anions [197]

Dihedral Parameters							
Dihedral	γ (deg)	K_{ϕ} (kcal/mol)	n^*	Dihedral	γ (deg)	K_{ϕ} (kcal/mol)	n^*
CT-CT-CT-CT	0	0.18	3	CT-CT-CT-N3*	0	0.2139	3
CT-CT-CT-P	0	0.1441	3	CT-CT-CT-H1	0	0.1561	3
C-CT-CT-CA	0	0.1561	3	CA-CT-CT-N3	0	0.1561	3
C-CT-CT-OH	0	0.1561	3	N3-CT-CT-OH	0	0.1561	3
CT-CT-C-O2	0	0	2	N3-CT-CT-H1	0	0.1561	3
HC-CT-C-O2	0	0.2299	2	OH-CT-CT-HC	0	0.1561	3
CT-CT-CT-C	0	0.1561	3	HC-CT-CT-HC	0	0.1501	3
C-CT-CT-N3	0	0.1561	2	HC-CT-CT-HP	0	0.1501	3
C-CT-CT-H1	0	0.1561	3	CT-CT-CT-N3	0	0.1561	3
C-CT-CT-HC	0	0.1561	3	CT-CT-CT-HC	0	0.1590	3
CA-CT-CT-H1	0	0.1561	3	CT-CT-CT-HP	0	0.1590	3
N3-CT-CT-HC	0	0.1561	3	C-CT-CT-N3*	0	0.1561	2
OH-CT-CT-H1	0	0.1561	3	N3*-CT-CT-HC	0	0.2139	3
P-CT-CT-HC	0	0.1441	3	HC-CT-CT-H1	0	0.1561	3
H1-CT-CT-H1	0	0.1561	3	N3-CT-C-O2	0	0.2299	2
H1-CT-C-O2	0	0	2	HC-CT-CA-CA	0	-0.125	2
CT-CT-N3-CT	0	0.056	3	C-CT-N3-CT	0	0.256	3
H-CT-N3-CT	0	0.1	3	H1-CT-N3-H1	0	0.1	3
HP-CT-P-CT	0	0.165	3	H1-CT-N3*-H	0	0.22	3
CT-CA-CA-HA	180	3.625	2	H1-CT-OH-HO	0	0.3	3
CA-CA-CA-HA	180	3.625	2	CT-CT-CA-CA	0	0.125	2

CT-CT-N3-H	0	0.1	3	CT-CT-N3*-H	0	0.1	3
H1-CT-N3-CT	0	0.056	3	CT-CT-OH-HO	0	1.2	1
CT-CT-P-CT	0	0.165	3	CT-CA-CA-CA	180	3.625	2
CA-CA-CA-CA	180	3.625	2	HA-CA-CA-HA	180	3.625	2

** n: The coefficient of periodicity of the angle*