RICE UNIVERSITY

The Behavior of Surfactants in Water / Oil System by Dissipative Particle Dynamics

by

Hassan Alasiri

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE

Dr. Walter G. Chapman, Chair
William W. Akers Professor
Chemical and Biomolecular Engineering

Dr. Francisco Vargas
Assistant Professor
Chemical and Biomolecular Engineering

Dr. Mason B. Tomson
Professor
Civil and Environmental Engineering

HOUSTON, TEXAS
December 2016
Abstract

The Behavior of Surfactants in Water / Oil System by Dissipative Particle Dynamics

by

Hassan Alasiri

Dissipative Particle Dynamics is a mesoscale simulation model that is widely used in simulation of complex fluids. This method simulates the fluid in the scales between microscopic and macroscopic scales. The scope of this research is to study the influence of different type of surfactants and the phase behavior into the water/oil system by using dissipative particle dynamics simulation. The DPD method shows to be a reliable tool to get a better understanding about the prediction of the phase behavior of surfactants/oil/water system and to estimate the properties of surfactant. The DPD simulation is applicable to support the complicated experiments or to obtain data unavailable from experiment. To avoid expensive experiments, this simulation can be used to predict the properties of surfactants by suggesting promising information about different type of surfactants. In this thesis, the DPD interaction parameters between the beads as an input for DPD simulations are estimated using the COSMO-RS model (Conductor-like Screening Model for Real Solvents) through the Flory-Huggins interaction parameter matching the infinite dilution activity coefficient. The outcomes of this thesis are:

1. Interfacial tension (IFT) study: The DPD simulation was used to study the interfacial phenomena of water/alkanes and surfactant/water/octane systems. The computed interfacial tension of water/alkanes systems agrees very well with the experimental value
for all temperatures. For surfactant/water/octane systems, dissipative particle dynamic (DPD) simulations were performed to study the interfacial properties such as interfacial tension, area compressibility, stress profile, and conformation of surfactant at water/octane interface. The IFT results of DPD agree qualitatively with experimental measurement. We perform a series of experimental study on the interfacial tension of surfactants with different structures at the octane/water interface to study the effect of different head group and tail group of surfactants, and the adsorption of Triton X-100 surfactant on water/octane interface. Moreover, the effect of sodium chloride (NaCl), calcium chloride (CaCl₂), and temperature for one surfactant concentration and varying concentrations of salt or temperature were investigated on water/octane interface.

2. Critical micelles concentration (CMC) of SDS surfactant study: dissipative particle dynamics to determine the CMC has been used for sodium dodecyl sulfate (SDS) surfactant. The effect of NaCl salt and temperature upon the critical concentration for micelle formation have been investigated. The effects of salt on the CMC values were found to be consistent with experimental data. From DPD results, the CMC increases with increasing the temperature but the experimental values propose a minimum in the CMC around 25 °C. The DPD simulation cannot capture the minimum value as cores grained model.

3. The adsorption of SDS surfactant on carbonate surface study: Various concentration of SDS surfactant in water/ calcium carbonate system are evaluated to determine the amount of adsorption of surfactant to the surface by DPD. Simulation results show that the Freundlich isotherm models were well fitted better than Langmuir model of adsorption on calcium carbonate surface with a good agreement with the experimental fitting parameters.
4. The phase behavior of C₈E₄ surfactant study: Several DPD calculations were carried out at different simulation conditions with the C₈E₄ surfactant for water/octane model. From the simulation results, we are able to find the phase transition with changing the fraction volume of oil and temperature. We found five different phase structure depending on the oil/water volume fractions and temperature: spherical (inverse spherical) micelles, cylindrical (inverse cylindrical), hexagonal (inverse hexagonal), lamellar, and bicontinuous phase.
Acknowledgments

Firstly, I would like to express my sincere gratitude to my advisor Prof. Walter Chapman for the continuous support of my Ph.D. study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D. study. Besides my advisor, I would like to thank the rest of my thesis committee: Prof. Mason Tomson, and Dr. Francisco Vargas, for serving on my thesis committee. I thank Prof. George Hirasaki, and Prof. Clarence Miller for helpful and valuable discussions for surfactant study. I thank all my groupmates from Chapman’s group for their support in my PhD research.

My sincere thanks also goes to Dr. Abdullah Sultan, who gave access to his laboratory and research facilities at King Fahd University of Petroleum and Minerals (KFUPM) in Saudi Arabia to do some experimental work.

Financial support from King Fahd University of Petroleum and Minerals (KFUPM) is acknowledged.

I would like to thank my parents, my brothers, and my sisters, for support and encouragement in my Ph.D. study.

At the end, I want to express my gratitude and deepest appreciation to my wife and my sons. Without supports and encouragements from my wife, I could not have finished this work, it was you who kept the fundamental of our family, and I understand it was difficult for you to deal with our son disability. I want just say thanks for everything and may Allah give you all the best in return.
Contents

Chapter 1 Introduction .............................................................................................................. 1
  1.1 Surfactants Motivation ......................................................................................................... 1
  1.2 Simulation motivation .......................................................................................................... 2
  1.3 Organization of Thesis ......................................................................................................... 4

Chapter 2 Literature review .................................................................................................... 6
  2.1 Surfactants .......................................................................................................................... 6
    2.1.1 Surfactant interfacial tension ......................................................................................... 7
    2.1.2 Critical micelle concentration (CMC) ........................................................................... 10
    2.1.4 Phase behavior of ternary systems water / oil / nonionic surfactant ......................... 13
    2.1.4 Adsorption at liquid-solid system .................................................................................. 15
  2.2 Molecular modeling tools for surfactants ........................................................................... 18
    2.2.1 Density functional theory (DFT) .................................................................................. 19
    2.2.2 Molecular dynamics (MD) ............................................................................................ 20
    2.2.3 Dissipative particle dynamics (DPD) .......................................................................... 21

Chapter 3 Dissipative particle dynamics (DPD) method .......................................................... 24
  3.1 Fundamentals of Dissipative Particle Dynamics (DPD) simulation .................................. 24
  3.2 Interaction forces in DPD ..................................................................................................... 25
  3.3 Thermostat .......................................................................................................................... 27
  3.4 Integration algorithm ........................................................................................................... 28
  3.5 Properties of DPD parameters .......................................................................................... 29
  3.6 Statistical thermodynamics to determine Flory-Huggins interaction parameters .......... 33
  3.7 Conductor-like Screening Model for Real Solvents (COSMO-RS) calculation for infinite
dilution activity coefficients ........................................................................................................ 36

Chapter 4 Dissipative particle dynamics (DPD) study of alkanes/water systems interfacial tension
.................................................................................................................................................. 40
Chapter 7 Phase behavior of a water-oil-surfactant study of nonionic surfactant by DPD ......... 110

7.1 Introduction ........................................................................................................................................ 110
7.2 Methodology ....................................................................................................................................... 114
7.3 Results and Discussion ..................................................................................................................... 116
7.4 Conclusion ........................................................................................................................................... 122

Chapter 8 Experimental study of the interfacial tension for water/octane/surfactant system .... 123

8.1 Introduction ........................................................................................................................................ 123
8.2 Experimental method ......................................................................................................................... 125
8.3 Results and Discussion ....................................................................................................................... 130
  8.3.1 Effect of Head and Tail Group of Surfactant ............................................................................... 130
  8.3.2 Adsorption of Triton X-100 surfactant on water/octane interface .............................................. 134
  8.3.3 Effect of Salts and Temperature at Interface ............................................................................. 135
8.4 Conclusion .......................................................................................................................................... 137

Chapter 9 Conclusion and Future Work ............................................................................................... 139

9.1 Conclusion .......................................................................................................................................... 139
9.2 Future Work ......................................................................................................................................... 141
  9.2.1 Interfacial tension ......................................................................................................................... 141
  9.2.2 Critical micelles concentration (CMC) ..................................................................................... 142
  9.2.3 Adsorption of surfactants onto surface ..................................................................................... 143

Bibliography ............................................................................................................................................. 144

Appendix A The steps for performing simulations .............................................................................. 166
Appendix B Sigma profiles ....................................................................................................................... 169
Appendix C Experimental IFT data ........................................................................................................ 172
List of Figures

Figure 1.1: Western Europe Annual production surfactants from 1994 to 2014 (CESIO) [21] .........................2
Figure 2.1: Classification of surfactants. ........................................................................................................7
Figure 2.2: The pattern formation and aggregation forms in surfactant solutions as a function of surfactant concentration [26]. .................................................................................................12
Figure 2.3: Schematic representation of a phase diagram of a ternary system of water / oil / nonionic surfactant [30]. Left: phase prism of a ternary system water / oil / nonionic surfactant; Right: schematic representation of the interface tension as a function of temperature. ..................................................14
Figure 2.4: Adsorbed structures of surfactants at solid surfaces [34]: monolayer, bilayer, admicelles, and hemimicelles ...........................................................................................................................................17
Figure 2.5: Typical adsorption isotherms for ionic surfactants on hydrophilic surfaces ..............................17
Figure 2.6: the major Multiscale molecular modeling tools ............................................................................19
Figure 3.1: The excess pressure depends the interaction parameter and quadratically on density [58]. ........31
Figure 3.2: The excess repulsion parameters as function of χ –parameter [58]. ............................................32
Figure 4.1: Sigma profiles of water (H2O) and alkanes (oils) molecules (C6 Hexane, C7 Heptane, C8 Octane, C9 Nonane, C10 Decane, C11 Undecane, and C12 Dodecane) ...........................................50
Figure 4.2: Infinite dilution activity coefficients of water in n-alkanes at 25°C. experimental [107], [108], COSMOtherm [105], Bastos 1988 [109], Gmehling 1993 [110], Hansen 1992 [111] .........................54
Figure 4.3: (a) Water (blue) and dodecane (red) DPD simulation box at 25 °C, (b) The density profile in the X-direction of the simulation ..............................................................................................................55
Figure 4.4: The interfacial tension as function of temperature for DPD (lines) and experimental data (dots) [90], (each molecule is represented by one bead for DPD calculations). ......................................................57
Figure 4.5: The interfacial tension as function of temperature for water/alkane system by using different monomer. m=1: methyl, m=2 ethyl, m=3: propyl, m=4: butyl (m=4), 1 bead: alkane is representing as one bead results from Figure 4.4, Exp; experimental results from [90], and DPD-lit: DPD results from [95] ..................................................................................................................................................61
Figure 5.1: (a) Atomistic model of surfactants (SDS, DTAB, and DDAO), octane, water, and ions salts with water. (b) Mesomoleculer model: the coarse-grained model of each surfactant is represented as 3 Tail (T) beads and one head bead A, C, and Z for SDS, DTAB, and DDAO surfactants head group respectively. Octane is represented by 2 Tail (T) beads. Water (W) bead has 4 water molecules. Beads containing ions have 3 water molecules plus the Cl-, Na+, and Ca+ ions for WCl, and WNa, and WCa respectively. .........................................................................................................................73
Figure 5.2: The experimental results of interfacial tension as a function of surfactant concentration at T = 25 °C for three different surfactants (SDS, DTAB, and DDAO) at the interface of water/octane system. ...77
Figure 5.3: The experimental results of interfacial tension of water / Octane system as a function of salt concentration (NaCl, and CaCl2) and temperature for fixed SDS concentration of 0.35mM T = 25 °C.78
Figure 5.4: The DPD results of interfacial tension as a function of number of surfactants at \( T = 25 \, ^\circ\text{C} \) for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system. 82

Figure 5.5: The DPD results of stress profile with fixed number of surfactants (120 surfactants) at \( T = 25 \, ^\circ\text{C} \) for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system. 82

Figure 5.6: The DPD results of root mean square (RMS) end-to-end distance as a function of number of surfactants at \( T = 25 \, ^\circ\text{C} \) for SDS, DTAB, and DDAO surfactants. 83

Figure 5.7: The change of the interfacial tension versus the reduced relative area change per surfactant at \( T = 25 \, ^\circ\text{C} \). 83

Figure 5.8: The DPD results of interfacial tension as a function of number of salts at \( T = 25 \, ^\circ\text{C} \) and as function of temperature at fixed number of SDS surfactant at 120 surfactants for water/octane system. 87

Figure 5.9: The DPD results of interfacial tension as a function of number of surfactants for three systems at fixing \( T = 85 \, ^\circ\text{C} \), 375 molecules of NaCl, and 375 molecules of CaCl\(_2\) at the interface of water/octane system. 87

Figure 5.10: Snapshots of the water/octane systems at fixed the number of SDS surfactant at 120 surfactants (A) without any salts (B) with 375 molecules of NaCl (C) 375 molecules of CaCl\(_2\). (The water beads are removed for clarity, octane beads: red; head beads: blue; tail beads: pink; WCl beads: green; WNa beads: yellow; WCa beads; orang). 88

Figure 5.11: The DPD results of stress profile at fixed number of SDS surfactants (120 surfactants) for four systems at fixed \( T = 85 \, ^\circ\text{C} \), 375 molecules of NaCl, and 375 molecules of CaCl\(_2\) at the interface of water/octane system compared with SDS system at 25 \( ^\circ\text{C} \). 89

Figure 5.12: The DPD results of root mean square (RMS) end-to-end distance as a function of number of surfactants for three systems at fixing \( T = 85 \, ^\circ\text{C} \), 375 molecules of NaCl, and 375 molecules of CaCl\(_2\) at the interface of water/octane system in comparison with SDS system at 25 \( ^\circ\text{C} \) without salts. 89

Figure 5.13: The change of the interfacial tension against the reduced relative area change per SDS surfactant for three systems at fixing \( T = 85 \, ^\circ\text{C} \), 375 molecules of NaCl, and 375 molecules of CaCl\(_2\) at the interface of water/octane system comparing with SDS system at 25 \( ^\circ\text{C} \) without salts. 90

Figure 6.1: The evolution of the free surfactants concentration (\( C_f \)) as a function of the total concentration of surfactants (\( C_T \)) for SDS surfactant in water. 100

Figure 6.2: Snapshots of the SDS in water at 25 \( ^\circ\text{C} \) as increasing the concentration of surfactants at equilibrium. (a) 12.1 mM (b) 15.6 mM (c) 19.1 mM (The water beads is removed for clarity; head beads: green; tail beads: red). 101

Figure 6.3: Temperature dependence of the CMC values of DPD and experimental for the SDS surfactants. (experimental CMC values from ref [156]) 102

Figure 6.4: Effect of NaCl salts on the CMC values of DPD and experimental for the SDS surfactants at 25 \( ^\circ\text{C} \). (experimental CMC values of slats from ref [142]) 102
Figure 6.5: The adsorption isotherm of SDS on calcium carbonate for DPD and experimental. Experimental data ref. [151]...

Figure 6.6: Snapshots of the SDS in water at 25 °C with calcium carbonate as increasing the concentration of surfactants at equilibrium. (a) 1250 ppm from first region (b) 2750 ppm from second region (c) 4500 ppm from last region (The water beads is removed for clarity; head beads: green; tail beads: red, calcium carbonate beads: pink).

Figure 6.7: Langmuir isotherm model fit from DPD results for adsorption of SDS surfactant on calcium carbonate at 25 °C.

Figure 6.8: Freundlich isotherm model fit from DPD results for adsorption of SDS surfactant on calcium carbonate at 25 °C.

Figure 7.1: Different microstructures of nonionic surfactants with the mass fraction of the oil in the binary mixture of oil and water at constant surfactants. (a) Phase prism of a ternary mixture at constant surfactants. (b) Schematic phase diagram [26].

Figure 7.2: Mesomorphic model: the coarse-grained of surfactant is represented as 2 Tail (T) beads and 4 head (H) beads. Octane is represented by 1 (O) bead. Water (W) bead has 1 water molecule. Water: green, Octane: red, Tail: blue, and Head: pink.

Figure 7.3: DPD phase structures transition with changing volume fraction and temperature at fixing the concentration of surfactants. Blue: spherical and inverse spherical micelles, red: cylindrical and inverse cylindrical, green: hexagonal and inverse hexagonal, yellow: lamellar, gray: bicontinuous phase.

Figure 7.4: Snapshots of phase structures transition from 0.1 to 0.5 volume fraction of oil ($\alpha O$) at fixing the temperature at 60 °C. (The octane beads is removed for clarity)

Figure 7.5: Snapshots of phase structures transition from 0.5 to 0.9 volume fraction of oil ($\alpha O$) at fixing the temperature at 60 °C (The water beads is removed for clarity)

Figure 7.6: Snapshots of phase structures transition between 20 °C and 60 °C at 0.5 volume fraction. (for bicontinuous phases the octane beads is removed for clarity)

Figure 8.1: Principle design of the Pendant drop apparatus (picture from manual of Attension Theta Optical Tensiometer equipment).

Figure 8.2: Shape of a dropping drop taken from a DVC camera.

Figure 8.3: The results of interfacial tension as a function of surfactants concentration at $T = 25 ^\circ C$ for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system.

Figure 8.4: The results of interfacial tension as a function of surfactants concentration at $T = 25 ^\circ C$ for four different surfactants (SDS, LDS, DTAB, and DTAC) at the interface of water octane system.

Figure 8.5: The results of interfacial tension as a function of surfactants concentration at $T = 25 ^\circ C$ for two different surfactants (DTAB, and CTAB) at the interface of water octane system.

Figure 8.6: The results of interfacial tension as a function of surfactants concentration at $T = 25 ^\circ C$ for Triton X-100 surfactant at the interface of water octane system.
Figure 8.7: The results of interfacial tension of water / octane system as a function of salts concentration (NaCl, and CaCl₂) and temperature for fixed SDS surfactants at 0.35 mM. (the IFT values for salts at T = 25 °C). .................................................................................................................................................................................. 136

Figure 8.8: The results of interfacial tension of water / octane system as a function of salts concentration (NaCl, and CaCl₂) and temperature for fixed Triton X-100 surfactant at 0.16 mM. (the IFT values for salts at T = 25 °C). ........................................................................................................................................................................................................ 137
List of Tables

Table 4.1: Infinite dilution activity coefficients of water in alkanes and interaction parameters aij as function of temperature over the range from 5 °C to 85 °C. .................................................................54
Table 4.2: Interfacial tension experimental and DPD for alkane/water systems with Relative Absolute Error percent (RAE %) at 25°C. ........................................................................................................56
Table 4.3: The calculation of rc for each monomer. .......................................................................58
Table 4.4: The calculation of interaction parameters aij(m) after scaling........................................59
Table 5.1: Molecule volume of water, head group surfactants, butane (tail), and ions salts from COSMO....74
Table 5.2: Interaction parameters calculation: the infinite dilution activity coefficient $\gamma_{ij}^{\infty}$, molecular volume ratio $v_j/v_i$, the Flory-Huggins interaction parameters before and after scaling ($\chi_{ij}^{\infty}$, $\tilde{\chi}_{ij(m)}^{\infty}$), DPD interaction parameters after scaling $a_{ij(m)}$, and m is scaling number.................................................................75
Table 6.1: Interaction parameters for all DPD beads for CMC study..................................................95
Table 6.2: The interaction parameters for calcium carbonate bead (S) with water (W), head (A), and tail (T) beads.........................................................................................................................97
Table 6.3: Adsorption isotherm parameters of SDS on calcium carbonite for DPD and experimental........108
Table 7.1: The calculation of $\chi_{ij}^{\infty}$ parameters of ethylene oxide (head group) against water (W), octane (O), and tail (T) beads from the infinite dilution activity coefficient........................................115
Table 7.2: Interaction parameters aij. ...............................................................................................115
Table 8.1: Name and the Structure of Surfactants ...........................................................................126
Chapter 1 Introduction

1.1 Surfactants Motivation

Amphiphilic compounds are in the form of soaps since ancient times. However, we began to understand what operations lead at the molecular level to this utility only a few decades ago. The combination of a hydrophilic (polar) and hydrophobic (non-polar) groups indicates the amphiphilic property. Amphiphilic compounds are also known as surfactant. Surfactants are key segments in numerous industrial processes such as detergents, cleaners, cosmetics, personal care products, textiles, fibers, paints, plastics, medicine, biochemical, oilfield chemicals and petroleum production, pharmaceuticals, food and packaging of food, pest control, and plant protection [1]–[7]. The production of surfactants has expanded throughout the most recent decades. According to the CESIO (Comité Européen des Agents de Surface et leurs intermediaries Organiques), ethoxylates and anionic surfactants are the most produced surfactants among the other kinds of surfactants and amphoteric surfactants are lower production of surfactants between 1994-2014 as seen in Figure 1.1. Therefore, the surfactants are one of the most important substance due to their diverse applications particularly in enhanced oil recovery (EOR). Enhanced oil recovery (EOR) has become an area of revived interest due to the ability of EOR to produce more oil. 3 % of oil comes from EOR and the number is increasing daily. It is expected that enhanced oil recovery will eventually produce the majority of the world’s oil. Around 60 % of the oil remains in many oil reservoirs and enhanced oil recovery (EOR) have been developed to recover the remaining oil after waterflood [8]. Enhanced oil recovery (EOR) such as alkaline/surfactant/polymer (ASP) flooding is an attractive technique because it modifies the interfacial tensions and improves the sweep efficiency of the water/oil system [9]–[20]. Determining the phases and structures of the
surfactants by experimental methods for the prediction of enhance oil recovery (EOR) is of great practical importance. The molecular modeling can provide valuable information for the surfactant for water/oil system and the prediction of surfactant properties such as structure of the surfactant, interfacial tension (IFT), and Critical Micelle Concentration (CMC). The combination of experiment, and molecular modeling allows a better understanding and clarify some characteristic patterns of behavior of the surfactant.

![Graph](image)

Figure 1.1: Western Europe Annual production surfactants from 1994 to 2014 (CESIO) [21].

### 1.2 Simulation motivation

The simulations can play an important role for scientific research. They are a way of doing science and can be used as a reductionist tool. The benefits from the simulations could be as: simulation models can be used to test theory or simulation data to compare with experimental data
to test the realism of the simulation models. Simulations of atomistic or molecular systems are useful because they can provide a molecular interpretation of experimental facts, some which can be difficult to obtain experimentally. In addition, the simulation can also be used to guide new experiments by allowing prediction of novel phenomena, emerging structures and properties of materials.

In this thesis, Dissipative Particle Dynamics (DPD) was introduced as the method for calculations of surfactant/water/oil systems. Dissipative particle dynamics (DPD) is used as coarse graining technique to simulate complex fluids at mesoscopic scales. Dissipative particle dynamics as mesoscopic modeling focuses on predicting the material properties that are determined by the structure and behavior between microscopic scales (atomistic) and macroscopic (continuous) and this scale is typically between 10 - 1000 nm and 1 ns - 10 ms. Many complex systems act at mesoscale such as surfaces and interfaces, microfluidics, biological membranes and phase behavior. The coarse graining is grouping atoms together and treating them as one object (bead). The advantages of using coarse graining are: reducing the degrees of freedom for particles, neglecting the atomistic details, and less computational cost for complex fluids. The advantage of DPD over atomistic methods such as molecular dynamics MD is less computational cost for complex fluids because of the coarse graining reduces the number of interactions necessary to compute. In addition, the soft potentials used in DPD make larger time steps than in MD. The expensive calculations on the atomistic scale in MD is not comparable with DPD. The lattice Boltzmann method which are on the same family level of DPD (mesoscopic level), can also be used for the calculation of hydrodynamic phenomena, however, have a serious disadvantage as compared to DPD simulation. The lattice symmetry description of liquids in many cases is physically incorrect and leads to artifacts for lattice Boltzmann method. Moreover, the flow
behavior under shear are difficult to describe with the lattice model. Although lattice models allow the correct description of the hydrodynamics in the system but are not as flexible as DPD models. The dissipative particle dynamics avoids the disadvantages of both the atomistic and the mesoscale grid methods. Dissipative particle dynamics (DPD) was initially introduced by Hoogerbrugge and Koelman in 1992 [22] and the important of DPD is increasing since that time. The DPD simulation has not only an area of interesting research for academia in recent years, industry has also shown great interest in DPD and have even been responsible for many achievements by using DPD method such as the DPD method was conceived in Shell and then developed in Unilever. In addition, it has also been used in industry in COMEX Mexican. Dissipative particle dynamics (DPD) is the method that could be the best practicability and performance to use as computer simulation methods for the behavior of water/oil/surfactant systems in this work.

1.3 Organization of Thesis

The work of thesis is divided into nine chapters. Chapter 1 presents the introduction and the motivation of the work. Chapter 2 consists of some background information about surfactants. It begins with some fundamental concepts of surfactant properties such as interfacial tension, critical micelle concentration (CMC), adsorption at liquid-solid system, and phase behavior of water / oil / surfactant. Then a short literature review about surfactant studies using density functional theory (DFT), molecular dynamics (MD), and Dissipative Particle Dynamics (DPD) as molecular modeling tools are discussed. Chapter 3 explained Dissipative Particle Dynamics (DPD) simulation method. It begins with some fundamental concepts of Dissipative Particle Dynamics (DPD), including the interaction forces in DPD, thermostat, integration algorithm, and properties of DPD parameters. In chapter 4, The interaction parameters with temperature dependence as input
for DPD simulations calculated from Flory-Huggins $\chi$ parameter and COSMO-RS (Conductor-like Screening Model for Real Solvents). We studied the interfacial tension as a function of temperature for alkanes (C6-C12)/water systems by DPD. In addition, interfacial tension was calculated by rescaled $\chi$ parameters as a function of bead size to treat alkanes as chains of beads. Chapter 5 focuses on the effect of different head group of surfactants, temperature, and salts at the water/octane interface. We discussed the orientation of surfactants, stress profile, and the area compression modulus, and the interfacial tension (IFT) using dissipative particle dynamics (DPD). Two studies are presented in chapter 6 for aqueous sodium dodecyl sulfate (SDS) surfactant by dissipative particle dynamics. The first one, the critical micelle concentration (CMC) of SDS and the effect of NaCl salt and temperature upon CMC have been investigated. The second study, the adsorption of SDS surfactant on carbonate surface has been studied by adding various concentration of SDS surfactant with water/ carbonate system. Chapter 7 depicts the phase behavior of C$_8$E$_4$ surfactant in water /octane system by dissipative particles dynamics. In this chapter, nonionic surfactant C$_8$E$_4$ /water/octane systems at constant concentration of surfactant with different temperature are simulated to study structural phase transitions and to evaluate lower temperature ($T_L$), upper temperature ($T_U$) and, the mean temperature $T_m$ at which the microemulsion is formed. In chapter 8, we perform a series of experimental studies on the interfacial tension of surfactants with different structures at the octane/water interface to study the effect of different head group and tail group of surfactants, and the adsorption of Triton X-100 surfactant on water/octane interface. Moreover, the role of sodium chloride (NaCl), calcium chloride (CaCl$_2$), and temperature for one surfactant concentration and varying concentrations of salt or temperature were investigated on water/octane interface. Chapter 9 provides a summary of the work, a summary of findings obtained and a future work based on these findings.
Chapter 2 Literature review

2.1 Surfactants

Surfactants are surface-active, amphiphilic components which are composed of a hydrophilic part and a hydrophobic part. The hydrophobic part is called a tail and is usually formed by a hydrocarbon chain. The hydrophilic part is the head of the surfactant and is usually composed of an ionic group or a structural group capable of forming hydrogen bonds. A classification of the surfactants can be carried out according to the type of the hydrophilic head group. There are surfactants with cationic, anionic and nonionic head groups. Figure 2.1 shows the classification of the surfactants. An anionic surfactant dissociates in aqueous solution into a surfactant with a negatively charged head and into a positively charged counterion. Anionic surfactants are very frequently used in the detergent industry. A cationic surfactant, on the other hand, dissociates into a positively charged surfactant and into a counterion with a negative charge. Cationic surfactants are used as preservatives and disinfectants. Nonionic surfactants do not dissociate in aqueous solution. Their water solubility is based on the oxygen atoms of the ether group, to which water molecules can associate. Nonionic surfactants are used both in the detergent industry and in cosmetics and in personal care products. The dissociation of amphoteric or zwitterionic surfactants depends on the pH of the solution. They behave as cationic surfactants in the acidic medium, while in the basic medium they are anionic. This section in this chapter summarizes surfactant properties such as interfacial tension, critical micelle concentration (CMC), adsorption at liquid-solid system, and phase behavior of water / oil / surfactant systems.
2.1.1 Surfactant interfacial tension

The interfacial tension of a liquid can be derived from thermodynamics as the free Gibbs enthalpy (G) of a system with an interface is a function of the temperature (T), the pressure (P), the mass (N) and the boundary surface (A) [23]. Therefore, the total differential is defined as follows:
\[ dG = \left( \frac{\partial G}{\partial T} \right)_{P,N,A} dT + \left( \frac{\partial G}{\partial P} \right)_{T,N,A} dP + \sum_i \left( \frac{\partial G}{\partial N_i} \right)_{T,P,N_{i \neq j},A} dN_i + \left( \frac{\partial G}{\partial A} \right)_{P,N,T} dA \] (2.1)

For isobaric (P = constant), isothermal (T = constant), and constant mass (N = constant), above equation simplified to:

\[ dG = \left( \frac{\partial G}{\partial A} \right)_{P,N,T} dA \] (2.2)

The interfacial tension is defined as:

\[ \gamma = \left( \frac{\partial G}{\partial A} \right)_{P,N,T} \] (2.3)

The interfacial tension (\( \gamma \)) represents the proportionality constant between the change in free enthalpy with an increase in the boundary surface. If this relationship is used in equation (2.2), it becomes clear that the change in free enthalpy of a system is directly proportional to the increase of the boundary surface. As a fundamental equation for the free enthalpy, the total differential equation (2.1) can be derived from the definition of the interfacial tension as follows:

\[ dG = -SdT + VdP + \gamma dA + \sum_i \mu_i d\tilde{n}_i \] (2.4)

The interfacial tension of a system, as described above, is a function of temperature, pressure and mass. Surfactants can influence the interfacial tension of a system.
Surfactants adsorb at interfaces, so changing many physical properties such as interfacial
tension of a system. A relationship between the interfacial tension and the boundary surface excess
can be derived from the Gibbs isotherm [7]:

$$d\gamma = - \sum_i \Gamma_i d\mu_i$$  \hspace{1cm} (2.5)

The chemical potential ($\mu_i$) for dilute solutions is defined as follows:

$$d\mu_i = -RTd\ln C_i$$  \hspace{1cm} (2.6)

The Gibbs isotherm for surfactants is obtained by substituting equation (2.6) in equation (2.5):

$$\left( \frac{\partial \gamma}{\partial C_s} \right)_T = \frac{RT\Gamma_s}{C}$$  \hspace{1cm} (2.7)

The boundary surface excess is a positive value; therefore, a negative value is obtained for the
change of the boundary surface tension with a change in the concentration of the surfactant ($C_s$).
As a result, the interfacial tension decreases with an increase in the concentration of surfactant.
Furthermore, the relationship shown in equation (2.7) provides the possibility of determining an
excess concentration in the case of known concentration dependence of the interfacial tension as
follows:

$$\Gamma = - \frac{1}{zRT} \left( \frac{\partial \gamma}{\partial C} \right)_T$$  \hspace{1cm} (2.8)
Where \( z \) equals 2.303 for nonionic surfactant and 4.606 for anionic surfactant.

2.1.2 Critical micelle concentration (CMC)

From this concentration (CMC), surfactant molecules agglomerate to form micelles, which are molecular clusters. The arrangement of the surfactants in their surroundings depends on the medium that surrounds them. If the polar solution form micelles, the hydrophilic head of the surfactant points outwards and the hydrophobic tail is located in the micellar core. If the solution is non-polar, inverse micelles are formed. Although the formation of micelles is a volume phenomenon, the critical micelle formation concentration can be determined by the described boundary surface phenomenon. At low concentrations, surfactants accumulate on the surface of the water/air interface, therefore reducing the surface tension of the solvent (e.g., water). With increasing the surfactant concentration to a certain concentration, surfactants form molecular aggregates called micelles instead of partitioning to the surface, resulting in constant surface tension. This limiting concentration is referred to as critical micelle concentration (CMC). In addition to determination of the interfacial tension as a function of the surfactant concentration method, spectroscopic analysis method, determination of density method, determination of viscosity method, determination of light scattering method, and determination of the equivalence conductivity method can also be used to determine the CMC [24].

The value of CMC depends on the nature of the surfactant. Depending on which surfactant type is present, these molecular clusters can consist of up to 10,000 molecules. For charged surfactants, agglomeration numbers of up to 100 molecules are common, while micelles from nonionic surfactants can have substantially more molecules [24]. Various parameters such as the
temperature, the composition of the solvent and the molecular structure of the surfactant have a
great influence on the CMC value. In ionic surfactants, the ionic strength and the pH of the medium
are also effect the CMC value. With increasing surfactant concentrations above CMC, different
structures of micelles are formed. Above the CMC the surfactant molecules form spherical,
cylindrical, cubic, or lamellar micelles (or reverse structure) as seen in Figure 2.2. The type of
micelles (spherical, cylindrical, cubic, or lamellar shaped) can be predicted with the help of the
critical packing parameter (CPP). The packing parameter was defined as the volume of the
hydrophobic group (ν) to the extended length (l) and head group space area requirement of the
surfactant (a) [25]:

\[
CPP = \frac{\nu}{l \cdot a}
\]  

(2.9)

Surfactants with P less than 1/3 tend to form spherical micelles, where P is between 1/3 and 1/2
cylindrical or hexagonal can be obtained and the P value, which are greater than 1/2, lamellar
shaped micelles are preferably formed. Surfactants with a higher P value (P > 1) tend to form cubic
aggregates or inverse micelles. Therefore, the packing parameter is one of the most important
factors for predicting the phase behavior of surfactants.
Figure 2.2: The pattern formation and aggregation forms in surfactant solutions as a function of surfactant concentration [26].
2.1.4 Phase behavior of ternary systems water / oil / nonionic surfactant

For ternary systems of the type water / oil / nonionic surfactant, they are strongly dependent on the temperature [27]. For a better understanding of the phase behavior of a ternary system consisting of water / oil / nonionic surfactant the three binary systems can explain more about the phase behavior. *Figure 2.3* illustrates the temperature dependence of a ternary system of water / oil / nonionic surfactant. A nonionic surfactant is considered to be more soluble in the aqueous phase at a certain temperature ($T_l$). If the temperature of this system is increased, the solubility of the surfactant changes. At a temperature ($T_u$) the surfactant is better soluble in the organic phase. The phase inversion temperature (PIT) can be represented by a measurement of the phase components and it lies between the lower temperature ($T_l$) and upper temperature ($T_u$). The result is a sigmoidal dependence between the temperature and the phase volume [28]. The tangent through the turning point of phase inversion temperature is called a critical line. As the temperature increases, the slope of this tangent decreases. For $T_l$ and $T_u$ temperature, the slope is zero value. The division of the curve produces two critical endpoints ($T_\alpha$ and $T_\beta$). In a system without a critical point, the surfactant is continuously transported into the organic phase with increasing temperature. In the case of a ternary system in which a critical point is present, the aqueous phase splits and a third phase is formed (bicontinuous phase). A further increase in the temperature leads to an improved oil solubility of the surfactant, two phases are formed again. Winsor [29] divided the phase states into three types:

Type I: Oil is in equilibrium with an aqueous surfactant solution. In the surfactant solution, oil is solubilized (O / W). R value is less than 1 (oil in water emulsion).

Type II: Water is in equilibrium with an oil surfactant solution containing solubilized water (W / O). R value is greater than 1 (water in oil emulsion).
Type III: oil and water phases are in equilibrium with a third phase containing surfactant, water and oil. This middle phase corresponds to a microemulsion. R value is 1.

The R value can be calculated according to the following formula [29]:

$$R = \frac{A_{HCO} + A_{LCO}}{A_{HCW} + A_{LCW}}$$  \hspace{1cm} (2.10)

Where $A_{HCO}$ is hydrophilic interactions between the oil and the surfactant, $A_{LCO}$ is hydrophobic interactions between the oil and the surfactant, $A_{HCW}$ is hydrophilic interactions between the surfactant and water, and $A_{LCW}$ is hydrophobic interactions between the surfactant and water.

Figure 2.3: Schematic representation of a phase diagram of a ternary system of water / oil / nonionic surfactant [30]. Left: phase prism of a ternary system water / oil / nonionic surfactant; Right: schematic representation of the interface tension as a function of temperature.
2.1.4 Adsorption at liquid-solid system

The adsorption on solid surfaces and phase interfaces is one of the important properties of surfactants. In many technical and industrial applications, such as the cleaning of surfaces, flotation, corrosion protection, coatings, and enhance oil recovery (EOR), the adsorption of the surfactants on the solid-liquid interface plays an important role [31]. Surfactant adsorption on solid surfaces is determined by three main factors. The nature and structure of the surfactant (type of head group and the hydrophobic chain, as well as the length and degree of branching of the chain). The nature of the surface (hydrophobic, charged, etc.). The properties of the surrounding aqueous solution (pH, temperature, additives, etc.). Any changes in one of the factors are sufficient to significantly change the adsorption properties of surfactants to the solid-liquid interface. Surfactant molecules adsorb to the solid surface due to dispersion forces, acid-base interactions, electrostatic interactions, hydrophobic bonds, and polarization effects [31]–[33].

Electrostatic interactions occur between the ionic head group of the surfactant and the oppositely charged surface, with the result that the head group is adsorbed to the surface and the surfactant chains are exposed to the aqueous solution due to the attractive coulomb forces. Hydrophobic interactions can occur between the hydrophobic surfactant chain and a hydrophobic surface so that the chain attaches to the surface or between the hydrophobic chains adsorbed to the hydrophilic surface and the hydrophobic chains of surfactants from the surrounding aqueous solution. The surfactants adsorb at the solid / liquid interface (structure, geometry) depends on the structure of the surfactants as well as on the nature of the surface itself. Figure 2.4 shows type of adsorbed structures of surfactants at solid surfaces (monolayer, bilayer, admicelles, and hemimicelles). The different adsorbed structures of surfactants at solid surfaces based on the balance of interactions between surfactant molecules and between the surfactant and surface.
There are different models to describe adsorption mechanisms of surfactant molecules on solid surfaces. In general, the adsorption of surfactants onto solid surfaces can be described by adsorption isotherms. Figure 2.5 shows a typical adsorption isotherm for ionic surfactants on surfaces. The adsorption Isotherms can usually be divided into four regions [7], [31], [33]. At low surfactant concentrations in the solution, the surfactants adsorb as monomers without interacting with each other (region I). The adsorption of nonionic and ionic surfactants onto hydrophilic surfaces occurs due to specific attractive interactions between the surface and the head group of the surfactant. The hydrophobic hydrocarbon chains protrude into the aqueous phase. Ionic surfactants additionally have electrostatic (Coulomb) interactions which are attractive when the surfactants and the surface are oppositely charged and repulsive when they have the same charge. The Coulomb interactions are dependent on the charge number of the surfactant, the pH and the ionic strength [31], [33]. As the concentration increases, a transition from region I to region II takes place, which is reflected by a sudden increase in surfactant adsorption. This point is corresponding to the critical micellization concentration of the surfactants in solution and stands for the critical admicelles concentration (AMC) or for the hemimicelles concentration (HMC). If the surfactant concentration is further increased, double layers (admixes) occur in region III. The hydrophilic head groups shield the hydrophobic chains from the aqueous solution to prevent unfavorable interactions between solvent and chains. Region IV occurs when the concentration exceeds the CMC of the surfactants.
Figure 2.4: Adsorbed structures of surfactants at solid surfaces [34]: monolayer, bilayer, admicelles, and hemimicelles.

Figure 2.5: Typical adsorption isotherms for ionic surfactants on hydrophilic surfaces.
2.2 Molecular modeling tools for surfactants

Molecular modeling tools can be used to predict surfactant properties. As a matter of fact, valuable information can be delivered from the molecular modeling tools such as the behavior of the surfactant into different systems, Critical Micelle Concentration (CMC), interfacial tension (IFT), structure of the surfactants, and thermodynamics properties. Figure 2.6 depicts the major molecular modeling tools from the quantum to the engineering design level. To start with small scale, the electronic density functional theory (eDFT) presents the electronic structure of matter ranges from atoms, molecules and solids to quantum and classical fluids. To understand the microscopic level of the surfactant, molecular modeling tools such as molecular dynamics (MD), Monte Carlo (MC) can be used. For upper scale model, dissipative particle dynamics (DPD) and molecular density functional theory can offer more understanding about the mesoscale level. This part of chapter 2 presents a short literature review about surfactant studies using DFT, MD and, DPD as molecular modeling tools.
2.2.1 Density functional theory (DFT)

Molecular DFT has been used as one of the computational methods to offer a deeper understanding of surfactant behavior based on surfactant architecture. An advantage of molecular DFT is that the free energy for the surfactant solution is calculated directly and it is related to the molecular structure and the polarity. Rosenfeld and Yu et al. [35], [36] provide information about free energy functional to calculate the force between two parallel hard walls separated by an inhomogeneous heard spear fluid mixture. SAFT based density functional theory (DFT) has been applied to assess the behavior of inhomogeneous associating molecular fluids in confined systems and at the vapor–liquid interface [37], [38]. Stoyanov et al. [39] presented local density functional
to calculate surface tension isotherms for nonionic surfactants at air-water or oil-water interface. The SAFT based DFT called the interfacial statistical associating fluid theory (iSAFT) density functional theory (DFT) is used to model both bulk and interfacial properties n-alkanes and polymers, allowing the theory to deal with thousands of segments [40]. The iSAFT theory based Wertheim’s first order perturbation theory is applied broadly to a range of systems such as lipids near surfaces, lipid bilayers, and copolymer thin films [41] with same manner of Tripathi and Chapman research [42] and it was shown to be in excellent agreement with the results from molecular simulations. The capabilities of classical density functional theory to model structure of branched copolymer/nanoparticle systems and surfactant systems was studied by Emborsky et al [43]. The parameter space of an oil-water-surfactant system and the effect of interfacial properties of amphiphiles were evaluated by using the iSAFT polyatomic segment-based DFT [44] and using Second-order classical density functional theory [45]. Llovell et al. have published review in the application of the SAFT DFT to prediction of the interfacial properties of mixtures [46].

2.2.2 Molecular dynamics (MD)

Molecular dynamics MD simulation has been used to study surfactants in complex systems during the last 25 years. One of the challenging tasks is simulating the aggregation of surfactants and the critical micelle concentration (CMC) that is used as an indication of surfactant molecules aggregation in EOR. The CMC variations with addition of salts for ionic surfactant was reported by Sammalkorpi et al [47], and it shows that the increase in ionic strength leads to an increase in aggregate size. Samanta et al. [48] have performed MD simulations to study the aggregation property of multiheaded surfactants. An increase in number of headgroups of the multiheaded surfactants drives an increase in CMC value and leads to increase the aggregation numbers. The
morphology of the aggregates of surfactant oligomers was investigate by using MD to find that with increase in degree of oligomerization the CMC values decrease [49]. Stephenson et al. [50]–[52] have employed MD simulation to study the aggregation of ionic and nonionic surfactants in water. Jang et al. [53] present MD simulations to describe the behavior of interfacial tension (IFT) of a benzene sulfonate surfactant in oil–water system. As a result, it was found that the interfacial tension has inverse behavior with interfacial thickness for surfactant that attached 4 carbon in a hexadecane backbone to benzene sulfonate group. The effect of different surfactants such as sodium dodecyl sulfate (SDS), Triton X-100, and tetraethylene glycol alkyl ethers on the surface tension of air–water and liquid–liquid interfaces was investigated using MD simulations [54]. Chenac and Hao [55] performed a recent study about the mechanism of aggregation to provide more understanding of cationic–anionic surfactant mixtures systems. Molecular dynamics (MD) simulations have been used to study the energy and the entropy at different surfactant concentrations and temperatures for a model heptane/water system by Urbina-Villalba et al. [56].

2.2.3 Dissipative particle dynamics (DPD)

Dissipative particle dynamics (DPD) is used as coarse graining to simulate complex fluids at mesoscopic scales which fills the gap between atomistic methods and CFD. An advantage of DPD over atomistic methods such as molecular dynamics (MD) is less computational cost for complex fluids because the coarse graining reduces the number of interactions necessary to compute and the soft potentials used in DPD allow larger time steps than in MD. Dissipative particle dynamics (DPD) was initially introduced by Hoogerbrugge and Koelman in 1992 [22] and the importance of DPD has increased since that time. It was slightly modified by Espanol and Warren [57] to ensure the proper thermal equilibrium state and deriving hydrodynamic variables. The total force
acting on each particle are represented by conservative, dissipative, and random forces. The dissipative and random forces depend on each other through a fluctuation-dissipation relation. Useful parameter ranges for simulations which is related to the Flory-Huggins chi parameter, were determined by Groot and Warren [58]. A wide variety of systems have been simulated using DPD such as colloidal systems, polymers, monolayers, mixtures, membranes etc. The micellization kinetics and equilibrium properties for diblock copolymers have been investigated by using DPD [59]. Simulated results are in agreement with previous experimental and theoretical studies. For IFT, the dissipative particle dynamics simulations were applied to study how interfacial tension depends on the surfactant branching or different concentration of water/oil system by Rekvig et al. [60]. In addition, the same group studied the effect of changing the size and structure of surfactants on the interfacial tension [61]. Furthermore, the DPD interaction parameters as a function of bead size for different systems were compared by Maiti and McGrother for the interfacial tension and the results were found to agree well with experimental results [62]. With oil/water/ nonionic surfactant mixtures, Ginzburg et al. studied interfacial tension through dissipative particle dynamics and self-consistent field theory [63]. The two methods showed a good semiquantitative agreement with experimental results. For the cetyltrimethylammonium bromide (CTAB) at the oil/water system, the mechanical properties such as structural properties, IFT, and surfactant concentration were investigated by using DPD simulation [64]. Yang et al. [65] have used dissipative particle dynamics (DPD) to simulate the system of an anionic surfactant aerosol OT (AOT) and water. Various aggregation structures of AOT, and the phase behaviors varied with concentration and temperature were investigated. The results are in good agreement with the experimental results. Fraaije and co-works [66]–[68] developed the method of moments (MOM) and implemented in DPD. They relate the surface torque at a tensionless interface to the optimal
salinity for microemulsion formation based on the stress profile. In the work of Lee et al. [69], the effect of chain rigidity on critical micelle concentration and micelle size was investigated by using DPD simulations and it was found that rigid surfactants had significantly reduced cmc and form larger micelles than flexible molecules with the same nonbonded interaction parameters.

Computer simulation methods that deal with the calculations in between the atomistic and macroscopic scales are called mesoscopic. Mesoscopic simulation includes the dissipative particle dynamics, the lattice gas model, and lattice Boltzmann method. In mesoscopic modeling, individual atoms lose their identity and are treated as a group. The mesoscopic simulation techniques use simple coarse grained models to allow the calculations of surfactant systems on a mesoscopic level. The DPD method allows the correct description of the hydrodynamics of the system to be simulated. The lattice gas or lattice Boltzmann method can also be used for the calculation of hydrodynamic system but they have a serious disadvantage as compared to DPD simulation. The lattice symmetry in description of liquids in many cases is physically incorrect. The flow behavior under shear are difficult to describe with the lattice model. The dissipative particle dynamics avoids the disadvantages of both the atomistic and the mesoscale grid methods. To illustrate the selection of the DPD methods used in this work, the next chapter gives a description of the dissipative particle dynamics methods.
Chapter 3 Dissipative particle dynamics (DPD) method

3.1 Fundamentals of Dissipative Particle Dynamics (DPD) simulation

Dissipative particle dynamics (DPD) is a simulation method to study the hydrodynamic behavior of complex fluids. It was first introduced by Hoogerbrugge and Koelman in 1992 [22]. The DPD method has already been applied successfully in the study of the dynamic properties of a wide variety systems such as colloidal systems, polymers, monolayers, mixtures, membranes etc. DPD fluid consists of a set of particles (or beads) with continuous movement of the particles governed by Newton's equations. This is a common framework for all simulation methods based on particles, such as molecular dynamics (MD) [70], [71]. In contrast to atomistic simulations, the physical interpretation in DPD of the particles and the specific form of the forces between particles are described differently. The interpretation of the particles is not representing individual molecules or atoms within the system. It considered a coarse graining construction of the system that allows a description of scales of mesoscopic length.

Dissipative particle dynamics is modelled by particles (or DPD ‘beads’) interacting using soft pairwise potentials. Particles move according to Newton’s equations of motion:

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i; \quad \frac{d\vec{p}_i}{dt} = \vec{f}_i$$

(3.1)

Where, \(\vec{r}_i\) is position of particle i, \(\vec{v}_i\) is velocity of particle i, and \(\vec{f}_i\) is force on particle i. The forces are pairwise additive, acting on the line joining the centers of the particles thus are central forces and they satisfy the third law of Newton. Furthermore, the forces only depend on their relative
positions and velocities by the system invariant under Galilean transformations (Galilean invariance).

### 3.2 Interaction forces in DPD

The total force acting on each particle or bead is represented by conservative, dissipative, and random forces:

\[
\vec{f}_i = \vec{f}^C_{ij} + \vec{f}^D_{ij} + \vec{f}^R_{ij}
\]  

(3.2)

The sum is calculated between all DPD particles within a cut-off radius \( r_c \).

**The conservative force:**

The conservative force takes the form of a gradient of potential interaction pairs, where \( r_{ij} \) is the separation of the particles i and j. The conservative force is a soft repulsive force and is calculated as follows:

\[
\vec{f}^C_{ij} = a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \frac{\vec{r}_{ij}}{r_{ij}} \quad (r_{ij} < r_c)
\]

\[
\vec{f}^C_{ij} = 0 \quad (r_{ij} \geq r_c)
\]

(3.3)

Where; \( a_{ij} \) is a “repulsion” parameter and \( r_c \) is an interaction cut-off range parameter.

**The dissipative force:**
The dissipative force depends on the relative particle velocities \( v_{ij} = v_i - v_j \) and is described by equation (3.4). If particle j moves in the opposite direction of particle i, the scalar \( \hat{r}_{ij} \cdot \vec{v}_{ij} \) is positive and the particles i and j attract each other with the force \( (f_{ij}^D) \), which is proportional to \( v_{ij} \). If particles j moves in the direction of particle i, a repulsive force is created between the particles. In the physical sense of the dissipative force term cools the system. The coefficient \( \lambda \) determines the strength of the dissipative force and is interpreted as a friction constant.

\[
\vec{f}_{ij}^D = -\lambda \omega_d (r_{ij}) (\hat{r}_{ij} \cdot v_{ij}) \hat{r}_{ij}
\]  

(3.4)

Where \( v_{ij} = \vec{v}_i - \vec{v}_j \) is the relative velocity, \( \lambda \) is a friction coefficient, \( \hat{r}_{ij} \) is a unit vector, and \( \omega_d \) is a distance dependent weight function that is zero for \( r_{ij} \geq r_c \).

**The random force:**

This random force provides the energy input into the system and the preservation of the thermal particle motion. The energy dissipation caused by the dissipative force is generated by a random force as seen equation (3.5). \( \delta \) is the amplitude of the random noise, the random variable \( \theta_{ij} \) which is generated independently for each particle pair in each time step of the Gaussian distribution

\[
\vec{f}_{ij}^R = -\delta \omega_r (r_{ij}) \theta_{ij} \hat{r}_{ij}
\]  

(3.5)

Where \( \delta \) is a fluctuation amplitude, \( \omega_r \) is a distance dependent weight function that is zero for \( r_{ij} \geq r_c \), and \( \theta_{ij} \) is a Gaussian distributed random number with zero mean and unit variance.
3.3 Thermostat

In the previous section we can see that the three forces are central forces and conserve both time and angular momentum, but not energy. $\omega_d$ and $\omega_r$ are distance dependent particle weight functions for the dissipative force and the random force to ensure that the total momentum is conserved in the system. These forces account for the effect of the thermal particle motion. Espanol and Warren [57] showed that the DPD system is simulated in the canonical (NVT) ensemble and the ensemble constants and weighting functions are selected according to equation (3.6) for the simulation. The dissipative and random forces depend on each other through a fluctuation-dissipation relation. Espanol and Warren derived the Fokker-Planck equation for DPD to determine this relation which was violated in the original paper by Hoogerbrugge and Koelman.

$$\omega_d(n_{ij}) = [\omega_r(n_{ij})]^2 \quad \text{and} \quad \delta^2 = 2\lambda k_B T$$  (3.6)

Where, $k_B$ is Boltzmann's constant, and $T$ is the temperature. This equation represents the fluctuation-dissipation theorem to the DPD method and fixes the DPD temperature at $k_B T = \delta^2 / (2 \lambda)$. It has exactly the same structure as the theorem of fluctuation dissipation dynamics of conventional Brownian motion, but the important difference between the two dynamics is that the Brownian dynamics does not satisfy Newton's third law and does not preserve the moment. The dynamic Brownian speed of particles are coupled directly to the dissipative force individually for each particle. This situation is not observed in simulations DPD, where the dissipative term includes contributions from particle pairs [72]. So the dissipative force together with the random force are a thermostat, which ensures that the DPD system reaches thermal equilibrium.
3.4 Integration algorithm

The DPD simulations use a modified Verlet velocity algorithm from the class of finite difference method. Because the temperature control in DPD simulations was an unsolved problem, the Hoogerbrugge – Koelmann [22] algorithm which introduced from the expression of the equilibrium temperature of an ideal gas, found that DPD temperature is always higher than the thermodynamic temperature of the system. The theoretical work of Espanol and Warren [57] showed that the two forces (dissipative, and random) are set by the dissipation fluctuation, therefore temperatures can be simulated. Many integration schemes which have been discussed in detail [72]–[75]; the best results for the DPD simulations were obtained by the Groot and Warren [58] algorithm to prevent this increase in temperature using a modified set of integration algorithm equations (3.7). The modified Verlet velocity algorithm is analogous to the predictor corrector method; an estimated value $\vec{v}_i'(t + \Delta t)$ velocity for the time $(t + \Delta t)$ is used to calculate the total force $f_i(t + \Delta t)$ at this time. Then, the value of the velocity is corrected $\vec{v}_i''(t + \Delta t)$ in the last integration step.

\[
\begin{align*}
\vec{r}_i(t + \Delta t) &= \vec{r}_i(t) + \Delta t \vec{v}_i(t) + \frac{1}{2} \Delta t^2 \vec{f}_i(t) \\
\vec{v}_i'(t + \Delta t) &= \vec{v}_i(t) + \lambda \Delta t \vec{f}_i(t) \\
\vec{f}_i(t + \Delta t) &= \vec{f}_i'(\vec{r}_i(t + \Delta t), \vec{v}_i'(t + \Delta t)) \\
\vec{v}_i(t + \Delta t) &= \vec{v}_i(t) + \frac{1}{2} \Delta t (\vec{f}_i(t) + \vec{f}_i(t + \Delta t))
\end{align*}
\]
3.5 Properties of DPD parameters

The choice of dissipative constant $\lambda$, the random noise $\delta$, and the time step in the dissipative particle dynamics is very important for the stability of the simulations. The dissipative constant $\lambda$ and the constant of the random noise $\delta$ by the fluctuation - dissipation theorem are interconnected as seen equation (3.6). Therefore, only one of the two parameters can be chosen freely. Groot and Warren (1997) [58] found that the integration process is unstable when the amplitude of the random noise $\delta$ is greater than 8. It was found that for $\delta = 3$, and the system in the temperature range $k_B T = 1 - 10$ quickly relaxed. The choice of the dissipation coefficient and the simulation temperature requires an amplitude of the random noise to a value which is not substantially greater than $\delta = 3$, because under other conditions, the simulation is unreliable. The temperature depends strongly on the time step. Groot and Warren showed that in the DPD calculations with a time step of $\Delta t = 0.04$, and $\delta = 3$ reached thermal equilibrium and increased the speed of simulation. The time step without loss in the temperature control can be increased up to $\Delta t = 0.06$.

The forces acting at the atomic level in physical systems can be expressed in DPD simulations by the repulsion parameters $a_{ij}$ of the conservative force. The thermodynamics of a DPD system is controlled by a simple repulsion parameter. The value obtained is usually tied through the DPD compressibility model to an actual system. On the DPD, the isothermal compressibility $\kappa_T$ connects to $a_{ij}$ parameter. This connection is made through compressibility $\kappa$ dimensionless by the following relationships:

$$\kappa^{-1} = \frac{1}{\rho_n k_B T \kappa_T} = \frac{1}{k_B T} \left( \frac{\partial p}{\partial \rho} \right)$$  \hspace{1cm} (3.8)
where $\rho_n = \frac{N}{V}$ is the number density of dissipative particles and $k_B T$ the isothermal compressibility of the liquid. Simulation results of Groot and Warren found that the excess pressure due to the interaction parameter is proportional to the repulsion parameters. These results are valid for $\rho_n > 2$ as can be seen in Figure 3.1. The equation of state of the DPD fluid can be described by equation (3.9) [58]:

$$
\frac{P}{\rho k_B T} = 1 + \frac{\alpha a_{ij} \rho}{k_B T}
$$

where $\alpha = 0.101 \pm 0.001$ is the curvature of the parabola in Figure 3.1. For water at room temperature, the dimensionless compressibility is $k^{-1} = 15.9835$. The interaction parameter of pure liquids ($a_{ii}$) (equation 3.10) has been derived from equation (3.8) after differentiating the equation of state with respect of $\rho$ (equation (3.9)). It was observed that the interaction parameter of pure liquids ($a_{ii}$) is the reciprocal of the density of the liquid in DPD. Equation (3.10) allows calculating the interaction parameter between the same DPD-particles:

$$
a_{ii} = \frac{75 k_B T}{\rho}
$$
In order to model the behavior of complex fluids, the DPD method also requires the interaction parameter $a_{ij}$ between unlike DPD particles. In polymer chemistry interactions between two polymer segments by the Flory-Huggins parameter $\chi$ are expressed. This parameter represents the excess of the free energy of mixing in the Flory-Huggins model. To establish a connection between the DPD method and the phase behavior of real fluids, the free energy of DPD liquid is compared with the Flory-Huggins theory. Therefore, it is possible to determine the value of the repulsive coefficient $a_{ij}$ when the compressibility of the system is known and that the density of simulation is set. Groot and Warren (1997) found that the relation between the Flory-Huggins interaction parameter $\chi$ and the DPD interaction parameter $a_{ij}$ is a linear relationship as seen Figure 3.2. The two different densities were studied giving relations as following:

$$\chi = 0.286 \left(a_{ij} - a_{ii}\right) \quad \text{at} \quad \rho = 3 \quad (3.11)$$

$$\chi = 0.689 \left(a_{ij} - a_{ii}\right) \quad \text{at} \quad \rho = 5 \quad (3.12)$$

Figure 3.1: The excess pressure depends the interaction parameter and quadratically on density [58].
Figure 3.2: The excess repulsion parameters as function of $\chi$–parameter [58].

It would be very important if the DPD model could reproduce correctly the thermodynamic properties of a real system beyond certain length scales, and time. It is performed in reduced units, based on the characteristic physical dimensions of the system under study. These units determine the distance scales ($r_c$), energy ($k_B T$) and mass ($m$), and therefore time via:

$$t_{DPD} = \frac{m r_c^2}{k_B T}$$  \hspace{1cm} (3.13)

All other units could be derived from the distance scales, energy and mass.
3.6 Statistical thermodynamics to determine Flory-Huggins interaction parameters

To calculate the DPD interaction parameters $a_{ij}$ between the unlike beads, it is important to compute $\chi_{ij}$, the Flory-Huggins parameter between the unlike beads. The relation between the statistical thermodynamics and Flory-Huggins interaction for the solvent $i$ in mixing with the solute $j$ is determined from the liquid lattice theory. The mixing behavior of solute can be described in solvents by this lattice theory. The Gibbs free energy $\Delta G$ change for solute is obtained from the thermodynamic expression which is composed of enthalpy change $\Delta H$ and entropy change $\Delta S$:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (3.14)

The enthalpy of mixing solution is calculated from the number of solute-solvent contacts while the entropy of mixing is determined from the number of different possible arrangements of the solute and solvent molecules on a grid. In case of entropy, the analysis of the problem is after any number solute molecules have been placed on an empty grid. The total number of possibilities to place the solute molecules on the grid is then given by the product of the options for each individual molecule. After the solute molecules are distributed on the lattice, there is a possibility to distribute the solvent molecules onto the still empty seats. The calculation of the total number of allowed options corresponds to the thermodynamic probability of a system. The thermodynamic probability is attached via the Boltzmann equation with the entropy of mixture. The molar entropy of mixing of solvent($i$) and solute($j$) molecules is finally obtained from following expression:

$$\Delta S_{mix} = -R(n_i \ln \phi_i + n_j \ln \phi_j)$$  \hspace{1cm} (3.15)
where \( n \) is the number of moles of solvent (i) and solute(j) and \( \phi \) is the volume fraction. A consideration of the pair interaction energy between the individual species based on a large number of existing particles and the consideration of the concentration dependence of the obtained result, eventually leading to the enthalpy of mixing a non-ideal solution:

\[
\Delta H_{\text{mix}} = RT\chi_{ij}n_i\phi_j
\]  

(3.16)

Where \( \chi_{ij} \) is Flory-Huggins interaction parameter and it corresponds to the expression \( Z\Delta W_{i,j}/RT \). \( W_{i,j} \) is here the change in the pair interaction energy, caused by the distribution of molecules on a lattice whose lattice sites have an average coordination number \( Z \). By combining equations (3.14-3.16), the Gibbs free energy of mixing of a binary solution is obtained as:

\[
\Delta G_{\text{mix}} = RT[\chi_{ij}n_i\phi_j + n_i \ln \phi_i + n_j \ln \phi_j] 
\]  

(3.17)

For the change of the chemical potential of the solvent, it is produced by forming the differential equation of Gibbs free energy of mixing respect to mole fraction of solvent and this means that the chemical potential of a solvent in a solution relative to that in the pure solvent:

\[
\mu_y - \mu_y^\circ = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_i}\right)_{p,T,n_j} = RT\left[\ln(1 - \phi_j) + \left(1 - \frac{1}{\nu_{ij}}\right)\phi_j + \chi_{ij}\phi_j^2\right]
\]  

(3.18)

where, \( \mu_y^\circ \) is pure solvent chemical potential, \( \mu_y \) is solvent chemical potential in solution, and \( \nu_{ij} \) is the ratio of molecular volume of the solute \( \nu_j \) to the solvent \( \nu_i \). To relate the simple form of this equation (3.18) to the activity coefficient of the solvent \( \gamma_y \) in a solution is defined by:
\[ \mu_{ij} - \mu_i^0 = RT \ln(x_i \gamma_{ij}) \]  

(3.19)

Where \( x_i \) is the solvent mole fraction. The expression for the chemical potential of the solvent, a binary solution in equation (3.18) has been derived from Flory-Huggins with the volume fraction of solute \( \phi_j \). Therefore, \( x_i \) can be drive from the definition of volume fraction of solute \( \phi_j = n_j / (n_j + n_i / \nu_i) \) and the solvent mole fraction \( x_i = n_i / (n_i + n_j) \) as:

\[ x_i = \frac{1 - \phi_j}{1 - \phi_j \left( 1 - \frac{1}{\nu_{ij}} \right)} \]  

(3.20)

Now, the relation between the statistical thermodynamics and Flory-Huggins interaction for the solvent i in mixing with the solute j is determine from the liquid lattice theory by combining equations(3.18-3.20) as [76]–[78]:

\[ \ln(\gamma_{ij}) = \ln \left[ 1 - \left( 1 - \frac{1}{\nu_{ij}} \right) \phi_j \right] + \left( 1 - \frac{1}{\nu_{ij}} \right) \phi_j + \phi_j^2 \chi_{ij} \]  

(3.21)

The interaction parameters \( a_{ij} \) of the solute j and solvent i can be determine from the infinite dilution limit ( \( \lim_{\phi_i \to 1} \chi_{ij} \) ) at the maximum of repulsion between the molecules i and molecules j because the maximum mixing enthalpy \( \Delta H_{\text{mix}} \) describes the interactions between the participating molecules i and j and the maximum transfer mixing heat around sites of molecules would occur at
the volume fraction of molecules $j$ goes to 1. The Flory-Huggins interaction parameter $\chi_{ij}^\infty$ at
infinite dilution activity coefficient $\gamma_{ij}^\infty$ of solvent $i$ in mixing with solute $j$ is described by:

$$
\chi_{ij}^\infty = \ln(\gamma_{ij}^\infty) + \ln(v_{ij}) - \left(1 - \frac{1}{v_{ij}}\right)
$$

(3.22)

3.7 Conductor-like Screening Model for Real Solvents (COSMO-RS)

calculation for infinite dilution activity coefficients

COSMO-RS (Conductor-like Screening Model for Real Solvents) has been used to calculate the chemical potential of a component in mixtures, allowing determination of the infinite dilution activity coefficient. Complete details about the COSMO-RS theory can be found in [79], [80][81]. The molecules are in the reference state in a vacuum and are transferred from this state in a dielectric continuum, which can be understood as an ideal conductor. In the dielectric continuum, the molecules are perfectly shielded. In this system, molecules move freely without change in energy since the molecules are shielded. The distribution of charge on the surface of molecules can be determined using quantum chemical COSMO calculations. By dividing the molecular surface in discrete segments, the average charge may be determined in each segment. The segments are characterized by the average segment surface charge. The interactions of surface segments that originate from the COSMO, go to a self-consistent expression for the chemical potential and the statistical thermodynamics allows the calculation of activity coefficient of a component. The $\sigma$-profile is the most important characteristic in the COSMO theory. The
probability distribution \( p(\sigma) \) present on the molecular surface charge densities \( \sigma \) to characterize each component clearly. The probability distribution of the charge densities is obtained by the weighted average of sigma profiles of pure components:

\[
P(\sigma) = \frac{\sum x_i A_i P_i(\sigma)}{\sum_i x_i A_i}
\]

(3.23)

\[
P_i(\sigma) = \frac{n_{i,\sigma}}{n_i} = \frac{A_i(\sigma)}{A_i}
\]

(3.24)

\[
n_i = \sum_i n_i(\sigma) = \frac{A_i}{a_{eff}}
\]

(3.25)

\[
A_i = \sum \sigma A_i(\sigma)
\]

(3.26)

where \( P_i(\sigma) \) is the sigma profile for a molecule \( i \), \( x_i \) is mole fraction of component \( i \), \( n_{i,\sigma} \) is the number of segments with a discretized surface charge density \( \sigma \), \( A_i \) is the total cavity surface area, \( A_i(\sigma) \) is the total surface area of all of the segments with a particular density \( \sigma \), and \( a_{eff} \) is effective surface area of a standard surface segment. The interactions of the surface segments derived from the COSMO calculations are expressed in a self-consistent expression of the chemical potential derived from the statistical thermodynamics and enable the calculation of the activity coefficient of a component. All the components involved in a mixture are characterized by the shielding charge densities which are formed on their surface, which would be adjusted when embedded in an ideal conductor. To find an effective surface-charge density, the surface-charge
densities is averaged by equation (3.27) and this procedure is necessary due to the need for constant charge densities on the effective contact surfaces:

\[
\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp \left( - \frac{d_{mn}^2}{r_n^2 + r_{av}^2} \right)}{\sum_n \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp \left( - \frac{d_{mn}^2}{r_n^2 + r_{av}^2} \right)}
\]  

(3.27)

where \(\sigma_m\) is the average surface-charge density on segment \(m\), from the COSMO output the summation is over \(n\) segments, \(d_{mn}\) is the distance between the two segments, \(r_n\) is the radius of the actual surface segment, and \(r_{av}\) is the averaging radius. As a result from COSMO-RS model, the chemical potential of a molecule \(i\) in a liquid mixture can be determined which is from the screening charge density surface (SCDs) by assuming the interactions between molecule \(i\) and molecule \(j\) are based on surface segments, the surfaces are in close contact, and there is only pair wise surface interactions. The microscopic interactions are transferred to macroscopic thermodynamics for calculating activity coefficient of the compound \(i\) in mixing with compound \(j\) from the statistical thermodynamics calculation of the pseudochemical potential [80]. After determination of the \(\sigma\)-profile of the whole systems, we can calculate the chemical potential of solute \(j\) in the solvent mixture \(S\) and the chemical potential of the contact surface segment \(\mu_s(\sigma)\) on the surface as following:

\[
\mu_s(\sigma) = -kT \ln \left[ \int p_s(\sigma') \exp \left\{ -\frac{E(\sigma, \sigma') - \mu_s(\sigma')}{kT} \right\} d\sigma' \right]
\]  

(3.28)

Where \(p_s(\sigma')\) is the probability distribution present on the molecular surface charge densities \(\sigma\) to characterize each component and \(E(\sigma, \sigma')\) is the interaction energies of a segment pair \((\sigma, \sigma')\).
The equation (3.28) has to be solved iteratively to obtain \( \mu_z(\sigma) \) where the chemical potential of the contact surface segment is a measure of the affinity of mixture S to a surface of polarity \( \sigma \). The chemical potential \( \mu_{j,s} \) of species \( j \) can be available in the mixture after integration over the cavities surface and is calculated by:

\[
\mu_{j,s} = \int p_j(\sigma)\mu_z(\sigma)d\sigma + \mu_{j,s}^c
\]  

(3.29)

The second term of the right hand side of equation (3.29) is a combinatorial contribution to the chemical potential that is accounting for size and shape differences of the molecules in the system and \( p_j(\sigma) \) is the fraction of those segments on the chemical potential of the solute \( j \). Now, we can calculate the activity coefficient of component \( j \) from chemical potential as following:

\[
\ln(\gamma_{ij}) = \frac{\mu_{j,s} - \mu^P}{RT}
\]  

(3.30)

Where \( \mu^P \) is chemical potential of pure component \( i \). From COSMO-RS, we can determine the infinite dilution activity coefficient \( \gamma_{ij}^\infty \) as function of temperature at \( x_i=0 \) and \( x_j=1 \) from equation (3.30) and molecular volume of the solute \( v_j \) and the solvent \( v_i \). Finally, we can calculate the maximum interaction parameters \( a_{ij} \) for DPD by combining equations (3.11) and (3.21).
Chapter 4 Dissipative particle dynamics (DPD) study of alkanes/water systems interfacial tension

4.1 Introduction

Accurate prediction of interfacial tension (IFT) is important in various applications, for example, formation of stable emulsions, the dispersion of droplets, Enhanced Oil Recovery (EOR), natural gas, and foam control in petrochemical industries. Several experimental techniques have been proposed for measurement of interfacial tension between two immiscible fluids such as pendant drop, sessile drop, the rising bubble, and spinning drop [82]–[84]. Molecular simulations of atomistic or coarse grained models can play an important role for scientific research because they can provide a molecular interpretation of experimental results, which often can be difficult to obtain experimentally. From the simulation point of view, the prediction of interfacial tension (IFT) of liquid-liquid systems is challenging due to the contributions of different forces such as van der Waals, electrostatic interactions, and hydrogen bonding among molecules. One promising method of coarse grained simulation is dissipative particle dynamics (DPD) to simulate complex fluids at mesoscopic scales. Dissipative particle dynamics focuses on predicting the material properties that are determined by the structure and behavior in mesoscopic systems of size typically between 10 - 1000 nm and time scales of 1 ns - 10 ms. The Advantage of DPD over atomistic methods such as molecular dynamics MD is lower computational cost for complex fluids due to the coarse graining that reduces the number of interactions necessary and the soft potentials that allow larger time steps than in MD simulation [85]. Dissipative particle dynamics (DPD) was initially introduced by Hoogerbrugge and Koelman in 1992 [22]. The importance of DPD has increased since that time as a wide variety of systems have been simulated using DPD such as colloidal systems, polymers, monolayers, membranes, etc [61], [86]–[89].
An important system for interfacial tension measurement is the system of alkanes and water. Numerous experimental studies for this system have been reported in the literature [90]–[94]. To the best of our knowledge, there is only one research paper that studies the IFT of alkane/water systems as function of temperature by dissipative particle dynamics [95]. In their work, the IFT calculations were based on two common methods in the literature using molecular dynamics to calculate solubility parameters to determine the DPD interaction parameters \( a_{ij} \) between the beads. The first method, that was proposed by Groot and Warren [58] and Maiti & McGrother [62], was used to calculate the interaction parameters from Flory-Huggins theory with fixed value for like bead interactions (\( a_{ii} = a_{jj} \)). That is the water-water beads and alkane-alkane interaction energies are the same. The second method was proposed by Travis [96] that determined the relation between DPD interaction parameters by including the inequality of interaction parameters between the beads (\( a_{ii} \neq a_{jj} \)) and it is based on Scatchard and Hildebrand’s (Regular Solution Theory RST). The results yielded by this study appear to suggest that IFT from the second method more closely agreed with experimental data for higher carbon number alkanes. A closer look at the results indicates that neither method showed a systematic way for calculating the interaction parameters of DPD or IFT results for alkanes/water systems. The motivation of this article is to compute the DPD interaction parameters in a systematic way by using the conductor-like screening model for real solvents (COSMO-RS) quantum chemical theory [79], [80]. Dissipative particle dynamics (DPD) is used to simulate spherical beads interacting via pairwise potentials that follow Newton’s equations of motion. The total forces that act on beads are conservative, dissipative, and random forces. The dissipative and random forces together act as a thermostat for the beads to keep the thermal equilibrium of the DPD system. The conservative force is a soft repulsion central force involving the interaction parameters \( a_{ij} \) between the beads to
represent the chemical behavior of the system. Groot and Warren [58] found a linear relationship between the Flory-Huggins interaction parameter $\chi$ and the DPD interaction parameter $a_{ij}$. The Flory-Huggins parameter $\chi$ has been determined by different computer simulation methods such as molecular dynamics simulations on the atomic level to determine the solubility parameters [62], Monte Carlo simulation of the contact interaction energies between molecules [97], and molecular simulations to determine binding energy values between the different components [98]. The accuracy of the previous simulations for computing $\chi$ depends on the adopted forcefields. In most cases, the simulation requires long simulation times to ensure reliable results. In a recent paper, Weiß et al. [99] used a method involving the Gibbs free energies of mixing and the volume fraction of species, where the Gibbs free energies are obtained from COSMO-RS, to calculate the Flory-Huggins $\chi$. In this work, an alternative methodology is presented to study the interfacial tension of alkane and water systems by using DPD simulation, where the interaction parameters of DPD are calculated based on the dependence of the Flory-Huggins $\chi$ parameters on temperature by using the liquid lattice theory through the infinite dilution activity coefficient. The infinite dilution activity coefficient as a function of temperature are determined from COSMO-RS.

The aim of this work is to determine the interaction parameters $a_{ij}$ with temperature dependence as input for DPD simulations for alkanes (C6-C12)/water systems by using COSMO-RS. Interfacial tension as a function of temperature for these systems is obtained from dissipative particle dynamics. We also calculate interfacial tension by rescaling $\chi$ parameters as a function of bead size to treat alkanes as chains of beads. Finally, the IFT results are compared with experimental and DPD data that are available in the literature.
4.2 Methodology and Theory

In dissipative particle dynamics, molecules are modelled by particles (DPD ‘beads’) interacting using soft pairwise potentials. These particles move according to Newton’s equations of motion. The total force acting on each particle is represented by the sum of conservative, dissipative, and random forces:

\[ \mathbf{f}_i = \mathbf{f}_{ij}^C + \mathbf{f}_{ij}^D + \mathbf{f}_{ij}^R \]  

(4.1)

The conservative force takes the usual form of a gradient of potential interacting between pairs of particles, where \( r_{ij} \) is the separation of the particles i and j, the potential is a soft repulsion. The conservative force is a repulsive force and is calculated according to equation (4.2):

\[ \mathbf{f}_{ij}^C = a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \mathbf{\hat{r}}_{ij} \quad (r_{ij} < r_c) \]

\[ \mathbf{f}_{ij}^C = 0 \quad (r_{ij} \geq r_c) \]  

(4.2)

Where \( a_{ij} \) is interaction (repulsion) parameter and \( r_c \) is the cut-off radius. The dissipative force \( (f_{ij}^D) \) depends on the relative particle velocities \( \mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j \) and is described by equation (4.3). If particle j moves in the opposite direction of particle i, the scalar \( (\mathbf{\hat{r}}_{ij} \cdot \mathbf{\hat{v}}_{ij}) \) is positive and the particles i and j attract each other with the force \( (f_{ij}^D) \). In the physical sense, the dissipative force term cools the system. The coefficient \( \lambda \) determines the strength of the dissipative force and is interpreted as a friction constant and \( \omega_d \) is a distance dependent weight function that is zero for \( r_{ij} > r_c \).
\[
\vec{f}_{ij}^D = -\lambda \omega_d (r_{ij})(\hat{r}_{ij} \cdot v_{ij})\hat{r}_{ij}
\]

(4.3)

The random force provides the energy input into the system and the preservation of the thermal particle motion. The energy lost by the dissipative force is balanced by energy generated by a random force as in seen equation (4.4). \( \delta \) is the amplitude of the random noise, and the random variable \( \theta_{ij} \) is generated independently for each particle pair in each time step from a Gaussian distribution and it is a random number with zero mean and unit variance. \( \omega_r \) is a distance dependent weight function that is zero for \( r_{ij} > r_c \).

\[
\vec{f}_{ij}^R = -\delta \omega_r (r_{ij})\theta_{ij}\hat{r}_{ij}
\]

(4.4)

\( \omega_d \) and \( \omega_r \) are the distance dependent weight functions for the dissipative force and the random force to ensure that the total momentum is conserved in the system. Espanol and Warren [57] showed that the DPD system is simulated in the canonical (NVT) ensemble if the ensemble constants and weighting functions are selected according to equation (4.5) for the simulation. The dissipative and random forces depend on each other through a fluctuation-dissipation relation.

\[
\omega_d (r_{ij}) = [\omega_r (r_{ij})]^2 \text{ and } \delta^2 = 2\lambda k_B T
\]

(4.5)

Where \( k_B \) is Boltzmann's constant and \( T \) is the temperature. So the dissipative force together with the random force are a thermostat, which ensures that the DPD system reaches thermal equilibrium.
In order to model the behavior of complex fluids, the DPD method also requires the interaction parameter $a_{ij}$ between DPD beads. Groot and Warren [58] proposed a relation between the Flory-Huggins interaction parameter $\chi_{ij}$ and the DPD interaction parameter $a_{ij}$ as a linear relationship as seen in equation (4.6). Groot and Warren showed that the sufficient DPD density is 3 to match the compressibility of liquid water where the repulsion parameter between water bead is recommended to be set at 25 and other repulsion parameters between beads of the same type are chosen as the same value as the water bead; more details are available in [58]. The repulsion parameters between beads of different types expressed as the Flory–Huggins parameter as following.

$$\chi = 0.286 \left( a_{ij} - a_{ii} \right) \text{ for } \rho = 3$$  \quad (4.6)

To calculate the DPD interaction parameters $a_{ij}$ between the alkanes and water, it is important to compute $\chi_{ij}$ the Flory-Huggins parameter between alkanes and water. To accomplish this, we relate $\chi_{ij}$ to water/alkane phase behavior using Flory-Huggins theory. The Gibbs free energy change on mixing a binary solution is obtained as [77], [78]:

$$\Delta G_{mix} = RT \left[ \chi_{12} n_1 \phi_2 + n_1 \ln \phi_1 + n_2 \ln \phi_2 \right]$$  \quad (4.7)

Where $n$ is the number of moles of component and $\phi$ is the volume fraction (1 for water and 2 for alkane). The change in chemical potential of a component is obtained by differentiating the Gibbs free energy of mixing respect to mole number of that component. The chemical potential of a water (1) in a solution relative to that of the pure water is:
\[
\mu_{12} - \mu_1^0 = \left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right)_{\mu,T,n_i} = RT \left[ \ln(1 - \phi_2) + \left( 1 - \frac{1}{\nu_{12}} \right) \phi_2 + \chi_{12} \phi_2^2 \right] \tag{4.8}
\]

where, \( \mu_1^0 \) is chemical potential of pure component (1), \( \mu_{12} \) is the chemical potential in solution, and \( \nu_{ij} \) is the ratio of molecular volume of the alkane \( \nu_2 \) to the water \( \nu_1 \). To relate the simple form of this equation (4.8) to the activity coefficient of water \( \gamma_{12} \) in a solution is defined by:

\[
\mu_{12} - \mu_1^0 = RT \ln(x_1 \gamma_{12}) \tag{4.9}
\]

Where \( x_1 \) is the water mole fraction. The water mole fraction is related to the volume fraction of alkane by:

\[
x_1 = \frac{1 - \phi_2}{1 - \phi_2 \left( 1 - \frac{1}{\nu_{12}} \right)} \tag{4.10}
\]

The activity coefficient of water can be related to the Flory-Huggins interaction by combining equations (4.8-4.10) as [76]-[78]:

\[
\ln(\gamma_{12}) = \ln \left[ 1 - \left( 1 - \frac{1}{\nu_{12}} \right) \phi_2 \right] + \left( 1 - \frac{1}{\nu_{12}} \right) \phi_2 + \phi_2^2 \chi_{12} \tag{4.11}
\]

We choose to determine the interaction parameters \( a_{ij} \) in equation (4.6) of the alkanes and water from the infinite dilution limit \( \lim_{\phi_2 \to 1} \chi_{12} \) of the Flory-Huggins \( \chi_{12} \). This limit isolates the unlike pair interaction energy. The Flory-Huggins interaction parameter \( \chi_{12}^\infty \) is related to the infinite dilution activity coefficient \( \gamma_{12}^\infty \) of component (1) in component (2) as [76]:

\[
\]
\[
\chi_{ij}^\infty = \ln(\gamma_{ij}^\infty) + \ln(v_{ij}) - \left(1 - \frac{1}{\nu_{ij}}\right)
\] (4.12)

We estimate the activity coefficient of water in alkane from COSMO-RS. The COSMO-RS model (Conductor-like Screening Model for Real Solvents) combines results of quantum chemical calculations of the distribution of electrostatic charge on molecules with statistical thermodynamics to estimate liquid phase nonideality. Complete details about the COSMO-RS theory can be found in [79], [80][81]. The distribution of charge on the surface of molecules can be determined using quantum chemical COSMO calculations. COSMO assumes the molecules to be in a conducting solution where the molecules are perfectly shielded. Since the molecules are shielded, the molecules move freely without change in energy. By dividing the molecular surface into discrete segments, the average charge can be determined in each segment. The chemical potential of a species is obtained by averaging over the interactions of surface segments using statistical thermodynamics. This allows the calculation of activity coefficient of a component.

All charge density calculations are performed in the ideal conductor based on the COSMO model which means that molecules are characterized only by the distribution function of their screen charge densities (SCDs) around the molecules. The SCDs are used to estimate the energy of interaction in real solvent, where the charge distribution and polarizability of molecule change the direct solvent environment. The COSMO-sigma profiles represent the electrostatic distributions on molecules. Figure 4.1 shows the COSMO-sigma profiles of water and alkanes in a range of -0.025 and 0.025 SCD. The water sigma (\(\sigma\)) profile is very broad and there are two maxima around \(\sigma = \pm 0.015 \text{ e/Å}^2\) due to the positive hydrogen atoms and the free electrons of the oxygen atom. The positive charged hydrogen atoms of water induce negative values for SCD. Similarly, the negative charged oxygen atoms induce positive values for SCD. The profiles are
fairly symmetrical so that the water molecules can play the role as charge accepter as well as charge donor and this reflects the capability of water to be a polar compound. Alkanes have large and narrow peaks in the non-polar region around zero e / Å² and the curves of sigma profile drops rapidly before the polar region of water. In general, non-polar molecules such as alkanes possess exclusively neutral segments. As a result, the sigma profiles of water and alkanes show that there is a weak interaction between water and alkanes; therefore the systems are immiscible.

After determination of the σ-profile, we calculate the chemical potential of the contact surface segment \( \mu_s(\sigma) \) of a component using the following [79]:

\[
\mu_s(\sigma) = -kT \ln \left[ \int p_s(\sigma') \exp \left\{ -\frac{E(\sigma,\sigma') - \mu_s(\sigma')}{kT} \right\} d\sigma' \right] 
\]  

(4.13)

Where \( p_s(\sigma') \) is the surface compositions functions with respect to the polarization charge density \( \sigma \) of a solvent S. \( E(\sigma,\sigma') \) is the interaction energies of a segment pair \((\sigma,\sigma')\) which is described as functions of the polarization charges of two interacting surface segments. The interaction energy is approximated by summation of the electrostatic contact interaction energy which results from the misfit of the two contacting polarization charge densities, and the extra energy of hydrogen bonding [100]. Equation (4.13) has to be solved iteratively to obtain \( \mu_s(\sigma) \). The chemical potential \( \mu_{j,S} \) of species j is obtained by integrating the chemical potential of all surface segments on the σ-profile of the molecule and adding the ideal proportion of solvation and a combinatorial contribution. The chemical potential \( \mu_{j,S} \) is calculated by [79]:

\[
\mu_{j,S} = \int p_j(\sigma) \mu_s(\sigma) d\sigma + \mu_{j,s}^c
\]  

(4.14)
The second term of the right hand side of equation (4.14) is a combinatorial contribution to the chemical potential that accounts for size and shape differences of the molecules in the system and $p_j(\sigma)$ is the surface compositions functions with respect to the polarization charge density of a solute j. Now, the activity coefficient of component j can be calculated as follows [79]:

$$\ln(\gamma_j) = \frac{\mu_{j,s} - \mu^p}{RT}$$  \hspace{1cm} (4.15)

Where $\mu^p$ is chemical potential of pure component j. From COSMO-RS, the infinite dilution activity coefficient $\gamma_{ij}^\infty$ as function of temperature at $x_i=0$ and $x_j=1$ can be determined from equation (4.15). Finally, we are able to calculate the interaction parameters $a_{ij}$ for DPD by combining equations (4.6) and (4.12).
Figure 4.1: Sigma profiles of water (H2O) and alkanes (oils) molecules (C6 Hexane, C7 Heptane, C8 Octane, C9 Nonane, C10 Decane, C11 Undecane, and C12 Dodecane).

4.3 Computational Details

The COSMO-RS model uses quantum mechanics to estimate the molecular interactions and statistical thermodynamics to predict the chemical potential of a component. Dmol3 was used for COSMO-RS calculations; more details are available in [81]. The GGA/VWN-BP functional and Double Numerical basis (DNP) v4.0.0 electronic basis set are considered to be adequate for computing accurate thermodynamic properties with fine quality $1.0 \times 10^{-6}$ hartree energy units, where GGA stands for generalized gradient approximation and VWN-BP stands for the Becke-
Perdew version of the Volsko-Wilk-Nusair functional [101]-[103]. The geometry optimization for molecular structure is important because it optimizes molecules to a stable geometry by minimizing the energy. The screening charge density (SCD) around the molecule was determined to perform the thermodynamic calculation of COSMO-RS.

COSMO based models generate a surface charge distribution used by COSMO-RS to compute infinite dilution activity coefficients as function of temperature. When the values of infinite dilution activity coefficients and volume ratios from COSMO-RS are obtained, the Flory-Huggins interaction parameter $\chi_{ij}$ are calculated from equation (4.12). We calculate the interaction parameters between the beads $a_{ij}$ from equation (4.6). According to equation (4.6), the interaction parameters of like beads $a_{ii}$ and $a_{jj}$ are assigned the value 25 as the Flory-Huggins interaction parameter ($\chi_{ii}$ and $\chi_{jj}$) are zero for pure components in Flory-Huggins theory.

The dissipative particle dynamics model was used to calculate the (IFT$_{DPD}$) based on the interaction parameters $a_{ij}$. The simulations were performed with 6000 particles (spherical beads) with equal volume fraction of water and alkane in a periodic boundary box size 20×10×10 DPD dimensionless units. A modified Verlet velocity algorithm from the class of finite difference methods was used to calculate trajectories of the particles [58] with time step of $\Delta t = 0.02$. The equilibration stage was lasted for 100000 steps followed by 100000 production steps. The dissipation strength or frictional constant $\lambda$ according to equation (4.5) is equal to 4.5, and the DPD density $\rho$ is number of DPD particles per unit volume was set to 3 [58], [62]. These values are commonly used in the literature. The interfacial tension can be represented by the difference between the normal and tangential stress integrated across the interface as follows:
$$IFT_{DPD} = 0.5 \int \left[ P_{zz}(z) - \frac{1}{2} \left( P_{xx}(x) + P_{yy}(y) \right) \right] dz \quad (4.16)$$

Where $P_{xx}(z) + P_{yy}(z)$ is the pressure parallel to the interface and $P_{zz}(z)$ is the pressure normal to the interface depending on the coordinate $z$ length. $P_{xx}$, $P_{yy}$, and $P_{zz}$ are diagonal components of the pressure tensor [58], [62]. The IFT can be converted from DPD unit to physical unit by using the following equation [62]:

$$IFT \left( \frac{mN}{m} \right) = \frac{k_B T}{r_c^2} IFT_{DPD} \quad (4.17)$$

where $k_B$ is the Boltzmann constant, and $T$ is the equilibrium temperature. The DPD mass, time, and volume are scaled to unity and kept dimensionless in the DPD calculations and the length ($r_c$) is expressed by the following equations [62]:

$$r_c = \sqrt[3]{\rho V^W} \quad (4.18)$$

Where $V^W$ is the volume of DPD bead. The value of $V^W$ will be discussed in the following section. The Materials Studio suite, version 7.0 of Accelrys was used to perform all Dmol3 calculations and DPD simulations [104].

### 4.4 Results and Discussion

The COSMO-RS model provides the activity coefficient of a component in the mixture. The results of the infinite dilution activity coefficients of water in n-alkanes at 25°C with the literature values are presented in Figure 4.2. A comparison of the results from experimental and
COSMOtherm [105] show that the proposed method performs very well as a function of alkane chain length. Table 4.1 shows COSMO-RS patterns of infinitely dilute activity coefficients for different temperatures which range between 5 - 85 °C. The interaction parameters between the alkanes and water particles were calculated according to equations (4.6) and (4.12), where the temperature dependent Flory-Huggins interaction parameter $\chi_{ij}$ of equation (12) needs $\ln(\gamma_{ij}^\infty)$ infinite dilution activity coefficients, molecular volume, and volume ratio which are determined from COSMO-RS. All values determined from these are summarized in Table 4.1. There is a linear relation between the temperature and $\ln(\gamma_{ij}^\infty)$ infinite dilution of activity coefficients or interaction parameters $a_{ij}$. The negative slopes indicate the decrease in $\ln(\gamma_{ij}^\infty)$ infinite dilution of activity coefficients and interaction parameters $a_{ij}$ by increasing temperature and the slope is almost the same for each water alkane system. The classical Flory-Huggins parameter $\chi$ can be determined from interaction energy between the components A and B divided by $kT$ [106]. The temperature dependence for the Flory-Huggins interaction parameter $\chi_{ij}^\infty$ depends not only on activity coefficients but also on the volume ratio as is the case in this paper. Since the calculation of Flory-Huggins interaction parameter $\chi_{ij}^\infty$ based on the volume of one water molecule, we can set the volume of the DPD bead is equal to the volume of one water molecule (bead volume ($V^W$) = volume of one water molecule). The values of the molecule volume come from COSMO calculation. Then, the length ($r_c$) is expressed by the following:

$$r_c = \frac{3}{\sqrt[3]{\rho V^W}} = \frac{3}{\sqrt[3]{3(25.58)}} = 4.25 \text{ Å} \quad (4.19)$$
Figure 4.2: Infinite dilution activity coefficients of water in n-alkanes at 25°C. experimental [107], [108], COSMOtherm [105], Bastos 1988 [109], Gmehling 1993 [110], Hansen 1992 [111] Lyngby 1987 [112].

Table 4.1: Infinite dilution activity coefficients of water in alkanes and interaction parameters aij as function of temperature over the range from 5 °C to 85 °C.

<table>
<thead>
<tr>
<th>Water/Alkane</th>
<th>ln((\gamma_{ij}^{\infty}))</th>
<th>Volume (Å³)</th>
<th>rij</th>
<th>aij</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane (C6)</td>
<td>-0.0095t(°C)+6.769</td>
<td>145.83</td>
<td>5.70</td>
<td>-0.0332t(°C)+51.899</td>
<td>0.9999</td>
</tr>
<tr>
<td>Heptane (C7)</td>
<td>-0.0095t(°C)+6.780</td>
<td>167.60</td>
<td>6.55</td>
<td>-0.0332t(°C)+52.345</td>
<td>0.9999</td>
</tr>
<tr>
<td>Octane (C8)</td>
<td>-0.0095t(°C)+6.791</td>
<td>189.59</td>
<td>7.41</td>
<td>-0.0332t(°C)+52.754</td>
<td>0.9999</td>
</tr>
<tr>
<td>Nonane (C9)</td>
<td>-0.0095t(°C)+6.801</td>
<td>211.38</td>
<td>8.27</td>
<td>-0.0332t(°C)+53.119</td>
<td>0.9999</td>
</tr>
<tr>
<td>Decane (C10)</td>
<td>-0.0095t(°C)+6.808</td>
<td>233.02</td>
<td>9.11</td>
<td>-0.0331t(°C)+53.447</td>
<td>0.9999</td>
</tr>
<tr>
<td>Undecane (C11)</td>
<td>-0.0094t(°C)+6.813</td>
<td>254.79</td>
<td>9.96</td>
<td>-0.0331t(°C)+53.743</td>
<td>0.9999</td>
</tr>
<tr>
<td>Dodecane (C12)</td>
<td>-0.0094t(°C)+6.820</td>
<td>276.51</td>
<td>10.81</td>
<td>-0.033t(°C)+54.027</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

volume ratio \(r_{ij}\) = volume of alkane/volume of water, volume of water = 25.58 Å³, and \(R^2\) is the fitting correlation.
A DPD result for liquid-liquid equilibrium of a water- dodecane system is shown in Figure 4.3. Figure 4.3 (a) depicts 3000 water beads and 3000 dodecane beads were placed in the simulation box where each molecule is represented by one bead. The water and the dodecane have separated into two phases after the system reached the equilibrium state and between phases well defined interfaces have formed. There are two interfaces because periodic boundary conditions have been used. In Figure 4.3 (b), the density profile of the water and oil as a function of distance (X) are represented by the interface. The interfacial tension was determined by integrating the difference between the normal and tangential components of the pressure tensor along the interface according to equation (4.16). Equation (4.17) is used to convert to physical units. The calculations were carried out for a range of alkane / water systems. The interfacial tensions obtained from DPD as well as the experimentally measured values from [90] at 25 °C are listed in Table 4.2. The interfacial tension from the DPD simulations agrees well with experimental results. The error decreases from 3.48% for small alkane to 0.78 % for large alkane.

Figure 4.3: (a) Water (blue) and dodecane (red) DPD simulation box at 25 °C, (b) The density profile in the X-direction of the simulation.
Table 4.2: Interfacial tension experimental and DPD for alkane/water systems with Relative Absolute Error percent (RAE %) at 25°C.

<table>
<thead>
<tr>
<th>Water/Alkenes</th>
<th>IFT DPD (mN/m)</th>
<th>IFT Experimental (mN/m) [90]</th>
<th>RAE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>48.63</td>
<td>50.38</td>
<td>3.48</td>
</tr>
<tr>
<td>Heptane</td>
<td>49.15</td>
<td>50.71</td>
<td>3.08</td>
</tr>
<tr>
<td>Octane</td>
<td>50.05</td>
<td>51.16</td>
<td>2.16</td>
</tr>
<tr>
<td>Nonane</td>
<td>50.95</td>
<td>51.63</td>
<td>1.31</td>
</tr>
<tr>
<td>Decane</td>
<td>51.13</td>
<td>51.98</td>
<td>1.63</td>
</tr>
<tr>
<td>Undecane</td>
<td>51.60</td>
<td>52.25</td>
<td>1.24</td>
</tr>
<tr>
<td>Dodecane</td>
<td>52.14</td>
<td>52.55</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The model parameters are functions of temperature as seen in Table 4.1. To perform DPD simulations at different temperatures, the interaction parameters $a_{ij}(T)$ were used for water/alkanes. Therefore, the temperature dependence of interfacial tension can be calculated. The comparison of measured values with literature is shown in Figure 4.4. As expected, the DPD interfacial tension decreases with increasing temperature for all systems and it shows a good agreement with experimental data. Although the DPD values do not match perfectly, the tendencies of interfacial tension values with the increasing the number of carbon and temperatures are acceptable considering the simplified intermolecular potential and the coarse-grained model of treating each molecule of water or alkane as one bead. The interfacial tension is nearly linearly dependent on the temperature. From both experimental and DPD results, the interfacial tension tends to increase with increasing molecular weight of alkanes.
Figure 4.4: The interfacial tension as function of temperature for DPD (lines) and experimental data (dots) [90]. (each molecule is represented by one bead for DPD calculations).

In the results above, the alkane is treated as a single bead in the water/alkane system. Although the results show good agreement with experimental IFT results, there are many other applications in which the alkane should be treated as chains of beads such as multiprotein complexes, surfactants or membranes simulations. In this part, we divide alkanes into chains of monomers representing methyl, ethyl, propyl, or butyl groups. For simplicity, the middle group containing CH₂ and the end group containing CH₃ are assumed to have the same interaction parameters. As seen in Table 4.3, we defined four types of monomer beads, namely methyl (C), ethyl (C2), propyl (C3), and butyl (C4), that can be bonded in a chain to represent an alkane. To keep the monomer beads in the alkane a similar volume to the water bead, the water bead is considered to contain multiple water molecules. In other words, one, two, three, and four water
molecules are represented inside the water bead for the methyl, ethyl, propyl, and butyl monomer bead respectively. As a result, each monomer would have different \( r_c \) values depending on the volume of the water bead.

Table 4.3: The calculation of \( r_c \) for each monomer.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Volume of monomer molecules (Å(^3))</th>
<th>Number of water molecules inside water bead (m)</th>
<th>Volume of water bead (Å(^3))</th>
<th>( r_c = \sqrt[3]{m \rho V^w} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl (C)</td>
<td>36.09</td>
<td>1</td>
<td>25.58</td>
<td>4.25</td>
</tr>
<tr>
<td>Ethyl (C2)</td>
<td>58.62</td>
<td>2</td>
<td>51.16</td>
<td>5.35</td>
</tr>
<tr>
<td>Propyl (C3)</td>
<td>80.42</td>
<td>3</td>
<td>76.74</td>
<td>6.12</td>
</tr>
<tr>
<td>Butyl (C4)</td>
<td>102.27</td>
<td>4</td>
<td>102.32</td>
<td>6.74</td>
</tr>
</tbody>
</table>

In this method, we need to scale the interaction parameters \( a_{ij} \) with bead size since equation (4.12) calculate \( \chi_{ij}^\infty \) based on the volume of water molecule and alkane molecule. In this way, we can avoid unphysical size discrepancies due to increasing the number of water molecules inside the water bead. Maitia and McGrother found that \( \chi_{ij} \) is proportional to the size of the bead. For example, the \( \chi_{ij}^\infty \) parameter for (m) water molecules coarse grained into a single bead scales as:

\[
\chi_{ij}^\infty (m) = m \chi_{ij}^\infty \quad \text{and} \quad a_{ii}(m) = a_{ii}
\]  

(4.20)

The \( \chi_{ij}^\infty (m) \) and \( a_{ij}(m) \) after the scaling for different monomer sizes are listed in Table 4.4 as a function of temperature. All interaction parameters \( a_{ij}(m) \) after scaling of the monomer were estimated from the \( \chi_{ij}^\infty (m) \) obtained from equation (4.20). With increasing the size of monomer and water bead the
interaction parameters is increased and the temperature slope dependence becomes more negative.

Table 4.4: The calculation of interaction parameters $a_{ij(m)}$ after scaling.

$\chi_{ij}^\infty$ parameters before scaling is calculated from equation (4.12), $\chi_{ij(m)}^\infty$ after scaling from equation (4.19), and $a_{ij(m)}$ interaction parameters is calculated from equation 6 by using $\chi_{ij(m)}^\infty$.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$\chi_{ij}^\infty$</th>
<th>$\chi_{ij(m)}^\infty$</th>
<th>$a_{ij(m)}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl (C)</td>
<td>-0.0096t(°C)+6.6754</td>
<td>-0.0096t(°C)+6.6754</td>
<td>-0.0335t(°C)+48.364</td>
<td>0.9999</td>
</tr>
<tr>
<td>Ethyl (C2)</td>
<td>-0.0095t(°C)+6.9411</td>
<td>-0.0190t(°C)+13.882</td>
<td>-0.0666t(°C)+73.588</td>
<td>0.9999</td>
</tr>
<tr>
<td>Propyl (C3)</td>
<td>-0.0095t(°C)+7.1742</td>
<td>-0.0285t(°C)+21.523</td>
<td>-0.0999t(°C)+100.33</td>
<td>0.9999</td>
</tr>
<tr>
<td>Butyl (C4)</td>
<td>-0.0096t(°C)+7.3733</td>
<td>-0.0382t(°C)+29.486</td>
<td>-0.1337t(°C)+128.23</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

The series of alkanes are modelled as monomer chains to determine IFT. The main difference to the previous work is the inclusion of increasing size of bead in order to match the water bead with monomer bead. Calculation of DPD interfacial tension for all possible alkanes coarse-graining system (hexane, octane, nonane, decane, and dodecane) of each monomer are shown in Figure 4.5.

To determine the number of beads for any system, it is used the following equation:

$$b = \frac{n}{m} \quad (4.21)$$
Where, \( b \) is the number of beads, \( n \) number of carbon inside the alkane, and \( m \) is the number of water molecules inside water bead. From all these results the interfacial tension decreases with an increase in the temperature. Comparison between this method with results from previous method, experimental, DPD in literature are shown in Figure 4.5. The slope of linear relation between IFT and temperature is clearly dependent on the bead size and monomer. The larger the bead size, the smaller the slope constant. A comparison to available experimental data shows better agreement for the alkane from butyl monomer (\( m=4 \)) than other monomers system such as methyl (\( m=1 \)) and ethyl (\( m=2 \)), in addition to that, DPD simulations shows good agreement with experimental much better than for a model described and tested earlier in Figure 4.4. The trend of IFT changes versus temperature for the systems of butyl monomer (\( m=4 \)), propyl monomer (\( m=3 \)), and one bead of alkane showed more accuracy compared with those reported from DPD by Rezaei and Modarress [95]. In Rezaei and Modarress research, DPD interaction parameter (\( a_{ij} \)) as a function of Flory–Huggins parameter, depends on the solubility parameter where molecular dynamics simulations on the atomic level was used to determine the solubility parameters.
Figure 4.5: The interfacial tension as function of temperature for water/alkane system by using different monomer. m=1: methyl, m=2 ethyl, m=3: propyl, m=4: butyl (m=4), 1 bead: alkane is representing as one bead results from Figure 4.4, Exp; experimental results from [90], and DPD-lit: DPD results from [95].
4.5 Conclusion

The dissipative particle dynamics simulation method offers a wide field of applications. As compared with molecular dynamics simulation, DPD offers a great benefit in terms of reduction of the computational cost. An important area of research for the DPD simulation is calculations of the interaction parameters, as well as the temperature dependence on different systems. In this work, a new approach to estimate the interaction parameters for the calculation of interfacial tension for alkanes/water systems was presented. The COSMO-RS model (Conductor-like Screening Model for Real Solvents) has been used to determine interaction parameters $a_{ij}$ as a function of temperature through the Flory-Huggins interaction parameter fit to infinite dilution activity coefficients from COSMO-RS. This method appears to yield reasonably interfacial tension values when compared with the experimental data for all temperatures. The predictions of the activity coefficient from the COSMO-RS method can be used for other complex fluid systems such ionic liquids [113]–[115] and liquid/solid [100], [116] systems.
Chapter 5 Dissipative particle dynamics (DPD) study of surfactant at interface of water/oil systems

5.1 Introduction

Surfactants or surface active agents are amphiphilic molecules which have a characteristic structure: a nonpolar (hydrophobic part) and a polar (hydrophilic part). Because of this structure surfactants prefer to stay at the boundary between two immiscible phases (such as oil and water) and arrange themselves at the interface with their hydrophilic part in the water phase and the hydrophobic part in oil phase to reduce the interfacial tension (IFT). The classification of surfactants is according to the head group as cationic, anionic, zwitterionic, and nonionic surfactants. The research in the field of water/oil/surfactant systems at interfaces is not only very important for scientific research but also for industry because of the variety of applications of these systems such as food technology, reaction processes, extractions, lubricants, coatings, pharmaceutical, plastic and enhanced oil recovery [1]–[6].

Although the interfacial properties of water/oil/surfactant systems have been investigated by using several experimental techniques [117]–[121], the molecular level description and properties of surfactants are not yet well understood. This is because the surfactant molecules form highly dynamic aggregates in aqueous solution and at interfaces with rapid fluctuations of structures that sometimes are difficult to be analyzed by experimental techniques. Through the development of modern high performance computers, the molecular dynamics computer simulation has become an alternative method for determining molecular structures and can provide a molecular interpretation to guide new experiments by allowing prediction of novel phenomena, developing structures, and understanding properties of materials. The combination of experiment,
and molecular modeling allows a better understanding and clarifies some characteristic patterns of behavior of the surfactants at an interface. In this work, dissipative particle dynamics (DPD), a mesoscopic simulation method, is presented for study of the interface of water/oil/surfactant systems. Hoogerbrugge and Koelman in 1992 [22] introduced the dissipative particle dynamics technique which is used as a coarse graining to simulate complex fluids at mesoscopic scales. The advantage of DPD is less computational cost and ability to simulate a large systems of complex fluids. The DPD simulations have been used successfully in a wide variety of systems [86]–[88], [122]–[125].

Research to study the interface of water/oil/surfactant systems by using dissipative particle dynamics simulations is fairly scarce. Rekvig and co-workers [60], [61] investigated interfacial tension of the linear and branched surfactants between oil and water by using a simple surfactant model. The results showed that the branched surfactants have important influence on the surface tension and more efficiency than the linear surfactants. The water-dodecane interfacial tension for a linear alkyl ethoxylate surfactants were studied by Ginzburg and co-workers [63]. Their research presented that interfacial tension decreases strongly with increasing surfactant concentration which show a good semiquantitative agreement with experimental results. Yiming and co-workers [64] examined the effect of cetyltrimethylammonium bromide (CTAB) surfactant at the oil/water interface using DPD simulations by varying the oil/water ratio. They observed that the surfactant molecules with increasing oil/water ratio is more ordered and more compressible at the interface. Yiming and co-workers [126] investigate how the absence and presence of polymer influences the oil/water/surfactant interfacial properties and the ability to reduce the interfacial tension. The results show that the interfacial tension decreased with increasing number of polymer chains in the system. The research by Menga et al. [127] demonstrated the influence of ethanol/water ratio in
reduction of interfacial tension for ethanol/water/CTAB surfactant system, finding the appearance of ethanol in the system lowered the efficiency of the surfactant.

In this study, the interfacial tension (IFT) is evaluated by using pendant drop method to study the effect of different head group of surfactants, temperature, and salts at the water/octane interface. In the same manner, the orientation of surfactants, stress profile, and the area compression modulus besides the IFT are investigated by using dissipative particle dynamics (DPD). The polarity of the head group, ions of salts, and temperature are crucial factors that change interfacial tension. The conductor-like screening model for real solvents (COSMO-RS) quantum chemical theory [79], [80] is used to determine the interaction parameters between the beads as input for DPD. Three surfactants with different types of head group and the same length of hydrocarbon tail (Sodium dodecyl sulfate SDS, dodecyldimethylamine oxide DDAO and Dodecyltrimethylammonium bromide DTAB) are selected for studying the head group effect at the interface. Moreover, SDS surfactant is chosen for water/octane system to exam the role of sodium chloride (NaCl), calcium chloride (CaCl₂), and temperature.

5.2 Methodology

5.2.1 Experimental Method and Materials

The following materials were used for study the interfacial tension of water/octane/surfactants systems: oil (octane ≥ 99% purity), salts (NaCl ≥ 99% purity, and CaCl₂ ≥ 99% purity), surfactants (SDS ≥ 99% purity, DTAB-99% purity, and DDAO ≥ 99% purity), and deionized water. Oil, salts, and surfactants were supplied by Sigma Aldrich. The method of the pendant drop was used to determine interfacial tension. The measuring principle of pendant drop
method is based on the detection of the geometrical shape of a pendant drop of a capillary. This is done by the axisymmetric drop shape, which is dependent on the force of gravity, and thus the weight of the drop and the interfacial tension. Both forces (gravity and interfacial tension) act here against each other: first force, the weight pulls the drop in the length and second force, the interfacial tension is anxious to keep the droplets in a spherical shape. At equilibrium state, a correlation between the interfacial tension and the curve of the drop can be determined mathematically by using Young–Laplace equation. More details are available in [82], [83]. Three different surfactants were chosen to study the effect of head group and each one was prepared at three different concentrations. For salts and temperature measurement, SDS surfactant at fixed concentration was selected. The concentration of salts were varied between 250 and 750 ppm and temperatures were between 25 and 75 °C. Each run was repeated 3 times and the average value for IFT was taken. Attension Theta Optical Tensiometer was used to perform IFT measurements.

5.2.2 Computational Method

Dissipative particle dynamics (DPD) is a mesoscopic simulation that models molecules as chains of spherical beads by using soft pairwise potentials [58], [62]. The motion of beads is described according to Newton’s equations of motion:

\[
\frac{d\vec{r}_i}{dt} = \vec{v}_i; \quad \frac{d\vec{p}_i}{dt} = \vec{f}_i
\]  

(5.1)

\[
\vec{f}_i = \vec{f}_{ij}^{c} + \vec{f}_{ij}^{p} + \vec{f}_{ij}^{R}
\]  

(5.2)
Where, $\vec{r}_i$ is position of particle $i$, $\vec{v}_i = \vec{p}_i / m_i$ is velocity of particle $i$, $\vec{f}_i$ is force on particle $i$, and $m_i$ is mass of particle $i$. The conservative $\vec{f}_{ij}^c$, dissipative $\vec{f}_{ij}^D$ and random $\vec{f}_{ij}^R$ forces are the total force $\vec{f}_i$ acting on a bead. The sum is calculated over all beads within cut-off radius $r_c$. The conservative force reflects the potential of interaction pairs which acts as soft repulsion between beads. The following equation describes the conservative force:

$$\vec{f}_{ij}^c = a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \frac{\vec{r}_{ij}}{r_{ij}} \quad (r_{ij} < r_c)$$

$$\vec{f}_{ij}^c = 0 \quad (r_{ij} \geq r_c) \quad (5.3)$$

Where $a_{ij}$ is the interaction (repulsion) parameter between the beads and $r_{ij}$ is the between bead $i$ and $j$. The second force is the dissipative force which can be interpreted as a frictional force. It is dependent on the position $r$ and the velocity $v$ of the particles:

$$\vec{f}_{ij}^D = -\lambda \omega_d (r_{ij}) \hat{r}_{ij} \cdot \vec{v}_{ij} \hat{r}_{ij} \quad (5.4)$$

Where the $\lambda$ coefficient is a friction constant and $\omega_d$ is a distance dependent weight function that is zero for $r_{ij} > r_c$. The third force is the random force that preserves the thermal particle motion:

$$\vec{f}_{ij}^R = -\delta \omega_r (r_{ij}) \theta_{ij} \hat{r}_{ij} \quad (5.5)$$

where $\delta$ the strength of the random noise, $\omega_r$ is a distance dependent weight function that is zero for $r_{ij} > r_c$, and $\theta_{ij}$ is standard random variable of the Gaussian distribution. Espanol and Warren
[57] have shown that DPD simulations run in NVT ensemble and the $\delta$ and $\lambda$ depend on each other as seen in equation (5.6).

$$\omega_d(n_{ij}) = [\omega_r(n_{ij})]^2 \quad \text{and} \quad \delta^2 = 2\lambda k_B T \quad (5.6)$$

Where, $k_B$ is Boltzmann's constant and T is the temperature. The dissipative force and the random force functions produce thermal equilibrium for the system during DPD simulation. Groot and Warren [58] have shown the theoretical foundations that the DPD repulsion parameters $a_{ij}$ have a direct linear relationship with the Flory-Huggins parameter $\chi_{ij}$ as seen in equation (5.7) and like-like bead interaction $a_{ii}$ is equal to 25.

$$\chi = 0.286 (a_{ij} - a_{ii}) \quad \text{for} \quad \rho = 3 \quad (5.7)$$

To model the behavior of complex fluids in DPD, the interaction parameters $a_{ij}$ between unlike beads are required. The Flory-Huggins liquid lattice theory is used to establish a connection between the interaction parameters for DPD beads and the phase behavior of real fluids. The computational details of using COSMO-RS for determining the Flory-Huggins parameter $\chi$ is presented in our previous work in chapter 4. To summarize, Dmol3 was used to calculate the screening charge densities (SCDs) around the molecule and the volume of molecules from COSMO calculation. After that, COSMO-RS was used to determine the infinite dilution activity coefficient $\gamma_{ij}^\infty$. Moreover, equation (5.8) was derived from the Flory-Huggins liquid lattice theory to determine the parameter $\chi_{ij}^\infty$. Finally, A combination of equation (5.7) and equation (5.8) is used to determine the interaction parameters $a_{ij}$ between different beads for DPD calculations.
\[
\chi_{ij}^\infty = \ln(y_{ij}^\infty) + \ln(v_{ij}) - \left(1 - \frac{1}{v_{ij}}\right)
\]

(5.8)

Where \(v_{ij}\) is the ratio of molecular volumes of the solute \(v_j\) to the solvent \(v_i\).

To build up the coarse-grained beads for DPD simulation requires that all beads has approximately the same volume size [62]. In this manner, the surfactants molecules (SDS, DTAB, and DDAO) are dissected into fragments of approximately similar volume size as seen in Figure 5.1. The hydrophobic tail of surfactants composed of three butyl groups and the hydrophilic head composed of [SO4\(^{-}\) Na\(^{+}\)], [N(CH\(_3\))\(_3\) Br\(^{-}\)], and [ N(CH\(_3\))\(_2\) O\(^{-}\)] to form A, C, and Z beads respectively. In order to match the volume of the tail and head group, the water bead lumps 4 water molecules. In a similar way, one water molecule is replaced by Cl\(^{-}\), Na\(^{+}\) and Ca\(^{+}\) ions to form water-salts beads of the form WCl, WNa, and WCa beads respectively. The octane bead represented by two tail T beads that contain butyl groups for each bead. This is consistent with Groot and Robane [128] for mapping one CH\(_2\) group in T bead to one water molecule in W bead. The volume of all single molecules proposed from the COSMO calculation for consistency with calculation methodology of the Flory-Huggins parameters \(\chi_{ij}^\infty\) from COSMO-RS is seen in Table 5.1.

In order to determine the DPD interaction parameters \(a_{ij}\) between bead i and bead j, we have used the same methodology in our previous work in chapter 4. Following this method, we first determined the value for interaction parameters between two identical beads \(a_{ii}\) or \(a_{jj}\). As the most of DPD simulations, the like-like beads interaction parameters is equal to 25 which was determined from the water compressibility as following Groot [58]. The like-like bead interaction represents the base for parameterization for unlike bead interactions \(a_{ij}\) as seen in equation (5.7).
The interaction parameters between unlike beads $a_{ij}$ was defined from the infinite dilution activity coefficients $\gamma_{ij}^{\infty}$ of binary solutions of i in j obtained from COSMO-RS. By using equation (5.8), the $\chi_{ij}^{\infty}$ parameters was measured based on the volume of molecule i and molecule j as well as the infinite dilution activity coefficients. The $\chi_{ij}^{\infty}$ parameters that related with water bead (W) and water salt beads (WCl, WN, and Ca) needs to be scaled as following from our previous work:

$$\chi_{ij}^{\infty}(m) = m\chi_{ij}^{\infty} \quad \text{and} \quad a_{ii}(m) = a_{ii}$$ (5.9)

Where $\chi_{ij}^{\infty}(m)$ is the parameter after scaling and m is the scaling number based on the number of water molecules inside the bead. Examples are given in Table 5.2. The reason for rescaling is because equation (5.8) measures the interaction energy within a volume of one water molecule or one salt ion molecule. By this way, any unphysical size discrepancies are avoided and we can have 4 water molecules inside water bead and 3 water molecules inside a water salt bead. Now, the interaction parameters $a_{ij}$ between the different types of beads for DPD can determined by combining equation (5.7), (5.8), and (5.9). The interaction parameters $a_{ij}$ can show how much beads like or dislike each other. For example, the interaction can be effectively repulsive if the interaction parameters $a_{ij}$ are larger than 25 as is the case of W bead and T bead. Alternatively, it can be effectively strong attractive if the interaction parameters are smaller than 25 as the case of W bead and Z bead. The attractive and repulsive behavior comes from negative or positive values of the $\chi_{ij}^{\infty}$ parameters that lead to phase separation of the system or direct the head group toward the water phase and tail group toward the oil phase. All these values and parameters are available in Table 5.2.
5.2.3 Simulation Details

Dissipative particles dynamics (DPD) simulations were performed in NVT ensemble (constant number of particles N, volume V, and temperature, T). There were a total of 6000 DPD beads in a cubic box (20 \( r_c \times 10 \ r_c \times 10 \ r_c \)) and all simulations began with a random distribution of the beads under periodic boundary condition. The density of the system \( \rho (\rho = N / V, \) Number of DPD beads per unit volume) is 3 DPD units and the friction constant \( \lambda \) is set equal to 4.5 [58]. The total length of each simulation run was \( 2 \times 10^6 \) steps with time step set to be equal to 0.02 DPD units. The first half of the total steps was to equilibrate the system and the second half was for production run. The spring constant is set to 4 for the bond between head-tail or tail-tail groups. The length (\( r_c \)) scale is expressed based on the volume of water bead that contain 4 water molecules (m) by the following equations [62]:

\[
r_c = \sqrt[3]{\rho m V^W} = \sqrt[3]{(3)(4)(25.58)} = 6.74 \text{ Å}
\]  

(5.10)

During all the simulation, the water and octane have the same volume fraction. From experimental results, the interfacial tension was studied as a function of concentration of surfactants or concentration of salts added to the water phase. In the simulation box, we have an inhomogeneous system and it is difficult to determine the concentration of the surfactants in the bulk water or octane phases. Since our interest here is to study the effect of head groups of surfactants and salts at the interface, we are looking for qualitative information about the IFT values and study the different properties at interface such as the orientation of surfactant, area compressibility factor, and stress profile for different system. In this manner, all surfactant and salt concentrations used in this chapter were determined by varying the number of surfactants and salt molecules in the box to determine the interfacial tension as a function of the surfactant and salt concentration from DPD.
The interfacial tension in DPD is obtained by the pressure parallel to the interface \( ( p_{xx}(z) + p_{yy}(z) ) \) and the pressure normal to the interface \( ( p_{zz}(z) ) \) as in equation (5.11). The calculation of the pressure in system is from the virial theorem which has two terms the kinetic energy and conservative interaction. Equation (5.12) was used to convert the interfacial tension from DPD units to real units.

\[
IFT_{DPD} = 0.5 \int \left[ p_{zz}(z) - \frac{1}{2} (p_{xx}(x) + p_{yy}(y)) \right] dz \tag{5.11}
\]

\[
IFT \left( \frac{mN}{m} \right) = \frac{k_B T}{r_c^2} IFT_{DPD} \tag{5.12}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the equilibrium temperature, \( z \) is the length. Simulations were performed using the Materials Studio suite, version 7.0 of Accelrys for all Dmol3 calculation and DPD simulations.
Figure 5.1: (a) Atomistic model of surfactants (SDS, DTAB, and DDAO), octane, water, and ions salts with water. (b) Mesomolecular model: the coarse-grained model of each surfactant is represented as 3 Tail (T) beads and one head bead A, C, and Z for SDS, DTAB, and DDAO surfactants head group respectively. Octane is represented by 2 Tail (T) beads. Water (W) bead has 4 water molecules. Beads containing ions have 3 water molecules plus the Cl\textsuperscript{−}, Na\textsuperscript{+}, and Ca\textsuperscript{2+} ions for WCl\textsuperscript{−}, WNa\textsuperscript{+}, and WCa\textsuperscript{2+} respectively.
Table 5.1: Molecule volume of water, head group surfactants, butane (tail), and ions salts from COSMO.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>25.58</td>
</tr>
<tr>
<td>SO₄²⁻ Na⁺</td>
<td>98.26</td>
</tr>
<tr>
<td>N(CH₃)₃⁺ Br⁻</td>
<td>138.65</td>
</tr>
<tr>
<td>N(CH₃)₂⁺ O⁻</td>
<td>86.68</td>
</tr>
<tr>
<td>(CH₄)₄</td>
<td>102.27</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>36.26</td>
</tr>
<tr>
<td>Na⁺</td>
<td>22.76</td>
</tr>
<tr>
<td>Ca⁺</td>
<td>40.75</td>
</tr>
</tbody>
</table>
Table 5.2: Interaction parameters calculation: the infinite dilution activity coefficient $\gamma_{ij}^\infty$, molecular volume ratio $\nu_j / \nu_i$, the Flory-Huggins interaction parameters before and after scaling ($\chi_{ij}^\infty$, $\tilde{\chi}_{ij(m)}^\infty$), DPD interaction parameters after scaling $a_{ij(m)}$, and $m$ is scaling number.

*For the calculation of water bead (W) against head groups and tail T water bead (W) $m=4$ related to $4$ water molecules inside the water bead, and for salt ions bead (WCl, WNa, and WCa) $m=3$ related to $3$ water molecules inside each salt ion beads. For the calculation of water bead against salt ion beads $m=4/3=1.333$ the scaling number depend on the ratio of number of water molecules inside the water and salt ion beads. For the calculation between the salt ion beads $m=3/3=1$ the scaling number is 1 since the salt ions beads have the same number of water molecules. The scaling number of any head group against tail is 1 because it does not need to rescaling the calculation.

**The calculation for W-A, W-T, and A-T beads are function of temperature to study the effect of temperature at interface.

<table>
<thead>
<tr>
<th>Bead i</th>
<th>Bead j</th>
<th>$\ln(\gamma_{ij}^\infty)$</th>
<th>$\nu_j / \nu_i$</th>
<th>$\chi_{ij}^\infty$</th>
<th>$m^*$</th>
<th>$\tilde{\chi}_{ij(m)}^\infty$</th>
<th>$a_{ij(m)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W**</td>
<td>A</td>
<td>0.0004 t(C) - 0.5393</td>
<td>3.842</td>
<td>0.0004 t(C) + 0.0670</td>
<td>4</td>
<td>0.0016 t(C) + 0.2679</td>
<td>0.0056 t(C) + 25.938</td>
</tr>
<tr>
<td>W</td>
<td>C</td>
<td>-0.955</td>
<td>5.421</td>
<td>-0.081</td>
<td>4</td>
<td>-0.322</td>
<td>23.871</td>
</tr>
<tr>
<td>W</td>
<td>Z</td>
<td>-5.186</td>
<td>3.390</td>
<td>-1.167</td>
<td>4</td>
<td>-4.670</td>
<td>8.655</td>
</tr>
<tr>
<td>W**</td>
<td>T</td>
<td>-0.0096 t(C) + 6.7372</td>
<td>3.842</td>
<td>-0.0096 t(C) + 7.3733</td>
<td>4</td>
<td>-0.0382 t(C) + 29.486</td>
<td>-0.1337 t(C) + 128.2</td>
</tr>
<tr>
<td>W</td>
<td>WCl</td>
<td>-0.854</td>
<td>1.418</td>
<td>-0.800</td>
<td>1.333</td>
<td>-1.066</td>
<td>21.277</td>
</tr>
<tr>
<td>W</td>
<td>WNa</td>
<td>0.227</td>
<td>0.890</td>
<td>0.234</td>
<td>1.333</td>
<td>0.312</td>
<td>26.090</td>
</tr>
<tr>
<td>W</td>
<td>WCa</td>
<td>-0.101</td>
<td>1.593</td>
<td>-0.008</td>
<td>1.333</td>
<td>-0.011</td>
<td>24.963</td>
</tr>
<tr>
<td>WCl</td>
<td>A</td>
<td>-0.964</td>
<td>2.710</td>
<td>-0.598</td>
<td>3</td>
<td>-1.794</td>
<td>18.720</td>
</tr>
<tr>
<td>WCl</td>
<td>T</td>
<td>0.535</td>
<td>2.820</td>
<td>0.927</td>
<td>3</td>
<td>2.781</td>
<td>34.733</td>
</tr>
<tr>
<td>WCl</td>
<td>WNa</td>
<td>-2.068</td>
<td>0.628</td>
<td>-1.940</td>
<td>1</td>
<td>-1.940</td>
<td>18.209</td>
</tr>
<tr>
<td>WCl</td>
<td>WCa</td>
<td>-1.642</td>
<td>1.124</td>
<td>-1.636</td>
<td>1</td>
<td>-1.636</td>
<td>19.274</td>
</tr>
<tr>
<td>WNa</td>
<td>A</td>
<td>-0.619</td>
<td>4.316</td>
<td>0.075</td>
<td>3</td>
<td>0.225</td>
<td>25.786</td>
</tr>
<tr>
<td>WNa</td>
<td>T</td>
<td>2.508</td>
<td>4.492</td>
<td>3.233</td>
<td>3</td>
<td>9.698</td>
<td>58.942</td>
</tr>
<tr>
<td>WCa</td>
<td>A</td>
<td>-0.236</td>
<td>2.411</td>
<td>0.059</td>
<td>3</td>
<td>0.176</td>
<td>25.615</td>
</tr>
<tr>
<td>WCa</td>
<td>T</td>
<td>6.327</td>
<td>2.510</td>
<td>6.645</td>
<td>3</td>
<td>19.936</td>
<td>94.778</td>
</tr>
<tr>
<td>A**</td>
<td>T</td>
<td>-0.0072 t(C) + 10.25</td>
<td>1.041</td>
<td>-0.0072 t(C) + 10.251</td>
<td>1</td>
<td>-0.0072 t(C) + 10.251</td>
<td>-0.0252 t(C) + 60.878</td>
</tr>
<tr>
<td>C</td>
<td>T</td>
<td>5.187</td>
<td>0.738</td>
<td>5.238</td>
<td>1</td>
<td>5.238</td>
<td>43.335</td>
</tr>
<tr>
<td>Z</td>
<td>T</td>
<td>1.838</td>
<td>1.180</td>
<td>1.851</td>
<td>1</td>
<td>1.851</td>
<td>31.479</td>
</tr>
</tbody>
</table>
5.3 Results and discussion

5.3.1 Experimental

The pendant drop method was used for determining the interfacial tension experimentally. As a result of these measurements, the interfacial tension is obtained as a function of three concentration values for SDS, DTAB, and DDAO surfactants to compare the efficiency of these surfactant and study the effect of change of the head group given the same tail group. Figure 5.2 shows the steady state interfacial tension between water or aqueous surfactant solution and octane as a function of surfactant concentration. A reduction in the interfacial tension with increasing surfactant concentration can be observed for each surfactant. For DDAO surfactant, at concentrations greater than 2.2 mM no variation in the interfacial tension was observed with increase of concentration. The CMC of DDAO is 2.1 mM [129], therefore the expectations are confirmed in this case the saturation concentration of the phase boundary is reached, and the interfacial tension will not be influenced. The CMC concentration of DDAO is lower than the CMC concentration of SDS (8.2 mM) [130], [131] and DTAB (16.4 mM) [132], [133]. This is explains the decrease of the interfacial tension as function of concentration for SDS and DTAB surfactants. The different values of interfacial tension between ionic (SDS), cationic (DTAB), and zwitterionic (DDAO) surfactants is related to the electric charge of the head groups and the interaction with water. We will see how this effect is handled by DPD with COSMO-RS based parameters. It can be seen that the efficiency of these three surfactants follows the order of DDAO>SDS>DTAB based on the decreasing interfacial tension.

Sodium dodecyl sulfate SDS surfactant was chosen to study the effects of salts and temperature on the IFT by fixing the concentration of SDS at 0.35 mM and varying the other parameters as seen on Figure 5.3. A linear decrease of the interfacial tension is observed with
increasing temperature. Al-Sahhaf et al., reported the same dependence on temperature for water/SDS/octane systems [134]. The interfacial tension decreases with increasing salt concentration of the aqueous phase with linear dependence for both salts. The CaCl$_2$ solutions have the higher reduction on the IFT values compared to NaCl solutions. Increasing the salt concentration, helps to transfer surfactants to the interface, resulting in a decrease in IFT values. In other words, the effect of salts is to increase partitioning of surfactant from the bulk solution to the interface [135].

![Figure 5.2](image-url)

Figure 5.2: The experimental results of interfacial tension as a function of surfactant concentration at $T = 25 \ ^\circ\text{C}$ for three different surfactants (SDS, DTAB, and DDAO) at the interface of water/octane system.
Figure 5.3: The experimental results of interfacial tension of water / Octane system as a function of salt concentration (NaCl, and CaCl2) and temperature for fixed SDS concentration of 0.35mM T = 25 °C.

5.3.2 DPD Simulations

*Effect of Head Group:*

The effect of head group of surfactants on the interfacial tension is shown in Figure 4 for the DPD results. With increasing number of surfactants in the system, the interfacial tension decreases because more surfactant molecules transfer to the interface between water and octane and arrange themselves as the head group into water phase and the tail group to octane phase. At a certain number of surfactants of SDS, DTAB, and DDAO, a plateau value is reached at which the surface tension does not change. The reason is that the surface is now completely covered with surfactant molecules. If the concentration is further increased, the molecules cannot adsorb at the interface. The concentration at which the interfacial tension no longer decreases further, is called
the critical micelle concentration (CMC). Since our interest is to compare the results qualitatively with experimental results, we found that the efficiency of surfactants from DPD follows the same order of experimental results DDAO>SDS>DTAB. The values of interaction parameters $a_{ij}$ between the beads calculated from $\gamma_{ij}^{w}$ and $\chi_{ij}^{w}$ in Table 5.2 are crucial parameters that give insight into the efficiency of the surfactants. The polarity between the head groups and water could be evaluated by the Flory-Huggins interaction parameters $\chi_{ij}^{w}$, the smaller the value means more charge attraction. The charge interaction between the head group and water increase as following for DDAO>DTAB>SDS head group. Although the polarity of head group of DTAB surfactant is higher than that of SDS, the efficiency of SDS is better than DTAB. The reason is that the oxygen atoms in the SDS head group make a strong repulsion versus the tail group. This increases the efficiency of SDS of surfactant over the DTAB surfactant.

The stress profile describes the stress distribution through the interface. Figure 5.5 shows the effect of head group in stress profile and it compares SDS, DTAB, and DDAO at same number of surfactants inside water octane system. The stress away from interface is equal zero since the pressure is isotropic, the same in the x-y plane as in the normal to the interface. At the interface, the stress is nonzero due to the different distributions of water, octane, and surfactants. For example, the positive contribution of stress at the interface arises from the repulsion between water and octane. DDAO surfactant changes the shape of the positive peak of stress by reducing and shrinking it as compared with other surfactants. Furthermore, the negative contribution near the bulk oil results from the interaction between the oil and tail of the surfactants. It is interesting to note that this part of the stress profile does not change much with changing surfactant type since all surfactants have the same tail. Lastly, the negative contribution near from the bulk water reflects the interaction between the head group and water. We can see clearly that DDAO has the major
contribution over the SDS and DTAB. From the stress profile results, the head group can play an important role at the interface especially for the positive contribution and the negative contribution near the bulk water side of the interface.

The orientation of the surfactants at the interface can give more justification that DDAO is a more efficient surfactant. Root mean square (RMS) end-to-end distance $\langle R^2 \rangle^{1/2}$ is a concept that is used to show the degree of extension or collapse in polymer chains. The RMS end-to-end distance is used here to describe the orientation and structure of surfactant at the interface of water/octane system. On increasing of the number of surfactants in the system, we observe an increase in $\langle R^2 \rangle^{1/2}$ until reaches a plateau for SDS, DTAB, and DDAO surfactants as seen in Figure 5.6. This implies that the orientation of the surfactant becomes straighter and more perpendicular at the interface with increasing $\langle R^2 \rangle^{1/2}$. DDAO surfactant is straighter and more perpendicular at the interface compared to SDS and DTAB surfactants since it has higher values of $\langle R^2 \rangle^{1/2}$. This could explain the behavior of the stress distribution inside the system of DDAO surfactants. As a result, the orientation of surfactants depends on the head group type of surfactants at the interface. In other words, the high values of $\langle R^2 \rangle^{1/2}$ for surfactants makes the surfactant chain more ordered at the interface and interfacial density increases which enhances the efficiency of the surfactants. When $\langle R^2 \rangle^{1/2}$ reaches a plateau, the interface is saturated by surfactants and surfactants begin forming micelles in the bulk phase.
The compressibility modulus of a monolayer film is evaluated from the IFT-area data isotherms to characterize monolayer mechanical properties. Area compressibility modulus $K_A$ is defined as [136]:

\[
IFT = \frac{K_A(A - A_0)}{A_0}
\]  

(5.13)

Where $A_0$ is saturated area per molecule and $A$ is the area per surfactant at the interface. The saturated area per molecule $A_0$ can be determined from the plot of IFT as function of the area occupied by surfactants at the water/octane interface where the intersection of straight fitting line with the horizontal line at zero IFT. The saturated area for the SDS monolayer is 47.98 Å²/molecule at water/octane interfaces, which agrees well with the experimental values of 48.3 Å²/molecule measured for water/octane interface at the critical micelle concentration [130]. The saturation value for DTAB and DDAO monolayer at water/octane interfaces are 51.20 and 41.86 Å²/molecule, respectively. The values are slightly lower than the value of 59 Å²/molecule and 47 Å²/molecule for DTAB and DDAO respectively reported in the literature for air/water interface [137], [138]. The area compressibility modulus of surfactants can be calculated from the slope of the variation of the interfacial tension against the reduced relative area change per molecule $(A - A_0)/A_0$ as seen on Figure 5.7. The values of the area compressibility modulus $K_A$ of SDS, DATB, and DDAO at water-octane interface are 30.06, 24.45, and 45.56 mN m⁻¹, respectively. Unfortunately, there are no experimental values available for making a comparison with our findings. It is interesting to note that this result shows the values for the area compressibility modulus increase with increasing the efficiency of the surfactants DDAO>SDS>DTAB a similar
dependence of IFT. The ordering of surfactants at the interface and the high compressibility indicates a more highly packed monolayer.

![Figure 5.4](image1)

**Figure 5.4**: The DPD results of interfacial tension as a function of number of surfactants at $T = 25 \degree C$ for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system.

![Figure 5.5](image2)

**Figure 5.5**: The DPD results of stress profile with fixed number of surfactants (120 surfactants) at $T = 25 \degree C$ for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system.
Figure 5.6: The DPD results of root mean square (RMS) end-to-end distance as a function of number of surfactants at $T = 25$ °C for SDS, DTAB, and DDAO surfactants.

Figure 5.7: The change of the interfacial tension versus the reduced relative area change per surfactants at $T = 25$ °C.
**Effect of salt and temperature at water/octane/SDS system:**

We performed DPD simulations for the water/octane/SDS surfactants system to study the effect of changing the temperature or adding salts at the interface. As expected, the interfacial tension decreases with increasing temperature without any salt as shown in Figure 5.8. Moreover, the results for the change in the interfacial tension when salts are added, is also shown in Figure 5.8. As expected in all type of salts, a decrease in the interfacial tension is obtained when salts are added. Our calculation assume that the salts are completely dissociated inside the system. It can be seen clearly that CaCl$_2$ salt is more efficiency than NaCl. We found that the DPD results for IFT as functions of temperature or of salt concentration agree qualitatively with experimental results.

To study the effect of concentration of SDS surfactant at the interface, we will consider three different systems: fixing the temperature at 85 °C, fixing the number of NaCl molecules, and fixing the number of CaCl$_2$ molecules. We will investigate the orientation of surfactants, stress profile, and the area compression modulus. Figure 5.9 shows variation of the interfacial tension as a function of concentration of SDS surfactant at the constant temperature as well as constant number of salts molecules inside the system (375 molecules NaCl and 375 molecules CaCl$_2$). Increasing temperature reduces the interfacial tension a little and a sharp decrease in interfacial tension is observed when salts are added to system compared with water/octane/SDS system at 25°C with no salt. The interaction parameters $a_{ij}$ of W-T and A-T is reduced with the increase of temperature which leads to the decrease of interfacial tensions between the two phases. Figure 5.10 shows the snapshot of 120 SDS inside water/octane system with and without salts. The figure reveals that all the ions are distributed in the water phases as well as accumulated at the interface around the hydrophilic groups of the surfactants. There is a strong charge interaction between the
WCl bead with SDS head group and water and medium charge interaction between the positive ions beads (WNa and WCa) with SDS head group and water as seen in Table 5.2. This indicates that the surfactant can tolerate the salts ions with the result a reduction in the interfacial tension. Figure 5.11 shows stress profile for four systems: 120 SDS surfactants at 25 °C, 120 SDS surfactants at 85 °C, 120 SDS surfactants at 25 °C with 275 NaCl molecules, and 120 SDS surfactants at 25 °C with 375 CaCl₂ molecules to make a comparison. The temperature reduces the peak of the positive contribution of stress profile a little. Moreover, the negative contribution near from the bulk oil increases which implies the reduction of IFT with increasing temperature due to reduced interactions between the water bead and tail bead. The salts have more impact on the peaks of the positive and negative contribution of stress profile and the peaks are affected by the type of salt as seen in Figure 5.11. As expected, the salts have an effect on the hydrophilic property of the head group of SDS surfactant.

Figure 12 shows the root mean square (RMS) end-to-end distance \( \left\langle R^2 \right\rangle^{1/2} \) of surfactants in the systems with salt and without salts. The root mean square (RMS) end-to-end distance \( \left\langle R^2 \right\rangle^{1/2} \) of SDS surfactant in the systems with NaCl or CaCl₂ salt is more than that of the system without salt. Introducing the salts in the system make surfactants becomes straighter and more perpendicular to the interface. The strong interaction between the ions and the head group of SDS surfactants let the surfactant to be more stretched at the interface and enhance the efficiency of the surfactant. From Figure 5.12, root mean square (RMS) end-to-end distance \( \left\langle R^2 \right\rangle^{1/2} \) of SDS surfactant at 85 °C is close to that for 25 °C which means the temperature shows little influence on the orientation of the surfactant.
The saturated area for the SDS monolayer at 85 °C is 50.01 Å²/molecule at water/octane interfaces, which is higher than value at 25 °C (47.98 Å²/molecule). The reason for increasing saturated area for the SDS monolayer with increasing temperature is due to the thermal motion [7]. The saturation areas of SDS with NaCl or CaCl₂ present at water/octane interface are 43.25 and 41.05 Å²/molecule, respectively. The values are lower than the value of the SDS monolayer without salts. This reduction in saturated area per molecule indicates that the salts enhance the orientation of the surfactant at the interface, thus increasing the number of surfactants when a full monolayer is formed. From Figure 5.13, The values of the area compressibility modulus $K_A$ for a temperature of 85 °C, NaCl, and CaCl₂ at water/octane/SDS interface are 28.48, 38.13, and 38.97 mN m⁻¹, respectively. The value for the area compressibility modulus decreases with increasing temperature because there are decrease in adsorption of surfactant at high temperature. The area compressibility modulus decreases for salts systems since the appearing of salts increases the adsorption of surfactant at the interface.
Figure 5.8: The DPD results of interfacial tension as a function of number of salts at $T = 25 \, ^\circ\text{C}$ and as function of temperature at fixed number of SDS surfactant at 120 surfactants for water/octane system.

Figure 5.9: The DPD results of interfacial tension as a function of number of surfactants for three systems at fixing $T = 85 \, ^\circ\text{C}$, 375 molecules of NaCl, and 375 molecules of CaCl$_2$ at the interface of water/octane system.
Figure 5.10: Snapshots of the water/octane systems at fixed the number of SDS surfactant at 120 surfactants (A) without any salts (B) with 375 molecules of NaCl (C) 375 molecules of CaCl$_2$. (The water beads are removed for clarity, octane beads: red; head beads: blue; tail beads: pink; WCl beads: green; WNa beads: yellow; WCa beads: orang).
Figure 5.11: The DPD results of stress profile at fixed number of SDS surfactants (120 surfactants) for four systems at fixed $T = 85$ °C, 375 molecules of NaCl, and 375 molecules of CaCl$_2$ at the interface of water/octane system compared with SDS system at 25 °C.

Figure 5.12: The DPD results of root mean square (RMS) end-to-end distance as a function of number of surfactants for three systems at fixing $T = 85$ °C, 375 molecules of NaCl, and 375 molecules of CaCl$_2$ at the interface of water/octane system in comparison with SDS system at 25 °C without salts.
Figure 5.13: The change of the interfacial tension against the reduced relative area change per SDS surfactant for three systems at fixing $T = 85 \, ^\circ C$, 375 molecules of NaCl, and 375 molecules of CaCl$_2$ at the interface of water/octane system comparing with SDS system at 25 $^\circ C$ without salts.

5.4 Conclusion

In this work, we performed a series of dissipative particle dynamic (DPD) simulations as well as experiments to investigate the effect of head group of surfactants, salts and temperature on the properties of the water/octane interface. Dissipative particle dynamics simulations were conducted to reveal the interfacial properties such as interfacial tension, area compressibility, stress profile, and conformation of surfactant at the interface. It was observed from DPD and experimental results that the efficiency of the three surfactants to reduce interfacial tension follows the order of DDAO>SDS>DTAB. DPD results indicate that of surfactants at the interface and area compressibility all followed the order of DDAO>SDS>DTAB which described more ordering of surfactants at the interface and the high compressibility indicates a highly packed monolayer.
We also investigated the influence of salts and temperature at water/octane/SDS surfactants interface. Both experiment and DPD showed a reduction in IFT with increase in temperature or salt concentration. The interaction parameters between W-T and A-T decreased with the increasing the temperature which caused a decrease of the interfacial tension. The temperature did not show too much effect on the orientation of SDS surfactant at the interface. In contrast, the area compressibility increased with increasing temperature. The salts demonstrated a major impact in reducing the interfacial tension sharply. The addition of salts in the system stretched and ordered the SDS surfactant more at the interface, which allowed the number of surfactants at the interface to increase, increasing the area compressibility.

The qualitative agreement between experiment and DPD model based on COSMO-RS derived parameters should be attractive for a researcher who is interested in designing surfactants. For specific application, the model also provides new insight into the molecular scale behavior of surfactants.
Chapter 6 Critical micelle concentration (CMC) and adsorption onto calcium carbonate for SDS ionic surfactant by DPD

6.1 Introduction

The arrangement of the surfactants in their environment depends on the surrounding medium. The concentration of surfactants, in which micelles are formed, is known as critical micelle concentration (CMC). If the solution is polar, the micelles form as the hydrophilic head of the surfactant is facing outwards and the hydrophobic tail is in the micelle core. If the solution is non-polar, it forms inverse micelles [139]. In the solution, there is a dynamic equilibrium between the surfactants and the micelles. As a result, the value of the CMC depends strongly on the type of surfactant [140], [141] as well as temperature [142], and salt [143], [144]. There are many experimental methods used for determining the value of CMC such as spectroscopic methods, the surface tension as a function of surfactant concentration, determination of the viscosity, determination of light scattering, determination of the equivalence conductivity [145]–[148]. Accurate results of CMC studies are very important for different research areas such as environmental, pharmaceutical, biological, and Enhanced Oil Recovery (EOR) [7].

The adsorption of surfactants to solid surface is dependent on the interaction between the surface and the surfactant. This means, the adsorption of surfactants is affected by the hydrophobicity of surface. For example, if the surfactant adsorbs onto a hydrophobic surface, the head group is exposed to the solution and the tail group adsorbs to the surface. And, if the surfactant adsorbs onto a polar surface, the head group adsorbs to the surface and the tail group is exposed to
the solution. If the surface has the same degree of polarity with head group and the tail group of the surfactant, the micelles could form at the surface. Micelle formation of surfactants at the surface is consequently a matter of balance between these two forces of interaction. The study of adsorption of surfactants on solid surface is important for a variety of interfacial processes such as detergency, emulsification, dispersion, and Enhanced Oil Recovery (EOR) [31]–[33].

In this work a mesoscopic simulation method (dissipative particle dynamics) is presented for the calculation of critical micelle concentration of SDS surfactants and the adsorption onto carbonate rocks based on various of surfactant concentration into water systems. The use of DPD method for determining the CMC values with effect of salt and temperature has not yet been studied. Using dissipative particle dynamics (DPD) simulations, Vishnyakov et al., proposed a model to predict micellar self-assembly of nonionic surfactants [149]. The CMC values showed reasonable agreement with experiment. Oviedo-Roa et al., selected dodecyltrimethylammonium chloride (DTAC) as a characteristic example to study aggregation number and critical micelle concentration [150]. Results indicate a quantitative agreement with the experiment where the CMC value is 0.0217 mol/kg, and the aggregation number ranges from 46 to 54 molecules. In order to determine the critical micelle concentration (CMC) of aqueous sodium dodecyl sulfate (SDS) and cationic surfactant cetyltrimethylammonium bromide (CTAB), Mao et al., proposed a model with various surfactant concentrations by performing dissipative particle dynamics (DPD) simulations [151]. The CMC values of SDS surfactants and CTAB are 19mM and 2.6mM respectively and both values are higher than the experimental values. To the best of our knowledge, the adsorption behavior of surfactant on carbonate surface is not yet reported in the literature by dissipative particle dynamics.
In this chapter, two type of studies are presented for aqueous sodium dodecyl sulfate (SDS) surfactant by dissipative particle dynamics. The first one, we consider the specifics of micellization in water phase to calculate the critical micelle concentration of SDS. The effect of NaCl salt and temperature upon the critical concentration for micelle formation in SDS solution has been investigated. The second part, the DPD have been used to study the adsorption of SDS surfactant on carbonate surface. Various concentration of SDS surfactant with water/Carbonate system are evaluated to determine the amount of adsorption of surfactant to the surface. For both CMC calculation and adsorption studies are compared with the experimental data.

6.2 Methodology

6.2.1 Critical micelle concentration (CMC) method

The building of coarse-grained beads for SDS and water is available in chapter 6. The SDS surfactants molecules are divided into 4 fragment of approximately similar volume size. The hydrophobic tail of surfactants composed of three tail (T) beads and the hydrophilic head composed of [SO\textsubscript{4} \textsuperscript{-} Na\textsuperscript{+}] to form one head (A) bead. Water (W) bead contains 4 water molecules to match the volume of the tail and head beads. Three water molecule plus ether Cl\textsuperscript{-} or Na\textsuperscript{+} are inside the salts beads to form WCl, and WNa beads respectively. The volume of all single molecules proposed from the COSMO calculation with calculation methodology of the Flory-Huggins parameters $\chi^\infty_{ij}$ from COSMO-RS are discussed in detail in chapter 5. The interaction parameters between beads are given in Table 6.1. The interaction parameters between water, tail, and head are set as function of temperature in °C to study the effect of temperature on CMC. It is
worth noting that the interaction parameters for W-T are strongly dependent on temperature and strongly unfavorable beads. The interaction between A-T is about half of interaction parameters for W-T but it is still an unfavorable interaction. The surfactant head bead with water bead are polar and have favorable interactions. It shows a weak dependence on temperature. All like-like beads interaction in diagonal $a_{ii}$ are equal to 25. The spring constant is set to 4 for the bond between head-tail or tail-tail groups.

Table 6.1: Interaction parameters for all DPD beads for CMC study.

<table>
<thead>
<tr>
<th>$a_{ij}$</th>
<th>W</th>
<th>T</th>
<th>A</th>
<th>WCl</th>
<th>WNa</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>25.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>-0.1337 t(°C) + 128.2</td>
<td>25.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.0056 t(°C) + 25.938</td>
<td>-0.0252 t(°C) + 60.878</td>
<td>25.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WCl</td>
<td>21.28</td>
<td>34.73</td>
<td>18.72</td>
<td>25.00</td>
<td></td>
</tr>
<tr>
<td>WNa</td>
<td>26.09</td>
<td>58.94</td>
<td>25.79</td>
<td>18.21</td>
<td>25.00</td>
</tr>
</tbody>
</table>

The Dissipative particles dynamics (DPD) simulation cubic box is set at $30.28 \, r_c \times 30.28 \, r_c$ with total of 83275 beads. In DPD, all beads have the same volume size and the value of length $r_c$ scale is 6.74 Å based on the volume of water bead that contain 4 water molecules. The density of the system $\rho$, and friction constant $\lambda$ are 3 and 4.5 respectively. The total length of simulations run is 200000 steps with time step is set to be equal to 0.02 DPD unite. The first half of the total steps 100000 is found to be sufficient to stabilize the micelle formation. The second one is for production run to make sure the number of free surfactants does not change after the equilibrium stage.
The concentration of SDS inside the DPD box varies from 12.1 to 19.1 mM. To calculate the concentration into physical unit (mol/l), equation (6.1) is used in order to convert the number of surfactant in the system to concentration (C) in real unit (mol/l) and we can compare with experimental values:

\[
C = \frac{n}{L^3r_c^3N_A}
\]

(6.1)

Where, \(n\) is the number of surfactant molecules in the box (there are two type of \(n\): \(n_{\text{total}}\) is the number of total surfactant molecules to determine the total concentration of surfactant (\(C_T\)) and \(n_{\text{free}}\) is the number of free surfactant molecules that, at the end of run, determine the free concentration of surfactant (\(C_f\)), \(L\) is the length side of simulation box, \(r_c\) is cutoff distance, and \(N_A\) is Avogadro number. To determine the \(n\) of free surfactant molecules from each simulation box, if any surfactant molecule is separated by more than \(r_c\) from any other surfactant molecule it is considered as free surfactant. This means that, free surfactants do not belong to any aggregation of surfactants inside the box. As a result, a micelle is considered to be any two or more surfactants that aggregate together.

6.2.2 Adsorption of SDS surfactant onto calcium carbonate method

The design of coarse-grained beads of calcium carbonate (\(\text{CaCO}_3\)) of solid phase is built to represent each \(\text{CaCO}_3\) as one bead (S bead). The interaction parameters for W, A, and T bead at 25 °C are available in Table 6.1. We need to calculate the interaction parameter between calcium carbonate bead with W, A, and T bead. We follow the same methodology that used in
chapter 5 to calculate the interaction parameters of solid bead against the W, A, and T beads. As seen Table 6.2. The interaction parameters between calcium carbonate bead with water bead shows a strong interaction between water and calcium carbonate. The head and tail of surfactant have same degree of polarity with calcium carbonate. Water, head, and tail beads have favorable with interactions solid beads. The screening charge density of calcium carbonate from COSMO calculation that is used to calculate the interaction parameters is available on appendix B.

Table 6.2: The interaction parameters for calcium carbonate bead (S) with water (W), head (A), and tail (T) beads.

<table>
<thead>
<tr>
<th>Bead i</th>
<th>Bead j</th>
<th>ln($\gamma_{ij}^{\infty}$)</th>
<th>$v_j / v_i$</th>
<th>$\chi_{ij}^{\infty}$</th>
<th>$m$</th>
<th>$\chi_{ij(m)}^{\infty}$</th>
<th>$a_{ij(m)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>S</td>
<td>-1.107</td>
<td>3.520</td>
<td>-0.565</td>
<td>4</td>
<td>-2.259</td>
<td>17.094</td>
</tr>
<tr>
<td>A</td>
<td>S</td>
<td>-0.226</td>
<td>0.916</td>
<td>-0.222</td>
<td>1</td>
<td>-0.222</td>
<td>24.222</td>
</tr>
<tr>
<td>T</td>
<td>S</td>
<td>-0.092</td>
<td>0.880</td>
<td>-0.083</td>
<td>1</td>
<td>-0.083</td>
<td>24.708</td>
</tr>
</tbody>
</table>

The simulation size for the liquid phase is the same as for CMC calculation in section 6.2.1 30.28 $r_e$ x 30.28 $r_e$ x 30.28 $r_e$. The volume ratio of liquid phase to solid phase is calculated from the experimental volumes [152]. From the experimental volume ratio and volume of the liquid phase in DPD, we can determine the volume size of solid phase that equal to 2176.56 $r_e^3$. The solid phase is placed perpendicular to the y direction of the simulation box for the liquid phase with area size 30.28 $r_e$ x 30.28 $r_e$, and then the thickness of the solid box is 2.374 $r_e$. In order to avoid the solid surface beads to mix with liquid beads, the solid surface beads are represented as fixed DPD beads and the periodic boundary condition is applied in the x and y directions. The SDS
concentration ($\Gamma$) at the surface as a function of the SDS surfactant concentration in the bulk (not adsorbed) in equilibrium, is calculated from the density profile $\rho(z)$ through equation (6.2):

$$\Gamma = \int (\rho(z) - \rho_b) \, dz \quad (6.2)$$

where $\rho_b$ is the SDS density in the bulk and the integral is performed over all the coordinate $z$ ($L_z = 32.564$ in all the cases).

Two well known adsorption models are introduced to characterize the number of surfactants that adsorb to the surface of calcium carbonate and the equilibrium concentration ($C_e$) of surfactant after contacting with surface of calcium carbonate: Langmuir adsorption model and the Freundlich model. The Freundlich isotherm assumes that the surfactant adsorption occurs on a heterogeneous surface by multilayer sorption and the model can be given as follows:

$$q_e = K_F C_e^n \quad \text{or} \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6.3)$$

Where $K_F$ is Freundlich coefficient, $n$ is Freundlich exponent, $q_e$ is amount adsorbed per unit of adsorbent. The Freundlich coefficient and exponent can be determined by plotting $\log q_e$ versus $\log C_e$. Langmuir suggested as one of the first theory of adsorption on surface. Langmuir isotherm is applicable for monolayer adsorption and it relates the amount of solid adsorbate adsorbed to the equilibrium liquid concentration at a fixed temperature. It is expressed in this nonlinear form as follows:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L} \frac{1}{C_e} \quad (6.4)$$
Where $Q_0$ is maximum amount adsorbed (monolayer) constant, and $K_L$ is Langmuir sorption constant. The Langmuir constants can be determined by plotting $1/q_e$ versus $1/C_e$.

6.3 Results and Discussion

6.3.1 Critical micelle concentration (CMC)

The determination of CMC is represented by the concentration of free surfactants ($C_f$) as a function of the total concentration of surfactants ($C_T$) as seen in Figure 6.1. When $C_T < CMC$ (micelles do not appear), the concentration of free surfactants is equal the total concentration. When the total concentration is above CMC, the concentration of the free surfactant decreases with increasing the total concentration. This decline of free surfactant concentration for ionic surfactants was noticed by experimental [153], [154], molecular dynamic simulations [140], [155], and theory calculation [156] and the reason for that because of the electrostatic interaction between free surfactants and micelles formation.

The CMC can be defined as the intersection of the linear line of $C_f$ as function of $C_T$ with $C_T = C_f$ line. The critical micelle concentration value of SDS at 25 °C is 6.02 mM from DPD which is very close to the experimental value 8.16 mM [157]. As an example, Figure 6.2 shows equilibrated configurations of different concentration of SDS at 25 °C. Addition of extra SDS surfactants to the systems causes to change the micelle size. As results of increasing the concentration, the micelles size become larger and the number of free surfactant reduce.
Figure 6.1: The evolution of the free surfactants concentration \( C_f \) as a function of the total concentration of surfactants \( C_T \) for SDS surfactant in water.
Figure 6.2: Snapshots of the SDS in water at 25 °C as increasing the concentration of surfactants at equilibrium. (a) 12.1 mM (b) 15.6 mM (c) 19.1 mM (The water beads is removed for clarity; head beads: green; tail beads: red).

The DPD simulation is performed at different temperatures 5 °C, 25 °C, 45 °C, and 65 °C to obtain the temperature dependent into the CMC. Figure 6.3 presents the values of CMC at different temperatures which are compared with experimental values [157]. From DPD results, the CMC increases with increasing the temperature but the experimental values propose a minimum in the CMC around 25 °C. The DPD simulation cannot capture the minimum value as a coarse grained model. The minimum value appears because of hydrogen bonds between water and surfactants break most rapidly at temperatures near to minimum temperature and it is very hard for a coarse grained model to deal with this feature [158].

We have studied CMC of SDS surfactants in the presence of NaCl salts and the values of CMC with salts are compared with experimental values as seen on Figure 6.4. The comparison of CMC values of DPD shows a reasonable agreement with experiment. As expected, the presence of NaCl salt appears to drive the systems toward increasing the micelles size and reduce the number of free surfactants in the system which is in good agreement with experimental observations [159]. As a result, addition of salt into the systems lowers the surfactants CMC values. Ion interactions (Na⁺ and Cl⁻) have been shown a major effect on SDS micelles grow. The micelles size changes as the salt concentration increases from 0.01 M to 0.02 M.
Figure 6.3: Temperature dependence of the CMC values of DPD and experimental for the SDS surfactants. (experimental CMC values from ref [157])

Figure 6.4: Effect of NaCl salts on the CMC values of DPD and experimental for the SDS surfactants at 25 °C. (experimental CMC values of slats from ref [143])
To study the degree of counterions associated $\alpha$ with the micelles, we introduce the semi-empirical theory to relate the free surfactant concentration $C_f$, the total surfactant concentration $C_T$, and the CMC:

$$\log(C_f) = (1 + \alpha) \log(CMC) - \alpha \log\left(\frac{(1 - \alpha)(C_T - C_f) + C_f}{1 - V C_T}\right)$$

(6.5)

Where $V$ is the molar volume of surfactants, and all concentrations in molarity unit. This empirical expression was developed by Quina and co-workers [156] and modified by Bales [160]. The reason for using this expression because of the interpretation of association and dissociation of ions is very difficult to describe by DPD simulation. The values of the degree of counterions associated $\alpha$ are determined from fitting the values of the free surfactant concentration $C_f$, the total surfactant concentration $C_T$, and the CMC by equation (6.5). The degree of counterions associated $\alpha$ describes the degree of association of counterions with head of surfactant to forming micelles. The degree of counterions associated $\alpha$ result is 0.58 for SDS surfactant at 25 °C and the experimental value is 0.73 [160], [161]. This obtained value of $\alpha$ is fairly acceptable with experiment if we take into account the design of coarse grained model in DPD of ionic compounds. The $\alpha$ values of SDS at different temperature are 0.57, 0.58, 0.58, and 0.59 for 5 °C, 25 °C, 45 °C, and 65 °C, respectively. It is clear that the $\alpha$ values are independent on temperature and this agrees with Sanders and co-workers [140]. On the other hand, the value of the degree of counterions associated is strongly dependent on salt concentration. The $\alpha$ values are 0.66 for 0.01 M NaCl and 0.68 for 0.02 M NaCl. Addition the salts in the systems increases the binding of the counterion and that make a decreasing in the CMC values [138].
6.3.2 Adsorption of SDS surfactant onto calcium carbonate

The adsorption isotherms of SDS onto calcium carbonate of DPD results and experimental data from ref. [152] are shown in Figure 6.5. From experimental results and as discussed in chapter 2, four type of regions can be clearly distinguished in the adsorption isotherm study. In this DPD results, the shapes of isotherms are close to experimental results. The main difference of DPD from experiment is that the adsorption of SDS surfactants for third region cannot expose by DPD. In other words, three type of regions can be distinguished in the adsorption isotherm study by DPD. The first region appears between 500 ppm to 1500 ppm of SDS equilibrium concentration. The second region which appears between 1750 ppm to 2500 ppm of SDS equilibrium concentration corresponds to the growth of aggregates already formed. The slope in second region is higher than the slope in first region. The different between the slopes in first and second regions can be explained by two reasons. First, the amounts of adsorption increase with increasing the concentration of SDS. Second, it is also indicated that admicelles appear on the surface in the second region because the critical micelle concentration is reached at around 2250 ppm. With increasing the concentration of SDS leads to last region where the maximum adsorption is observed. The maximum adsorption is reached at a concentration higher than the CMC. Figure 6.6 shows the snapshot of three different concentration systems at equilibrium where each one is representing different region. We can see that clearly as increasing the surfactant concentration on the system the amount of adsorption increases. Moreover, the type of micelles appears at the surface is admicelles (the type of micelles appears on surface was discussed in more details in chapter 2). The appearance of admicelles is related to the interaction parameters between the
surface and head or tail groups. Both head and tail groups are favorable to the surface that make admicelles formation because of the repulsion parameters between the SDS head groups and tail group to make a balance between the interaction of the surface, head group, and tail group.

Figure 6.5: The adsorption isotherm of SDS on calcium carbonate for DPD and experimental. Experimental data ref. [152].
Freundlich, and Langmuir adsorption isotherm models have been applied to quantify the adsorption capacity of SDS surfactant onto calcium carbonite. Figure 6.7 and Figure 6.8 depict Freundlich, and Langmuir adsorption isotherm models fittings from DPD results. The parameters result from the fitting of Freundlich, and Langmuir isotherm adsorption models and the experimental values have been compared in Table 6.3. The values of regression coefficient ($R^2$) of experimental indicate that both models are fitted better than DPD. The reason for well-fitting of experiment is that the experiment can be distinguished the adsorption isotherm into four type of regions but the DPD into three regions only. As a result, the Freundlich coefficient ($K_F$) and Langmuir sorption constant ($K_L$) for experimental is lower than DPD values. From both
experimental and DPD, Freundlich adsorption isotherm model show better accuracy compared with Langmuir isotherm models. From simulations point view, the appearance of admicelles on the surface let the Freundlich model has more accuracy fitting data than Langmuir model because of Freundlich are able to quantify admicelles on the surface by considering the assumptions of the Freundlich model as multilayer sorption and Langmuir model as monolayer adsorption.

Figure 6.7: Langmuir isotherm model fit from DPD results for adsorption of SDS surfactant on calcium carbonite at 25 °C.
Figure 6.8: Freundlich isotherm model fit from DPD results for adsorption of SDS surfactant on calcium carbonite at 25 °C.

Table 6.3: Adsorption isotherm parameters of SDS on calcium carbonite for DPD and experimental.

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>DPD</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$1/KQ_0$ (g/L)</td>
<td>62.601</td>
<td>117.58</td>
</tr>
<tr>
<td></td>
<td>$1/Q_0$ (g/mg)</td>
<td>0.0782</td>
<td>0.0648</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8236</td>
<td>0.9059</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg/g)</td>
<td>0.1533</td>
<td>0.0321</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.5400</td>
<td>0.7369</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9386</td>
<td>0.9569</td>
</tr>
</tbody>
</table>


6.4 Conclusion

Dissipative particle dynamics has been used to determine the CMC values of sodium alkyl sulfate (SDS) surfactant. We have investigated the effect of temperature and NaCl salts on the formation of micellar aggregates. We observed salt to play an important role in increasing micelles size and reduced the free surfactants concentrations on the systems. The effects of salt on the CMC values were found to be consistent with experimental data. The effects of temperature on the CMC values were not able to find a minimum in the CMC around 25 °C comparing with experimental data because of cores grained model cannot capture the minimum value as it was discussed before. The degree of counterions associated $\alpha$ results from the equation (6.5) are insensitive to temperature but it increased with increasing salt concentration which is in good agreement with literature values.

The adsorption of SDS surfactants onto calcium carbonate from aqueous solutions at 25 °C was studied by dissipative particle dynamics and compared with experimental data from ref. [152]. According to the results obtained, the adsorption of SDS surfactants onto calcium carbonate surface increased until the maximum adsorption reached with increasing in the surfactant concentration. Adsorption parameters for the Langmuir, and Freundlich isotherms models were determined by using DPD data. Simulation results show that the Freundlich isotherm models were well fitted better than Langmuir model of adsorption on calcium carbonate surface with a good agreement with the experimental fitting parameters.

To the best of our knowledge, these are the first dissipative particle dynamics simulations of studying the effect of temperature and NaCl salts on CMC as well as the adsorption of SDS surfactants onto calcium carbonate surface.
Chapter 7 Phase behavior of a water-oil-surfactant study of nonionic surfactant by DPD

7.1 Introduction

Microemulsions consist of a hydrophilic component, usually water, a hydrophobic component, e.g. oil or alkane, and an amphiphilic component, a surfactant. The surfactants arrange themselves at the interface between the aqueous phase and the organic phase due to their chemical structure. They form a monomolecular surfactant layer. With addition more surfactant, the overall system can behave differently depending on the conditions such as temperature, pressure, salts and type of surfactant. Micelles, liquid crystals, or a microemulsion can be formed based on the conditions. Microemulsions are optically isotropic, transparent oil-water dispersions of uniform round drops consisting of oil or water in the corresponding continuous phase. Microemulsions are thermodynamically stable and thus differ from macroemulsions on the basis of two criteria. In contrast to microemulsions, the macroemulsions are not thermodynamically stable. In addition, the aggregate size of the macroemulsion is between one and 10 μm clearly above the aggregate size of the microemulsion of 10 nm. The fields of application for microemulsions are versatile. In addition to cosmetics and personal care, detergents and dishwashers are major fields of application. The microemulsion enables a more effective and optimized use of surfactants with accurate knowledge of the corresponding phase behavior. The reduction in surfactant consumption e.g. of detergents and dishwashing agents, as well as the replacement of harmful ones with environmentally compatible and biodegradable surfactants lead both to the improvement and protection of our waters as well as to the reduction of the production costs. Further important applications of microemulsions are the size of their stable microstructures in nanotechnology. The production of foams (nanofoams) is another industrial application whose excellent insulation
properties could contribute to the reduction of greenhouse gases. In medicine, water-insoluble active substances can be packaged in self-organized nanostructures, such as microemulsions and vesicles, and thus transported into desired organs and cells. Food technology also offers a great challenge for stable emulsions and microemulsions. Further, microemulsions nowadays find versatile applications e.g. in the area of Enhance Oil Recovery (EOR) [162]–[164].

Figure 7.1 shows binary phase behavior in ternary microemulsion systems formed with nonionic surfactants. There are different types of microemulsions: water-in-oil or (W/O) microemulsions with oil as a continuous phase. Oil-in-water or (O/W) microemulsions with water as a continuous phase. Bicontinuous microemulsions with simultaneous continuous phases of water and oil. The structure of the microemulsion depends strongly on composition of oil and water. At low oil concentration, discrete oil droplets are dispersed in the continuous water phase. This is referred to as an oil-in-water microemulsion. A monolayer of surfactant molecules surrounds these oil droplets. In the case of W/O microemulsion, the oil is the continuous phase. The water droplets are separated from the oil phase by surfactant monolayers. Inverse micelles are formed. Other (e.g., lamellar, hexagonal, or cubic) structures also occur in the single-phase regions. In many cases, the transition from water-rich to oil-rich microemulsion proceeds continuously. In the single-phase region, it is possible by adding oil to the water phase with a constant surfactant content to form microemulsion phase. At 0.5 weigh friction region, it is possibly by changing the temperature between W/O and O/W phases without passing through a phase structure transition. Depending on the amount of the concentration (water and oil), temperature, and time, the microemulsion appears as a collection of larger and smaller drops or domains of oil in water until it comes to the formation of a structure in approximately the same proportions of oil and water in which both liquids simultaneously act as continuous phases side by
side. The water and oil areas as well as the surfactant, which is predominantly at the interface between oil and water, together form a bicontinuous microemulsion phase. The bicontinuous microemulsion can be compared with a sponge. The sponge body represents the water phase and the air in the sponge the oil phase. On the surface of the sponge are the surfactant molecules, which separate the water and the oil phase from each other. The structure of the sponge corresponds very well to the actual structure of a bicontinuous microemulsion. The lower temperature (\(T_L\)) and upper temperature (\(T_U\)) are the phase formation of water-in-oil (W/O) and oil in water (O/W) temperatures respectively. \(T_m\) is the mean temperature at which the microemulsion is formed and this temperature is also referred to as phase inversion temperature (PIT).

The phase behavior of water/alkane/ nonionic alkylpolyglycolether surfactants (C\(_i\)E\(_j\)) systems have been investigated with numerous experimental studies [27], [28], [30], [165]–[169]. The surfactants structure of the microemulsions as function of temperature has not been explored in detail by dissipative particles dynamics. The aim of this chapter is to investigate the phase behavior of C\(_8\)E\(_4\) surfactant in water /octane system by dissipative particles dynamics. In this work, C\(_8\)E\(_4\) /water/octane systems at constant concentration of surfactant with different temperature are simulated to carry out structural investigations and to evaluate \(T_L\), \(T_U\), and \(T_m\).
Figure 7.1: Different microstructures of nonionic surfactants with the mass fraction of the oil in the binary mixture of oil and water at constant surfactants. (a) Phase prism of a ternary mixture at constant surfactants. (b) Schematic phase diagram [26].
7.2 Methodology

For coarse-grained beads on the DPD, the C₈E₄ surfactant molecule composed of two tails (T) group and 4 heads (E) group as seen on Figure 7.2. For simplicity, Water (W) and octane (O) were treated as a separate DPD bead. For the DPD phase calculations, a total of 42000 DPD beads were placed in a cubic box (20 x 20 x 20 DPD unit) and calculated at different temperatures with fixed surfactant concentrations under periodic boundary conditions. The density $\rho (\rho = N / V$, number of DPD particles per unit volume) is set to 3 and the coefficient of friction is 4.5. The time step size was 0.02 DPD time units in all simulations. The spring constant was set to 4. The interaction parameters between the T, H, O and W DPD beads were calculated according to the methods described in Chapter 5 without rescaling the $\chi_{\infty}^{ij}$ parameters for simplicity. Table 7.1 the calculation of $\chi_{\infty}^{ij}$ parameters are shown of ethylene oxide (head group) against water (W), octane (O), and tail (T) beads from the infinite dilution activity coefficient. The temperature-dependent $\chi_{\infty}^{ij}$ values as well as the resulting DPD interaction parameters $a_{ij}$ for the W, O, T and H beads were calculated. The values of interaction parameters $a_{ij}$ determined from $\chi_{\infty}^{ij}$ are summarized in Table 7.2.
Figure 7.2: Mesomolecular model: the coarse-grained of surfactant is represented as 2 Tail (T) beads and 4 head (H) beads. Octane is represented by 1 (O) bead. Water (W) bead has 1 water molecule. Water: green, Octane: red, Tail: blue, and Head: pink.

Table 7.1: The calculation of $\chi_i^\infty$ parameters of ethylene oxide (head group) against water (W), octane (O), and tail (T) beads from the infinite dilution activity coefficient.

<table>
<thead>
<tr>
<th>Bead i</th>
<th>Bead j</th>
<th>$\ln(\chi_i^\infty)$</th>
<th>$v_j / v_i$</th>
<th>$\chi_i^\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>H</td>
<td>0.0021 t(°C)-0.0178</td>
<td>3.18</td>
<td>0.0021 t(°C)+0.4525</td>
</tr>
<tr>
<td>H</td>
<td>O</td>
<td>-0.0139 t(°C)+7.5099</td>
<td>2.33</td>
<td>-0.0139 t(°C)+7.786</td>
</tr>
<tr>
<td>H</td>
<td>T</td>
<td>-0.0138 t(°C)-7.4405</td>
<td>1.47</td>
<td>-0.0138 t(°C)+7.5069</td>
</tr>
</tbody>
</table>

Table 7.2: Interaction parameters $a_{ij}$.

<table>
<thead>
<tr>
<th>$a_{ij}$</th>
<th>O (C8)</th>
<th>W</th>
<th>T (C4)</th>
<th>H (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (C8)</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>-0.0485 t(°C)+52.251</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (C4)</td>
<td>0.00003 t(°C)+25.703</td>
<td>-0.0577 t(°C)+50.715</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>H (E)</td>
<td>-0.0485 t(°C)+52.251</td>
<td>0.0072 t(°C)+26.584</td>
<td>-0.0484 t(°C)+51.274</td>
<td>25</td>
</tr>
</tbody>
</table>
7.3 Results and Discussion

The dissipative particle dynamics (DPD) are determined phase transition of $C_8E_4$ surfactant in water/octane system as seen in Figure 7.3. There are five different phase structure depending on the oil/water volume fractions and temperature: spherical (inverse spherical) micelles, cylindrical (inverse cylindrical), hexagonal (inverse hexagonal), lamellar, and bicontinuous phase. We denote the volume fractions of water, oil and surfactant as $\varphi_W$, $\varphi_O$ and $\varphi_s$ respectively. The volume ratio of oil in the mixture of oil and water is:

$$\alpha_O = \frac{\varphi_O}{\varphi_W + \varphi_O} \quad (7.1)$$

The respective volume ratio of surfactant is fixed at 0.1 in the mixture and is given by:

$$\alpha_S = \frac{\varphi_S}{\varphi_W + \varphi_O + \varphi_S} \quad (7.2)$$

Micelles agglomerate into cylindrical micellar clusters which in turn agglomerate into hexagonal, or lamellar structures by changing the volume ratio of oil in the mixture. The biocontinuous phase appears between the lamellar phases. As an example, the results of the system of $C_8E_4$ surfactant in water/octane system at 60 °C are presented in Figure 7.4 and Figure 7.5 to visualize the structures transition as function of volume fraction. Figure 7.4 depicts the structures of the volume fraction between 0.1 and 0.5 and Figure 7.5 shows the structures of the volume fraction between 0.5 and 0.9. The structures transitions are divided into two figures for same temperature because we want to make the structure visualization clear for normal and inverse phases. Figure 7.4 and Figure 7.5 show seven characteristic regions for phases structures transition at 60 °C. At volume fraction lower than 0.2 of octane a spherical micellar phase has been found, which changes to a
cylindrical phase region between 0.2 and 0.3. At higher volume fraction the lamellar phase is formed until the volume fraction reaches 0.65, where the lamellar phase changes to the inverse hexagonal phase. The bicontinuous phase appears between the lamellar phase. The volume fraction increases from 0.7 to 0.8 leads to the formation of inverse cylindrical and a more increasing of volume fraction is found the formation of inverse spherical phase with more structured micelles.

One of more complex parameters on the formation of the microemulsions can be found in the PIT phase diagram (phase inversion temperature). The phase inversion temperature describes the reversal point of the phase formation from the O / W to the O / W type and vice versa. In the region of this point the individual phases are separated. For nonionic surfactants, phase transitions can occur by raising the temperature. This kind of transition has been shown in Figure 7.3. The formation of microemulsion system depends on different parameters such as temperature, oil to water ratio, surfactant concentration, and the type of surfactant. We keep all parameters constant except temperature to study the temperature effects. We have used volume fraction of surfactant $\alpha_S=0.1$ and volume fraction of oil $\alpha_O=0.5$ by changing the temperature as seen in Figure 7.6. We know that from Figure 7.3 the formation of microemulsion phase is between 20-60 °C at 0.5 volume fraction of oil. To determine the lower temperature ($T_L$), we increase the 20 °C temperature by 1 °C until we reach to microemulsion phase structure. On other hand, the 60 °C temperature decrease by 1 °C until microemulsion phase structure appears to determine the upper temperature ($T_U$). Figure 7.6 shows that the lower temperature ($T_L$) and upper temperature ($T_U$) are equal 21 °C and 52 °C respectively. The lower temperature and upper temperature are described the range of microemulsion phase. From these two temperature ($T_L$ and $T_U$), the mean temperature is defined [28], [30], [167]:
The results of the mean temperature ($T_m$) is 36.5 °C. Experimentally, it has been shown that for the C$_8$E$_4$ nonionic surfactant $T_L$, $T_U$, and $T_m$ are 35.25 °C, 47.95 °C, and 41.7 °C, respectively [169]. The DPD simulation results of the lower temperature ($T_L$), upper temperature ($T_U$), and mean temperature ($T_m$) are in fair agreement with experimentally results.

Figure 7.3: DPD phase structures transition with changing volume fraction and temperature at fixing the concentration of surfactants. Blue: spherical and inverse spherical micelles, red: cylindrical and inverse cylindrical, green: hexagonal and inverse hexagonal, yellow: lamellar, gray: bicontinuous phase.
Figure 7.4: Snapshots of phase structures transition from 0.1 to 0.5 volume fraction of oil ($\alpha_O$) at fixing the temperature at 60 °C. (The octane beads is removed for clarity)
Figure 7.5: Snapshots of phase structures transition from 0.5 to 0.9 volume fraction of oil ($\alpha_O$) at fixing the temperature at 60 °C (The water beads is removed for clarity)
Figure 7.6: Snapshots of phase structures transition between 20 °C and 60 °C at 0.5 volume fraction. (for bicontinuous phases the octane beads is removed for clarity)
7.4 Conclusion

A great advantage of computer simulations is that they provide an immediate picture of simulation after performing the calculations. Visualized results of the calculations allow completely new understanding at the molecular level of the phase structural transition and investigation of complicated structures and phases. Several DPD calculations were carried out at different simulation conditions with the C₈E₄ surfactant for water/octane model. As the analyzes of the simulation results, we are able to find the phase transition with changing the fraction volume of oil and temperature and we have an important structural details of individual phases which sometimes are not accessible by experimental methods. The phase structure changes of the surfactants are important for practical application in industry. Therefore, a more investigation look at the phase transition provides useful information by studying the different parameters such as oil to water ratio, surfactant concentration, type of oil, and the type of surfactant. The DPD results of the lower temperature, upper temperature, and mean temperature are shown reasonable agreement with experimentally results. These results suggest that a DPD can provide a more details about structural transitions of different surfactant model to show a better understanding of the structural transitions within phase regions.
Chapter 8 Experimental study of the interfacial tension for water/octane/surfactant system

8.1 Introduction

Surfactants are amphiphilic organic compounds which lower interfacial tension. They have both a hydrophobic group and a hydrophilic group. Depending on the nature of the hydrophilic group, anionic, cationic, zwitterionic, or nonionic surfactants are classified. The contact surface of two immiscible phases (e.g. water and oil) is generally referred as an interface. We can introduce an interface as a plane of contact between two phases. If two immiscible liquids are in contact with each other, a transition region is formed in which the composition of the first phase changes into the composition of the second phase. This plane has molecular dimensions and is known as the boundary phase. Adding Surfactants to a liquid two-phase system, which is soluble in one or both phases lead to an accumulation in the boundary phase. The Surfactants strive to establish a thermodynamic equilibrium between the surrounding phase and the boundary surface. This process typically consists of two steps: diffusion of the molecules within the solution phase as well as from the homogeneous phase to the boundary phase and adsorption of the molecules at the boundary surface. If the concentration of the surfactants is sufficiently high so that the surface is completely occupied, micelles are formed. These are spherical structures that interior consists of the hydrophobic radicals of the surfactants. The concentration from which micelle formation occurs is referred to as critical micellization concentration (CMC).

An important system for interfacial tension measurement is the system of alkanes/water/surfactants and it has many applications in the petroleum, natural gas, and
petrochemical industries. The experimental researches have been conducted to study the interface of water/hydrocarbon/surfactant systems are few in the literature. Rehfeld [130] investigated interfacial tension of various hydrocarbon-water interfaces for SDS surfactant to study the influence of hydrocarbon on the critical micelle concentration and the adsorption isotherms. The results showed that the cmc and area per molecule increased with increasing the chime of hydrocarbon. The effect of the oil chain length, effect of salinity, effect of concentration of surfactant on interfacial tension between the alkanes and water studied by Ruckenstein and Rao [170]. Their researches presented that interfacial tension decreased with increasing of surfactant concentration, the oil chain length, and salinity. Badakhshan and Bakes [171] examined the influence of temperature and surfactant concentration on interfacial tension of saline water and hydrocarbon systems. Liggieri and co-works [172] investigated of a hexane/water/Triton X-100 systems to measure the interfacial tension. The results show that the Freundlich isotherm describes the experimental data better than Langmuir model. The researches by Al-Sahhaf et al. [134] demonstrated the influence of temperature, pressure, salinity, and surfactant concentration on the interfacial tension of the octane-water system. The interfacial tension was found to be linearly dependent on pressure and temperature as well as the dependence of the IFT on salt concentration was found to be linear in the range of concentrations considered.

In this chapter, we perform a series of experimental study on the interfacial tension of surfactants with different structures at the octane/water interface to study the effect of different head group and tail group of surfactants. Five surfactants with different types of head group and the same length of hydrocarbon tail (Sodium dodecyl sulfate SDS, Lithium dodecyl sulfate (LDS) dodecyltrimethylamine oxide DDAO, Dodecyltrimethylammonium chloride DTAC and Dodecyltrimethylammonium bromide DTAB) are selected for studying the head group effect at
the interface. In addition, Cetyltrimethylammonium bromide CTAB and DTAB are selected for studying the tail group effect at the interface. The adsorption of Triton X-100 surfactant on water/octane interface is investigated for Triton X-100 surfactant to calculate surface concentrations and area per molecule at the interface by use of the Gibbs equation. SDS (ionic) and Triton X-100 (nonionic) surfactants are chosen for water/octane system to exam the role of sodium chloride (NaCl), calcium chloride (CaCl₂), and temperature at interface for one surfactant concentration and varying concentrations of salt or temperature. (note: part of discussion for head group effect and salts effect are repeated from chapter 5 for comparison and completeness)

8.2 Experimental method

The surfactants were used for study the interfacial tension of water/octane/surfactants systems are summarized in Table 8.1. The other materials were used for study the interfacial tension: oil (octane ≥ 99% purity), salts (NaCl ≥ 99% purity, and CaCl₂ ≥ 99% purity ), and deionize water. Oil, and salts were supplied by Sigma Aldrich.

The method of the pendent drop was used to determine interfacial tensions. The measuring principle of pendant drop method is based on the detection of the geometrical shape of a pendant drop of a capillary. The basic design of the measuring station is shown in Figure 8.1. Attension Theta Optical Tensiometer equipment was used to perform a complete IFT measurements. The drop image was taken by a Digital Video Camera (DVC) with zoom or a high-speed DVC with zoom. A specially developed software enables automatic storage of a digitized drop image at any time, as well as simultaneous automatic control of the dosing unit. The video recorder, which is
connected between the DVC camera and the computer, enables fast online image storage. The individual images are then accessible to a later evaluation. The sample stage can be carefully moved in all 3 dimensions. The liquid dispenser is used for placing a drop onto a cuvette and the liquid dispenser holder has motor to allow liquid dispenser move in different direction.

Table 8.1: Name and the Structure of Surfactants

<table>
<thead>
<tr>
<th>Name of Surfactant (Abbreviation name)</th>
<th>Type (Provider)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulfate (SDS) Anionic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium dodecyl sulfate (LDS) Anionic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyldimethylamine oxide (DDAO) Zwitterionic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyltrimethylammonium bromide (DTAB) Cationic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecyltrimethylammonium chloride (DTAC) Cationic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetyl trimethylammonium bromide (CTAB) Cationic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triton X-100 nonionic (Sigma Aldrich)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For IFT measurement, the sample or mixture of water/surfactants was filled into the cuvette. The cuvette was placed in the measuring cell. The time required to reach the thermal equilibrium depends on the system used and on the accuracy requirements regarding the interfacial tension. For temperature study, the temperature constancy is controlled by the temperature program with computer connected with thermocouple in the sample. Once the desired temperature has been reached, the measurement was taken.

Figure 8.2 shows a pending drop example. The droplet is irradiated with a light beam parallel to the optical axis. If the refractive indices of the two phases markedly different, the light from the droplet and the surrounding medium is differently broken, and the contour of the drop becomes visible. The boundary surface tension influences the shape and the size of a droplet in such a way that the droplet is formed with an axially symmetrical profile.
A droplet suspended from a capillary has a certain geometric shape which depends on the interfacial tension $\gamma$ and the density difference $\Delta \rho$ to the surrounding medium. The theoretical calculation is characterized by the Young-Laplace-equation:

$$\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$  \hspace{1cm} (8.1)

$\Delta P$ is the pressure difference at the curved boundary surface, $R_1$ and $R_1$ are the main radii of curvature at a certain point of the axisymmetric droplet surface. Due to its axial symmetry, the drop can be represented by the coordinates $x (s)$ and $z (s)$ by $s$ as arc length from the apex ($x = 0$; $z = 0$). The boundary surface tension can thus be determined from the drop shape. For this purpose, the radii of curvature must be determined by means of tangents at different points of the drop profile and the angle which occurs between the x-axis and the tangents. The principal radii of curvature $R_1$ and $R_2$ are given by:

$$R_1 = \frac{ds}{d\theta}$$  \hspace{1cm} (8.2)

$$R_2 = \frac{x}{\sin \theta}$$  \hspace{1cm} (8.3)

Due to the axial symmetry of the droplet, both radii of curvature on the apex are the same ($R_1 = R_1 = R$) and the pressure difference on the apex $\Delta P$ is given by:
\[ \Delta P = \frac{2\gamma}{R} \]  

(8.4)

Without external force the drop would assume a ball shape with the average curvature \( 1 / R \).
Gravitation leads to the deformation of the droplet and the pressure difference in equation (8.4) is a linear function of the coordinate:

\[ \Delta P = \frac{2\gamma}{R} - g\Delta \rho z \]  

(8.5)

Where \( g \) is acceleration due to gravity and \( \Delta \rho \) is density different. Substituting equation ((8.2)), equation (8.3), and equation (8.5) in equation (8.1) yields:

\[ \frac{ds}{d\phi} = \frac{2\gamma}{R} - \frac{g\Delta \rho z}{\gamma} \sin \phi \]  

(8.6)

When the density difference \( \Delta \rho \) is known, the interfacial tension \( \gamma \) for a given drop profile can be determined by solving the droplet profile differential equation system (8.6). The numerical integration system of differential equations has been solved by the program package coming with Attension Theta Optical Tensiometer for evaluation of the interfacial tension measurements.
Figure 8.2: Shape of a dropping drop taken from a DVC camera.

8.3 Results and Discussion

8.3.1 Effect of Head and Tail Group of Surfactant

The pendant drop method was used for determining the interfacial tension experimentally. The interfacial tension is obtained as a function of three concentration values for SDS, DTAB, and DDAO surfactants to compare the efficiency of these surfactant and study the effect of change the head group at interface if we know that SDS, DTAB, and DDAO surfactants have same tail and different head group. Figure 8.3 shows the steady state interfacial tension of the interface between water or aqueous surfactant solution in octane as a function of surfactant concentration. A reduction in the interfacial tension with increasing surfactant concentration can be observed for all type. For DDAO surfactant, at concentration about 2.2 mM of the surfactant concentration was
scarcely observed a variation in the interfacial tension with a further increase of concentration. The CMC of DDAO is 2.1 mM [129], therefore the expectations are confirmed in this case the saturation concentration of the phase boundary is reached, and the interfacial tension will not be influenced. The fact that the CMC concentration of DDAO is lower than the CMC concentration of SDS (8.2 mM) [130], [131] and DTAB (16.4 mM) [132], [133] and this is explaining the linear decrease of the interfacial tension as function of concentration for SDS and DTAB surfactants. The differences values in interfacial tension between ionic (SDS), cationic (DTAB), and zwitterionic (DDAO) surfactants can be justified by the electric charge of the head group. In other words, the head group can play an important role in the efficiency of the surfactants, means that the electrical repulsion changes the performance of surfactant on the boundary surface. It can be seen that the efficiency of these three surfactants follows the order of DDAO˃SDS˃DTAB based on the decreasing capability of interfacial tension.

The effects of counter-ions of surfactants on the interfacial tension for water/octane systems have been investigated. Figure 8.4 shows the interfacial tension as a function of surfactant concentration for SDS, LDS, DTAB, and DTAC. The investigated systems are two anionic surfactants (SDS, and LDS) and two cationic surfactants (DTAB, and DTAC). The counter-ions of anionic surfactants are Na⁺ and Li⁺ for SDS and LDS respectively. In addition, the counter-ions of cationic surfactants are Br⁻ and Cl⁻ for DTAB, and DTAC respectively. Changing the counter-ions of anionic surfactants does not influence the interfacial tension of water/octane system. On other hand, the cationic surfactants show that a small reduction into the interfacial tension for DTAB system when it is compared with DTAC system. This means that there is a small effect of the Br⁻ ions over the Cl⁻ ions into the adsorption of surfactant to interface.
Cetyltrimethylammonium bromide (CTAB) and Dodecyltrimethylammonium bromide (DTAB) are presented to study the effect of tail group at the interfacial tension of water/octane system by changing the length of tail group from 12 carbons for DTAB to 16 carbons for CTAB. The effect of increasing the chain length of surfactants on the interfacial tension is given in Figure 8.5. The results show that long tails (CTAB) reduce the interfacial tension more than short tail (DTAB). Increasing the tail length makes the surfactants more efficient. An increase in the size of tail length results in an increase the efficiency of adsorption of a surfactant at the interface of water/octane system a consequent decrease in interfacial tension.

![Figure 8.3](image-url)

Figure 8.3: The results of interfacial tension as a function of surfactants concentration at T = 25 °C for three different surfactants (SDS, DTAB, and DDAO) at the interface of water octane system.
Figure 8.4: The results of interfacial tension as a function of surfactants concentration at $T = 25\, ^\circ C$ for four different surfactants (SDS, LDS, DTAB, and DTAC) at the interface of water octane system.

Figure 8.5: The results of interfacial tension as a function of surfactants concentration at $T = 25\, ^\circ C$ for two different surfactants (DTAB, and CTAB) at the interface of water octane system.
8.3.2 Adsorption of Triton X-100 surfactant on water/octane interface

Measurement of interfacial tension of water/octane system with nonionic surfactant (Triton X-100) have been investigated. The measured values of interfacial tension are shown in Figure 8.6. As the surfactant concentration increases, the interracial tension decreases, and becomes constant at higher concentration because it reaches to CMC. The data were analyzed with Gibbs adsorption equation to determine the surface excess concentration ($\Gamma$) at the interface for water/octane/Triton X-100 system [7]:

$$
\Gamma = \frac{1}{2.303RT} \left( \frac{\partial \gamma}{\partial C} \right)_T
$$

Where R is gas constant, T is temperature, $\gamma$ is interfacial tension, and $C$ is surfactant concentration. The value of the surface excess concentration was determined from the slope of the linear region in a plot of IFT versus surfactant concentration. This analysis provides the values of the surface excess concentration ($\Gamma$) equal to $1.05 \times 10^{-10}$ mol cm$^{-2}$. The surface excess concentration value is slightly lower value $2.83 \times 10^{-10}$ mol cm$^{-2}$ calculated using data reported for water/air system of Triton X-100 versus by Szymczyk and Janczuk [173]. This difference agrees with the findings of Rehfeld [130] and Murphy [174] that is a slight decrease in the surface excess concentration of hydrocarbon compared with air.
Figure 8.6: The results of interfacial tension as a function of surfactants concentration at T = 25 °C for Triton X-100 surfactant at the interface of water octane system.

8.3.3 Effect of Salts and Temperature at Interface

Sodium dodecyl sulfate SDS surfactant was chosen as ionic surfactant to study the effects of salts and temperature on the IFT by fixing the concentration of SDS at 0.35mM and varying the other parameters as seen on Figure 8.7. The linear decrease of the interfacial tension is observed as increasing the temperature. Al-Sahhaf et al., reported the same dependence on temperature for water/SDS/octane systems [134]. The interfacial tension decreases with increasing in salts concentration of the aqueous phase with linear dependent for both salts. The CaCl₂ solutions have the higher reduction on the IFT values compared to NaCl solutions. With increasing the salts
concentration, it helps gradually transferred the surfactants to the interface, as a results decrease in IFT values. On other words, the effect of salts to the interface is accelerate the diffusion of surfactant from the bulk solution to the interface [135].

Triton X-100 surfactant was selected as nonionic surfactant to study the effects of salts and temperature on the IFT by fixing the concentration of surfactant at 0.16 mM and varying the other parameters as seen on Figure 8.8. Same as SDS surfactant, An increase in temperature results in a decrease in the interfacial tension. On the other hand, the interfacial tension increased as salt was added at constant concentration of surfactant. From the results, the Triton X-100 surfactants are not significantly affected by the salts. We can conclude that there was no interaction between the salt and the Triton X-100 nonionic surfactant.

![Figure 8.7: The results of interfacial tension of water / octane system as a function of salts concentration (NaCl, and CaCl2) and temperature for fixed SDS surfactants at 0.35mM. (the IFT values for salts at T = 25 °C).](image-url)

---

**Figure 8.7:** The results of interfacial tension of water / octane system as a function of salts concentration (NaCl, and CaCl2) and temperature for fixed SDS surfactants at 0.35mM. (the IFT values for salts at T = 25 °C).
Figure 8.8: The results of interfacial tension of water / octane system as a function of salts concentration (NaCl, and CaCl2) and temperature for fixed Triton X-100 surfactant at 0.16 mM. (the IFT values for salts at T = 25 °C).

8.4 Conclusion

From the results reported in this chapter, it can be concluded that:

- It was selected three surfactants that had the same hydrocarbon tail length but different head groups to study the effect of surfactant head group on the interfacial tension. The different surfactants were the zwitterionic DDAO, the anionic SDS, and the cationic DTAB. The values of the interfacial tension decrease in order DDAO>SDS>DTAB. The effect of head group indicates the following relations between the structure of the surfactant and its efficiency of adsorption at the interfaces.

- Changing the counter-ions of anionic surfactants does not influence the interfacial tension but the cationic surfactants show that a small reduction into the interfacial tension.
- Changing in the length of the tail group of straight chain of cationic surfactants from 12 to 16 carbon atoms appears to increase the efficiency of surfactant and enhance the adsorption of the surfactants at the interface to reduce IFT.

- The Gibbs adsorption model was used to model the data for the interfacial tension of Triton X-100 surfactants. Equation (8.7) was used to determine the surface excess concentration \( (\Gamma) \) of Triton X-100 at the interface of water/octane system and the value was \( 1.13 \times 10^{-10} \) mol cm\(^{-2}\) at 25 °C.

- For both ionic and nonionic surfactants, temperature increase causes a decrease in the interfacial tension.

- The Triton X-100 surfactants are not significantly affected by the salts. However, appearing the salts in water/octane systems with SDS surfactant causes a dramatic decrease in the interfacial tension. In addition, it has been found that the CaCl\(_2\) salts are more effective than the NaCl salts.
Chapter 9 Conclusion and Future Work

9.1 Conclusion

In this work, a mesoscopic simulation method (dissipative particle dynamics) for the calculation of water/oil/surfactants systems was presented and evaluated. The DPD method is a simulation technique, which was originally developed for the calculation of polymer systems. The determination of the interaction parameters for DPD beads was an unsolved problem with the application of this method especially for ionic system. A method for the determination of the interaction parameters for the DPD interaction parameters was discussed in chapter 3. For these calculations, a technique has been proposed that represents a combination of the Flory-Huggins theory and COSMO-RS. According to this method, the interactions between the DPD beads were determined by the calculations of the infinite dilution activity coefficient.

In chapter 4, Interfacial tension (IFT) between water and alkane liquid phases has been studied by dissipative particle dynamics (DPD) simulations. The DPD interaction parameters as a function of temperature are estimated using the COSMO-RS model (Conductor-like Screening Model for Real Solvents) through the Flory-Huggins interaction parameter matching the infinite dilution activity coefficient to estimate the repulsive interaction between the unlike beads. The computed interfacial tension agrees very well with the experimental value for all temperatures. The proposed method for determining DPD interactions provides the basis to estimate interactions for complex systems such as nonionic and ionic surfactant systems.

In chapter 5, dissipative particle dynamic (DPD) simulations were performed to study the interfacial properties such as interfacial tension, area compressibility, stress profile, and
conformation of surfactant at water/octane interface. Three surfactants with different head groups and same alkyl tail, SDS, DTAB, and DDAO were selected to study the effect of head group structure. The efficiency of surfactants from DPD follows the same order of experimental results DDAO>SDS>DTAB. The DDAO surfactant is more ordered at the interface and the high compressible area which indicates more highly packed monolayer. The effect of salts and temperature at water/octane/SDS surfactants at interface were investigated. Both experiment and DPD showed a reduction in IFT with increase in temperature or salt concentration. The addition of salts in the systems stretched and ordered the SDS surfactant more at the interface, as results, the area compressibility increased. The temperature shows a little effect on the orientation of the SDS surfactant at the interface and the area compressibility increased with increasing temperature. The interfacial tension was investigated by experiment using pendant drop method and the IFT results of DPD agree qualitatively with experimental measurement.

We have studied critical micelles concentration (CMC) of SDS surfactant using dissipative particle dynamics in chapter 6. The effects of temperature and NaCl salt on the CMC and the number of free surfactant after reaching the equilibrium have been investigated. The effects of salt on the CMC values were found to be consistent with experimental data. The effects of temperature on the CMC values were not able to find a minimum in the CMC around 25 °C comparing with experimental data because of cores grained model cannot capture the minimum value. In addition, Adsorption of SDS surfactants onto calcium carbonate was investigated as a function of concentration of surfactant at constant temperature by dissipative particle dynamics. In this case two adsorption isotherms were used; Freundlich and Langmuir isotherms. Simulation results show that the Freundlich isotherm models were well fitted better than Langmuir model of adsorption on calcium carbonate surface with a good agreement with the experimental fitting parameters.
In chapter 7, the phase behavior of C₈E₄ surfactant has been investigated by changing the volume ratio of oil/water and temperature by using dissipative particle dynamics study. We are able to find the phase transition such as spherical (inverse spherical) micelles, cylindrical (inverse cylindrical), hexagonal (inverse hexagonal), lamellar, and bicontinuous phase with changing these conditions. Visualized phase transition and have structural details of individual phases are important for practical application in industry which sometimes are not accessible by experimental methods.

In chapter 8, a series of experimental study were performed to study the effect of different head group and tail group of surfactants onto the interfacial tension of octane/water interface. In addition, the Gibbs-Langmuir model was used to model the data for the interfacial tension for Triton X-100 surfactant on water/octane interface. Moreover, the effect of sodium chloride (NaCl), calcium chloride (CaCl₂), and temperature for one surfactant concentration and varying concentrations of salt or temperature were investigated on water/octane interface.

9.2 Future Work

9.2.1 Interfacial tension

The combination of the simulations results, with experimental data which can be performed in our lab at KFUPM could give us a unique approach to understand the water/oil or water/oil/surfactant interfacial tension from simulation and experimental point of view.

The interfacial tension of binary and ternary systems of organic compound and water is a theoretical and practical interest. The availability of interfacial tension data of these systems in literature is a paucity. Dissipative particle dynamics simulations can be a powerful tool in the
further development of interfacial tension of organic compound and water over a wide range of temperature. This investigation will be similarly performed like water/alkane systems in chapter 4.

Research in chapter 5 and 8 enhanced the understanding of the effects of surfactants on the interfacial tension of octane. All the interfacial tensions in this thesis were measured for water/octane system. Some of these experiments or simulations can be repeated for different type of hydrocarbons encountered at to evaluate any changes in behavior. The number of surfactants considered in this thesis can be increased to include fluorosurfactants family. The interfacial tension of these surfactants can be determined in future work and compared the results with dissipative particle dynamics. The effect for salts has been studied for SDS and Triton X-100 (only experimental). It is recommended to investigate the interfacial tension of different surfactant with salts. It could be that the magnitude of surfactant adsorption at interface might depend on the strength between the salts ions and the head group of the surfactant. This can be verified by studying the effects of surfactants with varying head group. To extend the findings and understanding developed from interfacial tension work, the effect of pH can be studied which has not been considered in this thesis. A complex model such as mixture of surfactants could be developed for studying the interfacial tension.

9.2.2 Critical micelles concentration (CMC)

As shown in chapters 6, CMC of SDS surfactant can be predicted by dissipative particle dynamics. Thus, it is very interesting to extend the DPD simulation in this work to different single surfactant solutions, especially for cationic zwitterionic, and nonionic surfactants. Future works should be done in order to verify whether the type of surfactants will affect the value of CMC as...
compared with experiments values. In practical applications, CMC of mixed surfactant solutions are very important. The results of single surfactant solutions will help to establish a basis to extend to mixed surfactant solutions. From the investigations of salts effect on CMC value, dissipative particle dynamics based electrolyte model could be developed for electrolytes, especially for organic electrolyte solutions or ionic liquids.

9.2.3 Adsorption of surfactants onto surface

Throughout the research of adsorption of SDS surfactant onto calcium carbonate has been to investigate the importance of molecular interactions with surface. Many experimental have been studied different type of surfactant for the surface phenomena occurring in liquid-solid system. To the best of our knowledge, A studies by applying dissipative particle dynamics to illustrate the applicability to aqueous solution of surfactants adsorption onto solid surface are not yet reported in the literature. A lot of unsolved questions remain regarding not only from simulation point of view, but also the impact on more complex systems. Consequently, the following areas of research are suggested to be taken into consideration.

1. Explore the influence of different type of surfactants has on adsorption studies such as surfactant containing long tail, long head, or different head group (cationic, zwitterionic, and ionic)
2. Determine the effect of different solid surface in the adsorbed of surfactants
3. Expand upon the influence of solution conditions for the adsorption study (salts, temperature, adding oil).
Bibliography


B. C. Stephenson, K. Beers, and D. Blankschtein, “Complementary use of simulations and


[64] Y. Li, Y. Guo, M. Bao, and X. Gao, “Investigation of interfacial and structural properties


[114] M. G. Freire, S. P. M. Ventura, L. M. N. B. F. Santos, I. M. Marrucho, and J. A. P. Coutinho,


[145] I. M. Umlong and K. Ismail, “Micellization behaviour of sodium dodecylsulfate and dioctyl


[159] S. S. Berr and R. R. M. Jones, “Effect of added sodium and lithium chlorides on intermicellar interactions and micellar size of aqueous dodecyl sulfate aggregates as


Appendix A The steps for performing simulations

Figure A.1: The steps for performing DPD Dmol3 calculations and DPD simulations.
There are a number of steps to start studying the surfactant system in performing a DPD simulation:

1. **Selection the type of surfactant:** the selection of surfactant is based on the experimental work.

2. **Define the species:** the chemical structure of the surfactant, water, and oil are described to make up the system in terms of mesoscale molecules and bead types.

3. **Define the input system:** it needs to specify the composition, extent, and bead density of the mesoscale system you wish to simulate.

4. **Define bead interactions:** this is one of the important section. The repulsion parameter for pairs of like species is $a_i = (75/\rho)k_B T/r_c$. For unlike species in the system, they need first to determine the Flory-Huggins interaction parameters for each pair and convert these values into DPD interaction parameters. In this part, because the dissipative constant $\gamma$ and the constant of the statistical noise $\sigma$ are connected, one of them can be chosen. For example, noise $\sigma$ should not exceed more than 3 for simulation stability as seen on chapter 3.

5. **Define simulation conditions for the system:** it needs to choose conditions of simulation such as the adsorption phenomena of surfactant can be studied by including solid surface in DPD simulation. Defining the temperature of the simulation based on the temperature at which the repulsive and dissipative interaction parameters were determined

6. **Define how the run will be performed:** it needs to choose the length of the run and the frequency and nature of output information. Specifying the run length based on the Time step and either the number of steps or the total simulation time.
7. **Analyze the output**: it can be visualize and interpret the results of the simulation after finishing the simulation.
Appendix B Sigma profiles

The calculation of infinite dilution activity coefficient of head group of surfactant for SDS, DTAB, and DDAO were calculated by reducing the number of carbon of tail group from 12 to 2 carbons to determine the linear equation. Then, the calculation of head group was calculated from linear equation at number of carbon equal zero.

Figure B.1: Sigma profiles of water (H₂O), octane (C8), SDS surfactant (C12A), and reducing the number of tail group of SDS surfactant from 10 to 2 carbon (C10A, C8A, C6A, C4A, and C2A).
Figure B.2: Sigma profiles of water (H$_2$O), octane (C8), DTAB surfactant (C12C), and reducing the number of tail group of SDS surfactant from 10 to 2 carbon (C10C, C8C, C6C, C4A, and C2C).

Figure B.3: Sigma profiles of water (H$_2$O), octane (C8), DDAO surfactant (C12Z), and reducing the number of tail group of SDS surfactant from 10 to 2 carbon (C10Z, C8Z, C6Z, C4Z, and C2Z).
Figure B.4: Sigma profiles of water (H\textsubscript{2}O), octane (C\textsubscript{8}), water+Cl\textsuperscript{-} ion (WCl), water+Na\textsuperscript{+} ion (WNa), and water+Ca\textsuperscript{2+} (WCa).

Figure B.5: Sigma profiles of water (H\textsubscript{2}O) and CaCO\textsubscript{3}.
Appendix C Experimental IFT data

Table A.1: Experimental IFT values for anionic (SDS, and LDS) surfactants of water/octane system at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>SDS IFT (mN/m)</th>
<th>Concentration (mM)</th>
<th>LDS IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>51.935</td>
<td>0.000</td>
<td>51.935</td>
</tr>
<tr>
<td>0.347</td>
<td>43.005</td>
<td>0.367</td>
<td>43.320</td>
</tr>
<tr>
<td>1.734</td>
<td>26.486</td>
<td>1.836</td>
<td>27.831</td>
</tr>
<tr>
<td>3.468</td>
<td>20.273</td>
<td>3.672</td>
<td>19.491</td>
</tr>
</tbody>
</table>

Table A.2: Experimental IFT values for cationic (DTAB, DTAC, and CTAB) surfactants of water/octane system at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>DTAB IFT (mN/m)</th>
<th>Concentration (mM)</th>
<th>DTAC IFT (mN/m)</th>
<th>Concentration (mM)</th>
<th>CTAB IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>51.935</td>
<td>0.000</td>
<td>51.935</td>
<td>0.000</td>
<td>51.935</td>
</tr>
<tr>
<td>0.324</td>
<td>47.616</td>
<td>0.379</td>
<td>48.894</td>
<td>0.274</td>
<td>32.566</td>
</tr>
<tr>
<td>1.622</td>
<td>42.052</td>
<td>1.895</td>
<td>40.363</td>
<td>1.372</td>
<td>3.854</td>
</tr>
<tr>
<td>3.243</td>
<td>33.248</td>
<td>3.789</td>
<td>33.144</td>
<td>2.744</td>
<td>3.985</td>
</tr>
</tbody>
</table>
Table A.3: Experimental IFT values for zwitterionic (DDAO) surfactant of water/octane system at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>51.935</td>
</tr>
<tr>
<td>0.436</td>
<td>36.7652</td>
</tr>
<tr>
<td>2.180</td>
<td>2.925</td>
</tr>
<tr>
<td>4.359</td>
<td>3.575</td>
</tr>
</tbody>
</table>

Table A.4: Experimental IFT values for nonionic (Triton X-100) surfactant of water/octane system at 25 °C.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>51.935</td>
</tr>
<tr>
<td>0.0016</td>
<td>41.599</td>
</tr>
<tr>
<td>0.008</td>
<td>37.176</td>
</tr>
<tr>
<td>0.016</td>
<td>32.693</td>
</tr>
<tr>
<td>0.160</td>
<td>15.318</td>
</tr>
<tr>
<td>0.800</td>
<td>6.973</td>
</tr>
<tr>
<td>1.600</td>
<td>5.409</td>
</tr>
<tr>
<td>8.000</td>
<td>4.6447</td>
</tr>
</tbody>
</table>
Table A.5: Experimental IFT values as function of temperature for SDS and Triton X-100 surfactants of water/octane system by fixing the concentration of SDS at 0.347 mM and Triton X-100 at 0.16 mM.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Temperature (°C)</th>
<th>SDS IFT (mN/m)</th>
<th>Triton X-100 IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>43.005</td>
<td>15.318</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>39.5041</td>
<td>15.070</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>37.3629</td>
<td>14.823</td>
</tr>
</tbody>
</table>

Table A.6: Experimental IFT values as function of salts (NaCl, and CaCl₂) concentration for SDS surfactant of water/octane system at 25 °C by fixing the concentration of SDS at 0.347 mM.

<table>
<thead>
<tr>
<th>Salts</th>
<th>NaCl Concentration (ppm)</th>
<th>IFT (mN/m)</th>
<th>CaCl₂ Concentration (ppm)</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>43.004</td>
<td></td>
<td>43.004</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>29.038</td>
<td></td>
<td>18.722</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>16.075</td>
<td></td>
<td>7.552</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>9.500</td>
<td></td>
<td>3.610</td>
</tr>
</tbody>
</table>
Table A.7: Experimental IFT values as function of salts (NaCl, and CaCl₂) concentration for Triton X-100 surfactants of water/octane system at 25 °C by fixing the concentration of Triton X-100 at 0.16 mM.

<table>
<thead>
<tr>
<th>Salts Concentration (ppm)</th>
<th>NaCl IFT (mN/m)</th>
<th>CaCl₂ IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.318</td>
<td>15.318</td>
</tr>
<tr>
<td>500</td>
<td>16.057</td>
<td>16.778</td>
</tr>
<tr>
<td>1000</td>
<td>16.650</td>
<td>18.390</td>
</tr>
<tr>
<td>1500</td>
<td>17.105</td>
<td>18.284</td>
</tr>
</tbody>
</table>