SYNTHESIS, EVALUATION AND MOLECULAR DYNAMIC SIMULATIONS 
OF NOVEL ANIONIC POLYMERIC SURFACTANTS BASED ON 
POLYBENZOXAZINES

by

RIYAD AGELI SALEH MAHFUD

Submitted in partial fulfillment of the requirements 
For the degree of Doctor of Philosophy 

Department of Chemical Engineering 
Case Western Reserve University 

May 2014
SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis/dissertation of

RIYAD AGELI SALEH MAHFUD

candidate for the Doctor of Philosophy degree*

(signed) Dr. SYED QUTUBUDDIN

(Chair of the committee)

Dr. DANIEL LACKS

Dr. MOHANN SANKARAN

Dr. HATSUO ISHIDA

(date) December 19th, 2013

*We also certify that written approval has been obtained for any proprietary material contained therein.
DEDICATION

I would like to dedicate this work to my entire family. A special thank you goes out to my parents (Mr. Ageli Mahfud and Ms. Fatma AlQade) who were always so proud and supportive of their son. My wife (Wafa Zaroug) and my kids (Ahmed, Saviya and Omar) who have always been next to me on this long journey.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE</td>
<td>i</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>xvii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xviii</td>
</tr>
<tr>
<td><strong>CHAPTER 1. General introduction</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Classifications and synthesis of polymeric surfactants</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1 Block copolymers</td>
<td>4</td>
</tr>
<tr>
<td>1.2.2 Graft copolymers</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Polybenzoxazines</td>
<td>8</td>
</tr>
<tr>
<td>1.4 Scope of present work</td>
<td>12</td>
</tr>
<tr>
<td>1.5 References</td>
<td>15</td>
</tr>
<tr>
<td><strong>CHAPTER 2. Synthesis and Evaluation of Novel Anionic Polymeric Surfactants Based on Polybenzoxazines</strong></td>
<td>19</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>20</td>
</tr>
<tr>
<td>2.2 Experimental</td>
<td>22</td>
</tr>
<tr>
<td>2.3 Measurements</td>
<td>25</td>
</tr>
<tr>
<td>2.4 Results and Discussions</td>
<td>27</td>
</tr>
<tr>
<td>2.4.1 The molecular structure of synthesized monomers and oligomers</td>
<td>27</td>
</tr>
<tr>
<td>2.4.2 NMR analysis</td>
<td>29</td>
</tr>
<tr>
<td>2.4.3 FTIR analysis</td>
<td>30</td>
</tr>
<tr>
<td>2.4.4 DSC and TGA studies</td>
<td>32</td>
</tr>
<tr>
<td>2.4.5 Determination of MW by SEC</td>
<td>38</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.4.6 Surface tension measurements</td>
<td>40</td>
</tr>
<tr>
<td>2.5 Conclusions</td>
<td>49</td>
</tr>
<tr>
<td>2.6 References</td>
<td>50</td>
</tr>
<tr>
<td><strong>CHAPTER 3.</strong> Anionic Surfactants Based on Comb-like Polybenzoxazine Oligomers: Effects of Salinity and Temperature on Critical Micelle Concentration</td>
<td>54</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>55</td>
</tr>
<tr>
<td>3.2 Experimental</td>
<td>56</td>
</tr>
<tr>
<td>3.2.1 Chemicals</td>
<td>56</td>
</tr>
<tr>
<td>3.2.2 Preparation of solutions</td>
<td>57</td>
</tr>
<tr>
<td>3.3 Measurements</td>
<td>57</td>
</tr>
<tr>
<td>3.3.1 Surface tension measurements</td>
<td>57</td>
</tr>
<tr>
<td>3.3.2 Viscosity measurements</td>
<td>58</td>
</tr>
<tr>
<td>3.3.3 Dynamic light scattering</td>
<td>58</td>
</tr>
<tr>
<td>3.3.4 Foaming power measurements</td>
<td>59</td>
</tr>
<tr>
<td>3.3.5 Conductance measurements</td>
<td>59</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
<td>60</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
<td>85</td>
</tr>
<tr>
<td>3.6 References</td>
<td>86</td>
</tr>
<tr>
<td><strong>CHAPTER 4.</strong> Gemini (dimeric) benzoxazine surfactants: Synthesis, characterizations and molecular dynamics simulation of self-assembly</td>
<td>90</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>91</td>
</tr>
<tr>
<td>4.2 Experimental method</td>
<td>93</td>
</tr>
<tr>
<td>4.2.1 Materials</td>
<td>93</td>
</tr>
<tr>
<td>4.2.2 Preparation of di(4CaP-oca)</td>
<td>93</td>
</tr>
<tr>
<td>4.2.3 Ionization of di(4CaP-oca) into di(4CaP-oca - Na⁺)</td>
<td>93</td>
</tr>
<tr>
<td>4.3 Measurements</td>
<td>94</td>
</tr>
<tr>
<td>4.4 Computational Methods</td>
<td>94</td>
</tr>
<tr>
<td>4.5 Simulations Details</td>
<td>96</td>
</tr>
</tbody>
</table>
6.2.1 MD simulations of anionic dimeric benzoxazine

6.2.2 MD simulations of anionic polybenzoxazines

6.3 Future work

APPENDIX

i. The molecular dynamics algorithm

ii. Integrating the equations of motion

iii. Brendeson temperature and pressure coupling

iv. Trajectory analysis

v. References

CHAPTER 7. BIBLIOGRAPHY
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme No.</th>
<th>Legend</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The synthesis of benzoxazine monomers 4HBA-oca, 4HBA-dea and 4HBA-doa.</td>
<td>28</td>
</tr>
<tr>
<td>2.2</td>
<td>The proposed oligomer structures of poly(4HBA-oca), poly(4HBA-dea) and poly(4HBA-doa) and the ionization of these polymers into poly(4HBA-oca Na(^{+})), poly(4HBA-dea Na(^{+})) and poly(4HBA-doa Na(^{+})), respectively; (n) in Scheme 1, and the symbol (i) is the degree of polymerization.</td>
<td>29</td>
</tr>
<tr>
<td>4.1</td>
<td>Synthesis of dimeric benzoxazine 4CaP-oca.</td>
<td>98</td>
</tr>
<tr>
<td>4.2</td>
<td>The proposed dimeric benzoxazine structure of di(4CaP-oca) and the ionization of this dimer into the ionized form, di(4CaP-oca Na(^{+})).</td>
<td>103</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Legend</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of analytical results for molecular weight distributions and related properties determined from SEC with triple detector.</td>
<td>39</td>
</tr>
<tr>
<td>2.2</td>
<td>Influence of NaCl concentration on the cmc, $\gamma_{\text{cmc}}$, $\Gamma_{\max}$ and $a_s$ of poly(4HBA-oca Na$^+$), poly(4HBA-dea Na$^+$) and poly(4HBA-doa Na$^+$).</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>Summary of the surface activity properties of poly(4HBA-oca$^-$ Na$^+$), poly(4HBA-dea$^-$ Na$^+$) and poly(4HBA-doa$^-$ Na$^+$).</td>
<td>62</td>
</tr>
<tr>
<td>3.2</td>
<td>The cmc, $\Gamma_{\max}$, minimum surface area per molecule, $\Delta_{\text{mic}} G^0$ for poly(4HBA-oca$^-$ Na$^+$) at different temperatures.</td>
<td>76</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of the surface activity properties of di(4CaP-oca$^-$ Na$^+$) compared with values for anionic monomeric surfactant, SDS, from the literature.</td>
<td>104</td>
</tr>
<tr>
<td>4.2</td>
<td>The fractions of the guache and trans spacer conformers in aqueuos media.</td>
<td>113</td>
</tr>
<tr>
<td>5.1</td>
<td>The chemical structures and the snapshots of the used amphiphilic polybenzoxazines: The first column shows the abbreviated names, the second column shows the chemical structures using ChemDraw, and the third column shows the snapshots of the molecules at the minimum energy using VMD molecular viewer.</td>
<td>128</td>
</tr>
<tr>
<td>5.2</td>
<td>Structural Properties of the iBnXz clusters formed in the 49.8 mM simulation systems.</td>
<td>136</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Legend</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic represents the different types of block copolymers containing alternating hydrophilic and hydrophobic blocks.</td>
<td>5</td>
</tr>
<tr>
<td>1.2.a</td>
<td>Schematic represents the different types of graft copolymers containing a hydrophilic backbone and hydrophobic side chains (left), and hydrophobic backbone and hydrophilic side chains (right).</td>
<td>6</td>
</tr>
<tr>
<td>1.2.b</td>
<td>Synthetic methods for preparing Graft copolymers.</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Formation of polymeric micelles from different types of amphiphilic co-polymers (Extracted from Torchillin, 2001).</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Scheme showing the phenolic-type polybenzoxazine.</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>Representative structures of the three anionic polymeric surfactants, the symbol i is the degree of polymerization.</td>
<td>28</td>
</tr>
<tr>
<td>2.2</td>
<td>$^1$H NMR spectra of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.</td>
<td>30</td>
</tr>
<tr>
<td>2.3</td>
<td>FTIR spectra of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.</td>
<td>31</td>
</tr>
<tr>
<td>2.4</td>
<td>FTIR spectra of 4HBA-doa after polymerization at 80 °C, 120 °C and 160 °C for 30 min.</td>
<td>32</td>
</tr>
<tr>
<td>2.5</td>
<td>DSC thermograms of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.</td>
<td>34</td>
</tr>
<tr>
<td>2.6</td>
<td>Dynamic DSC plots for 4HBA-oca polymerization at various temperatures for 30 minutes.</td>
<td>35</td>
</tr>
<tr>
<td>2.7.A</td>
<td>TGA curves of poly(4HBA-oca), poly(4HBA-dea), and poly(4HBA-doa).</td>
<td>37</td>
</tr>
<tr>
<td>2.7.B</td>
<td>FTIR spectra of the condensate of the evolved gases at the peak rate degradation of poly(4HBA-oca) and octylamine.</td>
<td>37</td>
</tr>
</tbody>
</table>
2.8.A Surface tension at different weight concentrations.  41
2.8.B Surface tension at different molar concentrations.  41
2.9 Variation of cmc and γcmc with alkyl chain length.  42
2.10.A The effect of salinity on the surface tension of different poly(4HBA-oca` Na+) solutions.  43
2.10.B The effect of salinity on the surface tension of different poly(4HBA-dea` Na+) solutions.  44
2.10.C The effect of salinity on the surface tension of different poly(4HBA-doa` Na+) solutions.  44
2.11 The effect of salinity on the cmc and the surface tension at cmc (γcmc) of the solutions of poly(4HBA-oca` Na+), poly(4HBA-dea` Na+) and poly(4HBA-doa` Na+).  45
3.1 A schematic representation of micelles formation by a polymeric surfactant in aqueous media; unimer-to-aggregate transition.  61
3.2 Representative structures of the three anionic polymeric surfactants.  62
3.3 Surface tension variation over time for the poly(4HBA-doa` Na+) solutions with various viscosities.  63
3.4 The effect of poly(4HBA-oca` Na+) concentration on both the lamella height and the maximum force at 21±0.1 °C  64
3.5 The viscosities of poly(4HBA-oca` Na+), poly(4HBA-dea` Na+), and poly(4HBA-doa` Na+) solutions at different low concentrations, and constant temperature, 30±0.1 °C.  65
3.6 Variation of reduced viscosity of 0.1g/L poly(4HBA-doa` Na+) solution with added NaCl.  67
3.7 Kraemer plot (intrinsic viscosity =ln relative viscosity/concentration vs. concentration) for poly(4HBA-oca` Na+), poly(4HBA-dec` Na+) and poly(4HBA-doa` Na+).
solutions at different concentrations and 30±0.1 °C.

3.8 The effect of salinity on the cmc and the surface tension at cmc ($\gamma_{\text{cmc}}$) of the solutions of poly(4HBA-oca$^-\text{Na}^+$) (star), poly(4HBA-dea$^-\text{Na}^+$) (square), and poly(4HBA-doa$^-\text{Na}^+$) (triangle).

3.9 The variation of surface tension as a function of poly(4HBA-oca$^-\text{Na}^+$) concentration in aqueous solution at different temperatures (21, 38, and 48 °C).

3.10 The variation of cmc and $\gamma_{\text{cmc}}$ as a function of temperature for poly(4HBA-oca$^-\text{Na}^+$).

3.11 Thermodynamic parameters of micellization for poly(4HBA-oca$^-\text{Na}^+$).

3.12 $\Delta_{\text{mic}}H^\circ$ vs. $\Delta_{\text{mic}}S^\circ$ plot for poly(4HBA-oca$^-\text{Na}^+$).

3.13 Hydrodynamic diameter intensity of poly(4HBA-oca$^-\text{Na}^+$) micelles in aqueous solution at 25 °C measured by DLS at concentration of 0.5 g/L, and scattering angles of 60 ° (top), 90 ° (middle) and 130 ° (bottom).

3.14 Hydrodynamic diameter distributions $f(D_h)$ of poly(4HBA-oca$^-\text{Na}^+$) micelles in aqueous solution at 25 °C measured by DLS at concentration of 0.5 g/L, and scattering angle of 90 °C.

3.15 The dependence of the foam volume ratios on time, 150 ppm (left) and 75 ppm (right).

3.16 The decay rate plot (top) and the surfactants solution foams (bottom) after 1 min, a-poly(4HBA-oca$^-\text{Na}^+$), b- poly(4HBA-dea$^-\text{Na}^+$) and c- poly(4HBA-doa$^-\text{Na}^+$).

3.17 Temperature dependence of $\kappa$ in the systems of polymeric surfactant solutions, 0.05 wt% (poly(4HBA-oca$^-\text{Na}^+$), poly(4HBA-dea$^-\text{Na}^+$) and poly(4HBA-doa$^-\text{Na}^+$)). A sharp rise of $\kappa$ with temperature is due to the Krafft phenomenon, and shows the Krafft point of the polymeric surfactant species.
4.1 FTIR spectra of 4HBA-oca+HBZ-COOH (1:1) at 25 °C/0 hr, 140 °C/1 hr and 140 °C/3 hrs.

4.2 Dynamic DSC plots for (4HBA-oca) at 25°C, and for (4HBA-oca + HBZ_COOH) at 140°C after heating for 1 hr and 3 hrs.

4.3 TGA curves of di(4CaP-oca).

4.4 Representative structure of the anionic dimeric surfactant, represented by CPK model using VMD.

4.5 Surface tension at different weight concentrations.

4.6 Spontaneous aggregation of di(4CaP-ocaNa+) into a micelle; snapshots of the simulation at the start (t=0 ns), intermediate (t=3-10 ns), micelle and single molecule stage (t=10-16 ns), and micelle (16-20 ns) are shown. Water molecules are omitted for clarity and the black points represent the Na ions.

4.7 Radial distribution functions of water relative to the polar heads (W-Co), spacer (W-N), and carboxylic groups (W-OH) calculated from the MD simulations were carried out at 298K.

4.8 The RDFs between the charged head groups represented by the carbon atoms in the carboxylate groups [Co-Co] and between the spacers [N-N] (a). The RDFs between neighboring head groups [Co-Co] for each di(4CaP-ocaNa+) in aqueous media and in gas phase (b).

4.9.a Schematic definitions of the dihedral angles for the spacer.

4.9.b Distribution of the gauche and trans dihedral-angles for the spacer at vacuum system (left) and in aqueous media (right) that produced by the various dihedral angle sampling methods.

4.10 Distribution of the dihedral angle for the alkyl chain produced by the various dihedral angle sampling methods.

4.11 Density profiles along the Z axis.

4.12 The average values of the tilt angles and the spacer bend angle (a) that characteristic the geometric shape of the surfactant at air/water interface (b). The RDF between N and H of the hydroxyl groups in each individual di(4CaP-ocaNa+)
molecule (C). Equilibrium MD simulation snapshot (d) showing a dimeric benoxazine molecule at the air/water interface, Color legend: dark, di(4CaP-oca’Na+) molecule; gray, water molecule.

5.1 Snapshots represent the spontaneous aggregation of the amphiphilic polybenzoxazines (at a concentration of 49.8×10⁻³ M) into spherical and cylindrical micelles. Water molecules are omitted for clarity and the black points represents the Na ions.

5.2.a iBnXz-iBnXz (Atom_Atom) electrostatic short-range interactions (Coul-SR).

5.2.b iBnXz-iBnXz (Atom_Atom) van der Waals short-range interactions (LJ-SR).

5.3.a iBnXz-H₂O (Atom_Atom) electrostatic short-range interactions (Coul-SR).

5.3.b iBnXz-H₂O (Atom_Atom) van der Waals short-range interactions (LJ-SR).

5.4 The number of clusters as a function of time (a), and the relative clusters sizes during the simulations for all the iBnXz molecules based on 3BnXz cluster (b). The analysis was performed by using 1.2 nm cutoffs to define the interaction between iBnXz molecules.

5.5 Shows the eccentricity of the micelle over the last 5 ns of the simulation.

5.6 Overview of simulations performed: The snapshots at t= 20 ns represent the effect of both the molecule size and the molecules concentration on the micellization morphology. The letters in the first row define the systems. The numbers between the brackets represent the following: 1- millimolarity (mM), 2- iBnXz molecules, 3- water molecules, 4- Na ions, 5- wt% of amphiphile. The micelles in the center of the cell represented as van der Waals spheres; Red spots represent the oxygen atoms, cyan color represents the carbon and hydrogen atoms, and the nitrogen atoms are blue.
5.7 Plots of repeating units, i, in the iBnXz molecules vs. iBnXz concentration (mM)(a) and iBnXz wt% (b). The snapshots of micellar shape in the iBnXz system after 20 ns represent the spherical and the cylindrical regions. The dashed blue line represents the micelles shape transfer zone of iBnXz molecules and indicates the maximum available iBnXz concentrations for spherical micellar shape. The color legend is as described before.

5.8 (a) the end-to-end distances of the iBnXz backbones (left). The measured distances represented by the black lines (right). (b) The end-to-end distance distribution.
ACKNOWLEDGMENTS

My deepest gratitude goes to all my family members, parents, wife, kids, brothers and sisters for their support and encouragement during my time at Case Western Reserve University. Special recognition goes out to my little boys, Ahmed and Omar, and little daughter, Saviya, who missed out on a lot of daddy time.

I would like to express my sincerest thanks and appreciation to my advisors Professor Syed Qutubuddin and Professor Hatsuo Ishida for their guidance, advice and motivation throughout my Ph.D. studies. Their continued supports led me to the right way.

I would also like to extend my appreciation to the committee members, Professor Daniel Lacks and Professor Mohan Sankaran. I also want to thank Dr. Tarek Agag for introducing me to the polybenzoxazine field.

Finally, I would also like to thank my colleagues, who have supported me over the past several years. Special thanks to the research groups of Prof. Qutubuddin and Prof. Ishida for their advice and mentorship. I want to thank Professor J. Adin Mann for giving me access to his lab and equipments.
Polymeric surfactants attracted considerable attention in recent years for applications such as personal care product and stabilization of emulsions and suspensions. The characteristic properties of polymeric surfactants originate from the formation of aggregates through the association of the hydrophobic alkyl chains in aqueous solution, within a narrow concentration range. The aggregates are called micelles, and the narrow concentration range above which micelles are formed in the solutions is called the critical micelle concentration (cmc). The characteristics of micelles are easily controlled by changing the solution conditions such as temperature, concentration and ionic strength, and by changing the surfactant properties such as chain length, hydrophobic volume and head group area.

In present work, a novel platform of anionic polymeric surfactants, poly(4HBA-oça\textsuperscript{Na\textsuperscript{+}}), poly(4HBA-dea\textsuperscript{Na\textsuperscript{+}}), and poly(4HBA-doa\textsuperscript{Na\textsuperscript{+}}), has been synthesized by polymerizing benzoxazine monomers that are synthesized by reacting an aliphatic amine
of variable chain length ($C_8$, $C_{10}$ and $C_{12}$), with 4-hydroxybenzoic acid and paraformaldehyde. The structures of the monomers and polymeric surfactants are confirmed by NMR and FTIR. The ring-opening polymerization and thermal behavior of the benzoxazine monomers are studied by DSC and TGA. Size exclusion chromatography (SEC) coupled with Viscotek triple detection technique is used to characterize the molecular weight distribution of polybenzoxazine surfactants. The influence of the structure on the surface activity is investigated by measuring the surface tension of aqueous solutions of the polymeric surfactants using the Wilhelmy plate method. The tensiometry results indicate that the adsorption at the air/water interface is similar for the octylamine, decylamine and dodecylamine-based surfactants. Increasing the alkyl chain length from $C_8$ to $C_{12}$ does not significantly affect the surface tension at the critical micelle concentration ($\gamma_{\text{cmc}}$), while the critical micelle concentration (cmc) gradually increases due to increasing hydrophobic effect. The influences of salt addition on the surface tension at the cmc ($\gamma_{\text{cmc}}$) along with the thermodynamic properties of micellization in aqueous solutions surfactants are studied. Upon salt (NaCl) addition, the cmc initially decreases slightly and remains constant at 3wt% NaCl. For poly(4HBA-oca$^-$Na$^+$), micellization is affected by temperature as the hydrophobic and head group interactions change. As temperature increases the cmc of poly(4HBA-oca$^-$Na$^+$) decreases in the studied temperature range.

The synthesis of anionic gemini surfactant based on 4-carboxylphenol benzoxazine dimer, abbreviated as di(4CaP-oca) is described. Molecular dynamics simulations are employed to gain a fundamental understanding of the self-assembly of amphiphilic di(4CaP-oca$^-$Na$^+$); particularly the morphology and dynamics of the
aggregates. Starting with a randomly distributed surfactant molecules in water, the mechanism of micelle formation is observed at a molecular level. Simulation results show that this surfactant forms spherical micelles at concentrations higher than the cmc, and the conformation of the di(4CaP-oca`Na+) shows that the spacer is more flexible than the tail. The radial distribution functions (RDF) and the effect of electrostatic interactions between the head groups are investigated. Furthermore, fully atomistic molecular dynamic simulations are performed to address the self-assembly of amphiphilic and comb-like polybenzoxazines (iBnXz) in water, with i=3 (trimer), i=4 (tetramer); i=6 (hexamer), i=8 (octamer), and i=10 (decamer). Spontaneous aggregation of the comb-like polybenzoxazine molecules into a single micelle occurs in the simulations. The simulations show that the molecular size and concentration play important roles in micellar morphology. The micellar morphology is spherical at low concentrations, but undergoes a transition to cylindrical shape as the concentration increases. The transition point depends on the molecular size – both the true size as indicated by molecular weight, as well as an additional effective size dependent on molecular flexibility.
CHAPTER 1
GENERAL INTRODUCTION

1.1 BACKGROUND

Polymeric surfactants have become increasingly important for preparation of many dispersion systems such as oil-in-water (O/W) and water-in-oil (W/O) emulsions [1]. Interest in polymeric surfactants arises mainly from the fact that these materials have very low critical micelle concentration (cmc) values and low diffusion coefficient as compared to low molecular weight surfactants. The low cmc of the polymeric surfactants is attributed to their relatively high molecular weights [2], and it can be precisely measured for polymeric surfactant solutions in water [2]. At cmc or at higher concentrations the solution contains both micellar aggregates and single molecules [3]. The self-assembly of polymeric surfactants depends on the molecular structure of the amphiphile and on the solution conditions including concentration, temperature, pH and salinity [4]. Some studies on the synthesis and characterization of the surface activity of polymeric surfactants have been carried out via in the literature. For example, nonionic polymeric surfactants based on carboxymethylcellulose and alkyl poly(etheroxy) acrylate were synthesized by using ultrasonic irradiation to produce macroradicals and the solutions show low surface tension [5]. Further, nonionic polymeric surfactants show good interfacial properties, for example, poly(N-acylethylenimines), which is synthesized based on cationic polymerization of 2-alkyl-2-oxazolines [6]. A general overview of the polymeric surfactants types including classifications and the synthesis methods will be introduced in a later section. The high molecular weight polymeric surfactants is a result
of the large number of the repeating molecular units, hence it is called polymeric. Further, the phrase oligomeric is used to describe the polymeric surfactants with a few repeating units or of low molecular weights (< 15,000) [7].

The most prominent advantage of the polymeric surfactants is the wide variability of the chemical structure of the polymer. Because of their structural variables such as backbone length, branch length, and branch spacing, they generally have great potential to realize desirable properties such as micelles formation and surface tension reduction of liquids. The external factors that influence the micellization process, aggregation and the morphology of micelles include surfactant structure [8], concentration of the surfactant [9], temperature [9], and the surfactant-solvent interactions [9]. The critical micelle concentration (cmc) is known as the onset of intermolecular chain association [10], where the onset of these associations occurs at very dilute concentrations of polymeric surfactants [2].

The value of the cmc can be determined by measuring the change in the physical properties of the surfactant solution as the surfactant concentration increases [11]; any physical parameter can be used to register that change. Many techniques are used to determine the cmc such as UV-absorption spectroscopy [12], fluorescence spectroscopy [12], electrical conductivity for ionic surfactant [12], capillary electrophoresis [13], surface tension [14], static and dynamic light scattering [14, 15], self-diffusion measurements [16], viscosity and cryo-electron microscopy (Cryo-TEM) [17]. The most common technique for determining the cmc is surface tension measurements, based on either Wihelmy plate or du Nouy ring. The measurements show a break at the cmc after
which the surface tension remains constant with further increase in surfactant concentration.

1.2 Classifications and synthesis of polymeric surfactants

Classical surfactants are classified into four primary groups according to the composition of their head group: (a) anionic, containing a negatively charged head group, such as carboxylic acids and salts, and alkyl benzene sulfonates; (b) cationic, containing a positively charged head group, such as quaternary ammonium salts and amines; (c) zwitterionic, electrically neutral compounds have both cationic and anionic centers attached to the same molecule and separated by intervening atoms, such as octadecyl dimethyl betaine (C18DMB); and (d) non-ionic, having a hydrophilic head group that is not charged, such as ethers, alcohol ethoxylates, and carboxylic acid esters. Anionic polymeric surfactants, which are most relevant to the present study, have been synthesized by many different methods such as polymerization of monomeric surfactant with a sulfonate head group, namely poly(sodium undecylenic sulfate) [18], polymerization of sulfonated styrene with allyl fatty ester [19], based on sodium poly(oxyethylene) lauryl ether sulfate[20], chemical modification of dextran with epoxy group containing phenoxy resin and then with sodium sulfopropyl groups [21], polymerization of carboxymethyl cellulose and alkyl poly(etheroxy) acrylate under ultrasonic irradiation [22], etc.

Block and graft copolymers are the most common types of polymeric surfactants and the most efficient for stabilization of emulsions and suspensions [1]. Hence, the polymeric surfactants are designed along two main routes as described below.
1.2.1 Block copolymers

Block copolymers consist of alternating blocks of hydrophobic groups (B) and blocks of hydrophilic groups (A) connected in a wide variety of ways such as A-B diblock copolymers, A-B-A triblock copolymers and (A-B)$_n$ multiblock copolymers, see Figure 1.1. The poly(ethylene oxide)/poly(propylene oxide) (PEO/PPO) copolymers are examples of this type and are well known as Pluronic (PEO/PPO/PEO) or inverse Pluronic (PPO/PEO/PPO). These nonionic polymeric surfactants form micelles in aqueous solution when the concentration is higher than the cmc for a wide range of molecular weights (2900-14600) [23, 24]. In general, the most convenient approach to the synthesis of block copolymers is by creating an active site on the end of one polymer to initiate the polymerization of another monomer. The active site can be created by free radicals, anions, Ziegler catalyst, or cations [2]. Niwa and coworkers [25] synthesized polyoxyethylene-block-polystyrene (POE-b-PS) copolymers by using organometallic catalyst to generate macroradicals. The disadvantage of the polymerization by free radical is in the simultaneous formation of homopolymers, which is formed from the same repeating units with little surface activity at interface [1]. Khan and coworkers [26] prepared polystyrene-block-polyoxyethylene (PS-b-POE) by anionic polymerization using cumyl potassium as the styrene block initiator. The main problem with anionic polymerization lies in difficulty of required conditions such as high vacuum, inert atmosphere, low temperatures, and high purity of the reactants [1]. Thus, anionic polymerization is not typically used industrially.
1.2.2 Graft copolymers

Graft copolymers consist of either hydrophilic chains grafted to a hydrophobic backbone, or hydrophobic chains grafted to a hydrophilic backbone, see Figure 1.2.a. The polymeric surfactants of the graft type are designed to produce molecules suitable for use as emulsifiers or dispersants under extreme conditions such as high salinity, low or high pH, and different temperatures [2]. In general, three methods are used to synthesize graft copolymers [2], see Figure 1.2.b: (1) grafting-from approach, where the monomer is grafted from the backbone, such as the hydrophilic poly(2-(dimethylamino)ethyl acrylate) (PDMAEA) side chains grafted from the hydrophobic poly(6-methyl-1,2-heptadiene-4-ol) (PMHDO) backbone [27]; (2) grafting-onto approach, where the functional end groups of one kind of polymer react with other reactive groups, of the other polymer (backbone) that are distributed randomly on the main chain, such as the hydrophilic poly(ethylene oxide) side chains linked to α-C of carbonyl of polyacrylate-based backbone using CuBr as catalyst [28]; (3) grafting-through or macromonomer approach, where a monomer is copolymerized with a low molecular weight prepolymer containing

![Figure 1.1 Schematic represents the different types of block copolymers containing alternating hydrophilic and hydrophobic blocks.](image)
a polymerizable double bond, such as the free radical copolymerization of distilled methyl methacrylate with the poly(oxyethylene) macromonomer (PEO-MA), 2,2-azobisisobutyronitrile (AIBN) was used as initiator and toluene as solvent [29].

**Figure 1.2.a** Schematic represents the different types of graft copolymers containing a hydrophilic backbone and hydrophobic side chains (left), and hydrophobic backbone and hydrophilic side chains (right).

**Figure 1.2.b** Synthetic methods for preparing Graft copolymers.
Figure 1.3 presents a schematic representation of mechanism of micelle formation for polymeric surfactants in aqueous media. The micellar core consists of the hydrophobic segments and the shell region consists of the hydrophilic segments. The size of the segments plays a critical role in controlling the micellization process; for example, if the hydrophobic segments are slightly shorter than the hydrophilic segments, then spherical micelles are formed in aqueous solution. Further, if the hydrophilic segments are too long, polymeric surfactant molecules exist as unimer (individual molecules), while polymeric surfactants with very long hydrophobic segments form non-spherical structures such as rods and lamellae [11]. The cmc plays the main role in determining the polymeric surfactants concentration above which micelles are formed; the micelles become more stable at concentrations higher than the cmc. Thus the micelles are more stable at a given concentration for surfactants with low cmc [11].

This thesis presents new and easy approach to synthesize the amphiphilic graft copolymers that show surface activity better than the classical surfactant. In particular, this study illustrates the novel application of benzoxazine chemistry to make polymeric surfactants.
1.3 Polybenzoxazines

In 1944, Holly and Cope reported the synthesis of 1,3-benzoxazines by combining a primary amine, a phenolic derivate, and formaldehyde [30]. The synthesis and characterization of polybenzoxazines was first reported by Ning and Ishida in 1994 [31]. Since then, extensive studies of the synthesis, characterization, and applications of benzoxazine monomers and polymers have been reported [32]. Benzoxazines exhibit various unusual properties, including near-zero shrinkage upon polymerization [33], fast property development at low conversion [34], high char yield [35], very low surface energy [36, 37], and low water absorption despite having hydrophilic chemical repeat
units [38]. Of particular interest in the current study is the extremely versatile molecular design of benzoxazines [33]. While the majority of polybenzoxazines are hydrophobic, some show potential for applications in hydrophilic environment. Benzoxazines may have hydrophilic functionalities such as carboxylic [39], amine [40], and hydroxyl groups [41], and a comonomer in the main chain, including polyether chain [42].

Advantages of polymeric surfactants based on benzoxazine chemistry have been reported using a Jeffamine family with long hydrophilic chain based on polyethylene oxide [43, 44]. Sawaryn et al. [43] synthesized nonionic polymerizable benzoxazine surfactants that were used to stabilize miniemulsions. High molecular weight nonionic benzoxazine surfactants, with hydrophilic polymeric blocks and benzoxazine moieties in the polymer backbone, have also been synthesized and used as protective colloids to stabilize o/w miniemulsions of benzoxazine resins [44]. Ishida et al. [45] synthesized a water soluble phenolic-type polybenzoxazine that was obtained by cationic ring-opening polymerization of monofunctional benzoxazine monomers. This Mannich base phenolic-type polybenzoxazine has methylene groups in the molecule repeating unit as shown in Figure 1.4.

![Figure 1.4 Scheme showing the phenolic-type polybenzoxazine](image_url)
The polybenzoxazine structure obtained via thermal polymerization can be thought of as the phenolic-type [45, 46]. Thermal polymerization proceeds through an autocatalytic mechanism where the formed phenol groups at the beginning of the polymerization promote the benzoxazine ring-opening and accelerate the process due to their acid character [47, 48]. Further, the polymerization temperature can be decreased by adding acidic catalysts such as carboxylic acids or phenols [49-51]. In earlier studies [39, 46], the curing temperature of benzoxazine was improved by using monomers contain both carboxylic groups and benzoxazine ring. These carboxylic groups acted as catalyst that reacts with the amine moieties formed during the curing process. The existence of the carboxylic groups in the phenolic-type polybenzoxazine increases the hydrophilic property of the polymer. However, the inter/intra-molecular hydrogen bonding of the hydroxyl groups that exist in the phenolic-type polybenzoxazine increases its hydrophobicity [52, 53]. Water molecules might break intermolecular hydrogen bonds among the hydroxyl groups, resulting in the unusual hydrophilic property of this polymer [45]. Originally, the phenolic-type polybenzoxazine is hydrophobic, and must be converted to amphiphilic nature in order to make it compatible with the amphiphilic graft-type copolymers. Normally, this can be done via neutralization of ion exchange resins of the inorganic cations by adding equivalent amount of sodium hydroxide. The neutralization depends on the type of functional groups such as strongly acidic (sulphonate -SO₃H), and weakly acidic (carboxylate –COOH). The carboxylic functional groups reach the maximum hydrolysis at pH> 7.0 [54].

The polybenzoxazine-based amphiphilic graft copolymers possess methylene groups and tertiary amine along the backbone, alkyl side chains and the head which
consists of benzene groups that hold a hydroxyl and a carboxylate ion. They all self-assemble in aqueous media to form spherical micelles at concentrations above critical micelle concentrations [55]. The amphiphilic graft copolymer can aggregate in water to form micelles with non-spherical morphologies [56, 57]. The molecular dynamic (MD) simulation technique can provide microscopic level information which is used to study amphiphile aggregates, such as the determination of geometrical characteristics of aggregates and the concentration of free surfactant that may supplement experimental and theoretical studies [58].

MD simulation allows one to obtain the structure of aggregates and conformations of amphiphilic molecules by using appropriate force fields and equations of motion. Thus, MD simulations were conducted as part of this thesis. A model system is built at the atomic level with prescribed potentials (the force field) acting between the atoms. These interactions may consist of site-site type interactions, such as van der Waals dispersion and Coulombic forces, as well as intramolecular forces such as chemical bonds, angle bending and dihedral torsional barriers. The intramolecular forces are often treated to be a good approximation with simple harmonic or periodic functions [59], but recently more detailed OPLS (Optimized Potential for Liquid Simulations) is a set of force fields introduced to increase accuracy [60]. A surfactant molecule can be modeled as a collection of atoms in the presence of solvent such as water. These approaches provide an elegant way to predicate the polymeric surfactant structure and how it affects the micellization process. Thus a new simulation approach which incorporates all relevant parameters is presented for the analysis of surfactant micellization in aqueous media. Another important application of MD simulations in this field is the designing of
new amphiphiles in order to obtain desirable aggregate properties. Since MD simulations can also provide information on dynamics, the amphiphile self-assembly and other dynamical processes can be studied in the future.

1.4 Scope of present work

Many industrial processes rely on surfactants to decrease the surface tension of aqueous solutions at a relatively low surfactant concentration. Polymeric surfactants gained increasing interest due to their low cmc values. The raw materials cost and the design of the molecular structure are regarded as influential factors in selection of methodology for polymeric surfactant synthesis. The hypothesis of this work is that benzoxazine chemistry can be used to synthesize new polymeric surfactants with a variety of molecular structures based on relatively inexpensive raw materials and the molecular design flexibility for desired performance properties. While the majority of polybenzoxazines are hydrophobic, some show potential for applications in hydrophilic environment. The synthesis of carboxylic acid-functionalized benzoxazine monomers of various hydrophobe chain lengths, the polymerization of these monomers to obtain anionic polymeric surfactants, and the ability of these polymeric surfactants to reduce the water/air surface tension are the main experimental objectives. The results justify that these polybenzoxazines offer a superior alternative to conventional surfactants. The specific objectives of this study are the following:

1. Synthesize and characterize carboxylic acid-functionalized benzoxazine monomers of various chain lengths, and obtain anionic polymeric surfactants via polymerization of the monomers.
2. Demonstrate the ability of these surfactants to reduce the water/air surface tension, as a surface active agent, by measuring the critical micelle concentration, cmc, and the surface tension at cmc, $\gamma_{\text{cmc}}$.

3. Evaluate the effects of solution conditions such as concentration, temperature and salinity on micellization, and the significance of the enthalpy and entropy of micellization of anionic polymeric surfactants.

4. Apply molecular dynamic (MD) simulations to predict or model the micellization behavior of introduced surfactants and to improve the understanding at the molecular level.

Chapter 2 describes the synthesis of three anionic polymeric surfactants, poly(4HBA-oca$^+$Na$^+$), poly(4HBA-dea$^+$Na$^+$), and poly(4HBA-doa$^+$Na$^+$) via polymerizing benzoxazine monomers by reacting an aliphatic amine of variable chain length ($C_8$, $C_{10}$ and $C_{12}$), with 4-hydroxybenzoic acid and paraformaldehyde. In chapter 3, the physiochemical properties, such as critical micelle concentration (cmc), surface tension at cmc ($\gamma_{\text{cmc}}$), and surface activity parameters of the solutions of three anionic polymeric surfactants have been studied. The influences of salt addition, temperature change, chain length on the surface tension at the critical micelles concentration ($\gamma_{\text{cmc}}$) are discussed. Chapter 4 describes the synthesis of anionic dimeric surfactants based on dimeric benzoxazine, 3,3’-(octylazanediyl)bis(methylene)bis(4-hydroxybenzoic acid), or, 4-carboxylphenol-based benzoxazine dimer abbreviated as di(4CaP-oca), which contains only one hydrophobic alkyl tail and two hydrophilic carboxyl groups is described. MD simulations are employed to gain a molecular-level understanding of the self-assembly of amphiphilic di(4CaP-oca$^+$Na$^+$), particularly the morphology and dynamics of the
aggregates. The results of MD simulations of the aggregation behavior of five amphiphilic anionic polybenzoxazines are presented in chapter 5. The effect of the Mannich-bridge backbone length on the surfactant micellization is discussed, and the transition from spherical to cylindrical shape is predicted as a function of concentration and molecular size. Finally, Chapter 6 summarizes the overall conclusions and suggestions for future work.
1.5 References


Chapter 2

2. Synthesis and Evaluation of Novel Anionic Polymeric Surfactants
   Based on Polybenzoxazines
2.1 Introduction

Surfactants constitute one of the most versatile and powerful class of materials used in the chemical industry. Their surface activity and self-assembly behavior make surfactants useful for many applications including detergents, coatings, inks, pharmaceuticals, personal care products, and advanced materials such as nanocomposites, for the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsions and microemulsions, as well as solid/liquid dispersions [1, 2]. Polymeric surfactants may be used as an alternative to classical surfactants in most of the above applications, and based on the stability criteria, perform the best in dispersions [3, 4]. The characteristic properties of polymeric surfactants originate from the formation of micellar aggregates in aqueous solution through the association of hydrophobic segments. The polymeric surfactants may form monomolecular-layer micelles or aggregate to form multimolecular structures of various shapes [5]. The aggregation behavior of polymeric surfactants depends on the molecular structure of the amphiphile and on the solution conditions including concentration, temperature, pH and salinity [6-8]. Some studies on the synthesis and characterization of the surface activity of polymeric surfactants have been carried out via designing the molecular structure. For example, block copolymers were synthesized via ring opening reaction of cyclic imide [9], and comb-like copolymers were obtained using ethoxylated alkyl-phenol and formaldehyde for oil recovery applications [10]. Polymerizable surfactants have reactive functionalities that can exist in the hydrophobic tail or the polar headgroup. The most widely-used reactive group is a vinyl that can polymerize via thermal or photolytic initiation [11, 12]. It is important to
distinguish between polymeric surfactants from polymerizable surfactants such as used in microemulsion polymerization [13] and nanocomposites [14]. Polymerizable cationic surfactants such as vinylbenzyldimethyldecylammonium chloride (VDAC) can homopolymerize as well as copolymerize with monomers like styrene [13].

This study illustrates the novel application of benzoxazine chemistry to make polymeric surfactants. In 1944, Holly and Cope reported the synthesis of 1,3-benzoxazines by combining a primary amine, a phenolic derivate, and formaldehyde [15]. The synthesis and characterization of polybenzoxazines was first reported by Ning and Ishida in 1994 [16]. Since then, extensive studies of the synthesis, characterization, and applications of benzoxazine monomers and polymers have been reported [17]. Benzoxazines exhibit various unusual properties, including near-zero shrinkage upon polymerization [18], fast property development at low conversion [19], high char yield [20], very low surface energy [21, 22], and low water absorption despite having hydrophilic chemical repeat unit [23]. Of particular interest in the current study is the extremely versatile molecular design of benzoxazines [18]. While the majority of polybenzoxazines are hydrophobic, some show potential for applications in hydrophilic environment. Benzoxazines may have hydrophilic functionality such as carboxylic [24-27], amine [28-30], and hydroxyl groups [31, 32], and a comonomer in the main chain, including polyether chain [33-35]. Recently, Sawaryn et al. [36] synthesized nonionic benzoxazine polymerizable surfactants that were used to stabilize miniemulsions. High molecular weight nonionic benzoxazine surfactants, with hydrophilic polymeric blocks and benzoxazine moieties in the polymer backbone, have also been synthesized and used as protective colloids to stabilize o/w miniemulsions of benzoxazine resins [37].
However, the synthesis of anionic surfactants based on benzoxazine has not been described in the literature. This paper is the first to report anionic polybenzoxazine surfactants. The goals of this research are twofold: (a) the synthesis and characterization of carboxylic acid-functionalized benzoxazine monomers of various hydrophobe chain lengths, and (b) polymerization of these monomers to obtain anionic polymeric surfactants. The ability of the synthesized polymeric surfactants to reduce the water/air surface tension and form micelles is evaluated by measuring the critical micelle concentration, cmc, and the surface tension at cmc, $\gamma_{\text{cmc}}$. Comparison of the cmc and $\gamma_{\text{cmc}}$ of the new anionic polymeric surfactants with literature values for both low and high molecular weight surfactants are made to justify that these polybenzoxazines offer a superior alternative to conventional surfactants. Furthermore, the polymeric surfactants reported herein are thermally stable up to about 170 °C and do not contain sulfur, and therefore are more ecofriendly than many commercial surfactants.

2.2 EXPERIMENTAL

Paraformaldehyde (96%) was used as purchased from Acros Organics USA. 4-Hydroxybenzoic acid (99%), octylamine (99%), decylamine (95%), and dodecylamine (98%) were used as received from Sigma-Aldrich. 1,4-Dioxane was purchased from Fisher Scientific.

The benzoxazine monomers were prepared from 4-hydroxybenzoic acid, paraformaldehyde, and primary amines, including octylamine, decylamine and dodecylamine by using a modified solvent method reported in the literature [15].
2.2.1 Preparation of 3-octyl-3, 4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-oca)

In a 100 mL flask were mixed together octylamine (5 mmol, 0.646 g), 4-hydroxybenzoic acid (5 mmol, 0.69 g), and paraformaldehyde (12.5 mmol, 0.3877 g) and heated at 90 °C with magnetic stirring in dioxane (10 mL) for 24 h. The mixture was allowed to cool to room temperature and poured into 100 mL deionized water in a 200 mL flask to give a yellowish precipitate. The product was filtered and washed three times with deionized water and dried at 60 °C. The monomer was dissolved in chloroform and then filtered by using filter paper to remove the dispersed material, followed by drying under vacuum in a rotary evaporator. (Yield: 72%).

$^1$H NMR (DMSO-d$_6$, frequency: 300 MHz, ppm: δ, 298K): 1.31-1.48 (10H, CH$_2$–CH$_2$–CH$_2$), 3.96 (2H, Ar–CH$_2$–N), 4.89 (2H, O–CH$_2$–N), 6.76-7.66(3H, Ar–H). FTIR (KBr, cm$^{-1}$): 1700 (the C=O stretching of the carboxylic group), 1240 (the stretching of Ar–O–C), 938 (out-of-plane vibration, benzene ring to which oxazine is attached).

2.2.2 Preparation of 3-decyl-3, 4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-dea)

4HBA-dea was prepared from decylamine (5 mmol, 0.786 g), 4-Hydroxybenzoic acid (5 mmol, 0.690 g), and paraformaldehyde (12.5 mmol, 0.387 g) as previously described for 4HBA-oca, (Yield: 73%).

$^1$H NMR (DMSO-d$_6$, frequency: 300 MHz, ppm: δ, 298K): 1.31-1.47 (10H, CH$_2$–CH$_2$–CH$_2$), 3.96 (2H, Ar–CH$_2$–N), 4.87 (2H, O–CH$_2$–N), 6.77-7.68(3H, Ar–H).
2.2.3 Preparation of 3-dodecyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-doa)

4HBA-doa was prepared from dodecylamine (5 mmol, 0.945 g), 4-Hydroxybenzoic acid (5 mmol, 0.690 g), and paraformaldehyde (12.5 mmol, 0.387 g) as previously described for 4HBA-oca, (Yield: 78%)

^1^H NMR (DMSO-d₆, frequency: 300 MHz, ppm: δ, 298K): 1.31-1.47 (10H, CH₂─CH₂─CH₂), 3.95 (2H, Ar─CH₂─N), 4.87 (2H, O─CH₂─N), 6.77-7.68(3H, Ar─H).

FTIR (KBr, cm⁻¹): 1700 (the C═O stretching of the carboxylic group), 1240 (the stretching of Ar─O─C), 938 (out-of-plane vibration, benzene ring to which oxazine is attached).

2.2.4 Polymerization of benoxazine monomers and ionization of polymeric benoxazines

1.0 gram of each monomeric benoxazine, 4HBA-oca, 4HBA-dea, and 4HBA-doa, was polymerized on separate glass plates by following the same heating procedure in an air circulating oven at 160 °C for 30 minutes.

1.0 gram of each polymerized benoxazine monomer, abbreviated as poly(4HBA-oca), poly(4HBA-dea) and poly(4HBA-doa), was weighed separately into a 50 mL beaker. Since the starting monomers are monofunctional benoxazines, the polymers
formed are at best small oligomers with molecular weight in the range of 2000-6000 [38]. The designated amount of NaOH (to neutralize all carboxylic acid groups) was dissolved in 20 mL of deionized water, and then added to the polybenzoxazine oligomer. The beaker containing polybenzoxazine oligomer sample and base solution was placed in an ultrasonic bath until the solid was dissolved. The solution was then filtered with a filter paper and cooled to room temperature. The resulting polymer was dried overnight at 60 °C in an air circulating oven to a constant weight.

### 2.3 Measurements

Proton nuclear magnetic resonance (¹H NMR) spectra were taken on a Varian Gemini 2000 NMR operating at a proton frequency of 300 MHz. All samples were dissolved in deuterated dimethylsulfoxide (DMSO-d₆).

Fourier transform infrared (FTIR) spectroscopic analysis was carried out on a Bomem Michelson MB100 Spectrophotometer with a deuterated triglycine sulfate detector. After casting a thin film onto a KBr plate and purging with dry air, coadded spectra of 64 scans were recorded at a spectral resolution of 4 cm⁻¹.

Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC Model 2920 at a heating rate of 10 °C/min from 25 to 300 °C and nitrogen flow rate of 62 mL/min; 2mg samples were sealed between aluminum hermetic pans and lids for all tests.

Thermogravimetric analysis (TGA) was performed with a TA Instruments High Resolution 2950 Thermogravimetric Analyzer at a heating rate of 10 °C/min from 25 to
800 °C and nitrogen purge at a flow rate of 40 mL/min; 5 mg samples were placed in an open platinum crucible for all tests.

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), was performed with a triple detector array from Viscotek GPCmax instrument (Malvern instruments, Worcestershire, UK). The Viscotek SEC apparatus equipped with three-column set-up with pore size of 10, 50 and 1000 nm with common particle size of 5 mm using THF as an eluent, was pumped through the columns at a rate of 1.0 ml/min. Volume of injection was 75µL. The Viscotek system contains the following detectors in order: a 90° angle light scattering detector (LS), a refractive index detector (RI, concentration detector), and a four-capillary differential viscometer. The wavelength of the light scattering laser used was 670 nm. OmniSEC software was used for data analysis and acquisition. The number average molecular weights (M_n) and polydispersity index (M_w/M_n) were calculated relative to polystyrene standards.

Surface tension measurements of aqueous solutions were carried out with KRÜSS Tensiometer (K100) using the Wilhelmy platinum plate method. All measurements were carried out at 23±0.1 °C. Reproducibility was checked by frequent determination of the surface tension of de-ionized distilled water (72–73 mN/m).
2.4 Results and Discussion

2.4.1 The molecular structures of synthesized monomers and oligomers

Benzoxazines are typically hydrophobic materials and show limited solubility in water. The interfacial and association behavior of anionic polymeric surfactants based on benzoxazine chemistry are reported for the first time by observing the surface tension change of water versus surfactant concentration. The polymerized benzoxazines contain alkyl chain as hydrophobic segment, carboxylic moieties attached to phenolic rings as hydrophilic segment, and the rings connected by Mannich bridge as the backbone. Formation of the Mannich bridge structure is due to the ring-opening of benzoxazine in acidic media [39]. The segments are distributed throughout the whole polymer backbone in the form of a comb-like polymer. Figure 2.1 shows the hydrophilic and hydrophobic segments of the proposed structures for the three surfactants. The anionic polymeric surfactants introduced here have quite unusual properties in terms of high affinity for the air/water interface at low concentration, low critical micelle concentration, cmc, and high water-solubility. The hydrophobicity of the synthesized polymeric surfactants was varied by using three different chain lengths of the primary amine, C8, C10, and C12. The three benzoxazine monomers were synthesized following the same procedure as shown in Scheme 2.1. Scheme 2.2 shows the ionization of the oligomers which correspond to Figure 2.1.
Figure 2.1 Representative structures of the three anionic polymeric surfactants, the symbol i is the degree of polymerization.

\[
\begin{align*}
\text{poly(4HBA-oca-Na^+)} & \quad \text{poly(4HBA-dea-Na^+)} & \quad \text{poly(4HBA-doa-Na^+)} \\
\end{align*}
\]

Scheme 2.1 The synthesis of benzoxazine monomers 4HBA-oca, 4HBA-dea and 4HBA-doa.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Amine</th>
<th>n+1</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>4HBA-oca</td>
<td>CH₃(CH₂)₇NH₂</td>
<td>8</td>
<td>243</td>
</tr>
<tr>
<td>4HBA-dea</td>
<td>CH₃(CH₂)₉NH₂</td>
<td>10</td>
<td>271</td>
</tr>
<tr>
<td>4HBA-doa</td>
<td>CH₃(CH₂)₁₁NH₂</td>
<td>12</td>
<td>299</td>
</tr>
</tbody>
</table>
Scheme 2.2 The proposed oligomer structures of poly(4HBA-oca), poly(4HBA-dea) and poly(4HBA-doa) and the ionization of these polymers into poly(4HBA-oca` Na+), poly(4HBA-dea` Na+) and poly(4HBA-doa` Na+), respectively; n in Scheme 1, and the symbol i is the degree of polymerization.

2.4.2 NMR analysis

The $^1$H NMR spectra shown in Figure 2.2 clearly reveal the benzoaxazine ring formation for 4HBA-oca, 4HBA-dea, and 4HBA-doa. The characteristic resonances attributed to benzoaxazine structure are observed at 3.95-3.96 ppm (s, Ar─CH$_2$─N) and 4.87-4.89 ppm (s, N─CH$_2$─O─), which are consistent with the formation of benzoaxazine ring [15].
Figure 2.2 The $^1$H NMR spectra of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.

2.4.3 FTIR analysis

Moreover, the FTIR spectra of 4HBA-oca, 4HBA-dea, and 4HBA-doa as illustrated in Figure 2.3 show the characteristic absorption bands of benzoxazine structure at 1240 cm$^{-1}$ due to the stretching of C─O─C and at 940 cm$^{-1}$ due to the out-of-plane bending vibration of the benzene ring attached to the oxazine [40]. The IR spectrum taken at room temperature shown in Figure 2.4 indicates the weakening of the characteristic bands of benzoxazine at 1460, 1240, and 940 cm$^{-1}$. Disappearance of these bands after polymerizing at 80 °C, 120 °C and 160 °C confirms ring-opening of
benzoxazine moieties and the formation of polybenzoxazine. Similar thermal behavior was also observed for 4HBA-oca and 4HBA-dea.

Figure 2.3 FTIR spectra of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.
Figure 2.4 The FTIR spectra of 4HBA-doa after polymerization at 80 °C, 120 °C and 160 °C for 30 min.

2.4.4 DSC and TGA studies

Thermally accelerated ring-opening polymerization of 1,3-benzoxazines is an autocatalytic, exothermic process having a maximum around 200-270 °C depending on the functionalities of the benzoxazines [17]. The polymerization behavior of the monomers was examined by DSC. The melting point, onset temperature, maximum temperature and the amount of exotherm for 4HBA-oca, 4HBA-dea and 4HBA-doa are illustrated in Figure 2.5. The exotherm corresponding to the ring opening polymerization is observed for all three monomers. 4HBA-oca has an exotherm with an onset at 130 °C and a maximum peak at 184 °C, corresponding to the polymerization of benzoxazine with
a heat of polymerization, ΔH, of 75 J/g. For 4HBA-dea, the exotherm starts at 135 °C with a maximum at 187 °C and ΔH of 67 J/g. Finally, for 4HBA-doa, the exotherm starts at 142 °C with a maximum at 190 °C and ΔH of 61 J/g. These exotherm temperatures are unusually low in comparison to ordinary benzoxazine monomers [17] due to the effective catalytic role of carboxylic acid in the polymerization [41]. Benzoxazine monomers containing carboxylic acid groups show similar acceleration of the rate of polymerization [24, 42]. The melting points for 4HBA-oca, 4HBA-dea and 4HBA-doa are sharp indicating good purity of the monomers used. 4HBA-oca with chain-length C8 has a melting point of 92 °C and 4HBA-doa with chain-length C12 has a melting point of 99 °C. This increase in melting point with chain length is attributed to the increase of the hydrophobic interactions between the nonpolar alkyl groups. These benzoxazine monomers have low melting points compared to other benzoxazine monomers with aromatic functional groups [24].
Figure 2.5 The DSC thermograms of benzoxazine monomers 4HBA-oca, 4HBA-dea, and 4HBA-doa.

Figure 2.6 shows the DSC thermograms of 4HBA-oca at various thermal treatments. After each polymerization cycle for 4HBA-oca, the exotherm decreases with increasing temperature and almost disappears after polymerization at 120 °C for 30 minutes. The heat of polymerization decreases from 75 J/g to 0 J/g as the temperature is increased from 80 °C to 160 °C, indicating the disappearance of benzoxazine structure. The endotherm around 218 °C is due to the degradative evaporation of the amine moiety, as discussed later. The overlap of this endothermic peak with the polymerization exotherm makes the determination of the heat of polymerization slightly inaccurate, especially at high conversion.
The ring opening behavior was also monitored by the decreasing intensity and final disappearance of C-O-C band at 1240 cm\(^{-1}\) in sequential FTIR spectra in Figure 2.4. Moreover, Figure 2.6 reveals that ring-opening of benzoxazine moieties at 160 °C is almost complete after 30 minutes, and these cycles were also investigated by FTIR.

![Figure 2.6](image)

**Figure 2.6** Dynamic DSC plots for 4HBA-oça polymerization at various temperatures for 30 minutes.

The thermal stability of benzoxazine polymers was analyzed by TGA and the results are shown in Figure 2.7.A. The first weight loss of about 45% that was observed around 200 °C for the three polymers is attributed to the degradation of linear aliphatic amine. Figure 2.7.B shows the FTIR spectrum of the condensate from poly(4HBA-oça) after heating at 200 °C for 20 min and collecting the vapor phase. The FTIR spectrum of
octylamine used to produce poly(4HBA-oca) is included in Figure 2.7.B for comparison. Comparison of the two spectra indicates the cleavage of the alkyl chain in the polymer due to thermal cracking. Expectedly, the cleaved species did not show the NH stretching mode at 3330 cm\(^{-1}\) due to the lack of the primary amine structure. Detailed molecular mechanisms of fragmentation and the structure of the fragmented species have been reported in the literature [43-47].

Furthermore, the DSC endotherms of benzoxazine monomers shown in Figure 2.5 in the temperature range from 205 °C to 230 °C \((T_{\text{max}}=218 °C)\) are mainly attributed to the cracking reactions that lead to the cleavage of aliphatic side chain: These endotherms are consistent with the TGA weight loss from 200 °C to 230 °C. The second weight loss of about 15% observed between 300 °C and 400 °C can be ascribed to decarboxylation of acid groups on the polybenzoxazines. The temperatures with 5% and 10% weight loss under nitrogen environment are: 176 and 192 °C for poly(4HBA-oca), 177 and 193 °C for poly(4HBA-dea), 179 and 200 °C for poly(4HBA-doa), respectively. These polymers show a low char yield of 20-25% when the residual weight is examined under nitrogen at 800 °C. This char yield is low because of the existence of aliphatic chains.
Figure 2.7.A TGA curves of poly(4HBA-oca), poly(4HBA-dea), and poly(4HBA-doa).

Figure 2.7.B FTIR spectra of the condensate of the evolved gases at the peak rate degradation of poly(4HBA-oca) and octylamine.
2.4.5 Determination of molecular weights by SEC

Size exclusion chromatography (SEC) coupled with Viscotek triple detection technique (light scattering, viscometry and refractometry) was used to determine the molecular weight of each peak coming off the column and simultaneously measure the hydrodynamic radius and polydispersity of polymeric benzoxazines. Table 2.1 shows the analytical results for molecular weight distributions and related properties. The experimental results demonstrate that the polydispersity is large probably because of the presence of long-chain branched polymers. The branching leads to poor separation in SEC, and significantly changes the hydrodynamic volume [48].

To know the shape of the polybenzoxazines in the eluting solution (THF) the radius of gyration \( R_g \) was calculated by using the Flory-Fox and Ptitsyn-Eisner equations [49]:

\[
R_g = \left( \frac{1}{6} \right)^{1/2} \left( \eta \left( \frac{M}{F} \right) \right)^{1/3}
\]

Where \( M \) is the molecular weight, \( [\eta] \) is the intrinsic viscosity, and \( F \) is obtained from

\[
F = 2.86 \times 10^{21} (1 - 2.63\varepsilon + 2.86\varepsilon^2)
\]

and

\[
\varepsilon = \left( \frac{2a-1}{3} \right)
\]

Here \( a \) is the exponent of the Mark-Houwink-Sakurada equation:

\[
[\eta] = K M^a
\]

The shape ratio \( \frac{R_g}{R_h} \) can be used as a qualitative measure in judging what architectural structure may be present [50]. The ratio \( \frac{R_g}{R_h} \approx 0.77 \) represents a sphere of uniform
density [51- 53]. The data obtained are fairly close to 0.77 and suggest spherical shape of uniform density for all three polybenzoxazines.

**Table 2.1**

Summary of analytical results for molecular weight distributions and related properties determined from SEC with triple detector.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ $^a$ (Da)</th>
<th>$M_w / M_n$</th>
<th>$R_h$ $^c$ (nm)</th>
<th>$[\eta]$ $^d$ (dl/g)</th>
<th>$\alpha$ $^e$</th>
<th>$R_g$ $^f$ (nm)</th>
<th>$R_g / R_h$ $^g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(4HBA-oct)</td>
<td>2248</td>
<td>3.319</td>
<td>1.364</td>
<td>0.0283</td>
<td>0.135</td>
<td>0.942</td>
<td>0.690</td>
</tr>
<tr>
<td>Poly(4HBA-dea)</td>
<td>6021</td>
<td>1.328</td>
<td>1.378</td>
<td>0.0242</td>
<td>0.090</td>
<td>1.215</td>
<td>0.881</td>
</tr>
<tr>
<td>Poly(4HBA-doa)</td>
<td>4936</td>
<td>1.232</td>
<td>1.334</td>
<td>0.0251</td>
<td>0.057</td>
<td>1.133</td>
<td>0.849</td>
</tr>
</tbody>
</table>

$^a$ Number average molecular weight  
$^b$ Polydispersity  
$^c$ Hydrodynamic radius  
$^d$ Intrinsic viscosity  
$^e$ Mark-Houwink constant  
$^f$ Radius of gyration  
$^g$ Shape ratio  

The molecular weights of the polybenzoxazines depend on the polymerization mechanism as well as interchain hydrogen bonding and the interactions between the alkyl chains. The ring opening initiation of benzoxazine polymerization produces a carbocation and an iminium ion in equilibrium [54], and the propagation rate is controlled by the carbocation. If the iminium ion is stable the propagation rate is low. However, if the iminium ion is unstable the propagation rate is high [54]. The length of the alkyl chain attached to the iminium ion obviously affects its stability. In this work, the results indicate a wide range of polybenzoxazines molecular weights (2200 to 6000 Da), where the poly(4HBA-dea) and poly(4HBA-doa) exhibit a narrow range of molecular weights.
(5000 to 6000 Da) and the poly(4HBA-oct) shows a lower molecular weight (2200 Da). This variation is attributed to the short chain length of poly(4HBA-oct) that results in low hydrophobicity in the polar eluent. These observations in the molecular weights are consistent with the values of the radius of gyration presented in Table 2.1.

The values of the degree of polymerization for poly(4HBA-oca), poly(4HBA-dea) and poly(4HBA-doa) are 9, 22 and 16, respectively. The carboxylic acid group of the three polybenzoxazines were neutralized by adding required amount of NaOH as shown in Scheme 2.2, and converted to polymeric surfactants, poly(4HBA-oca\(\text{Na}^+\)), poly(4HBA-dea\(\text{Na}^+\)) and poly(4HBA-doa\(\text{Na}^+\)), respectively.

2.4.6 Surface tension measurements

The variation of surface tension with the concentration of the anionic polymeric surfactants in water is shown in Figure 2.8.A and B. The reduction of the surface tension by the polymeric surfactants due to adsorption at the air–water interface is observed at very low concentrations. In addition, Figure 2.8.B shows the surface tension as a function of the molar concentration of the polymeric surfactants. The cmc decreases with increasing molecular weight of the polybenzoxazine surfactants. Least square regression analysis was performed to find the best equation for each of the linear portion below the cmc (the pre-cmc line) and the portion above the cmc (the post-cmc line). The surface tension plots exhibit a shallow minimum which indicates the effect of polydispersity as observed in SEC analysis. Figure 2.9 shows that the cmc increases quite significantly.
from 0.12 g/L to 0.17 g/L with increase in alkyl chain length from C8 to C12 due to the hydrophobic effect. However, varying alkyl chain length does not affect the cmc.

Figure 2.8.A Surface tension at different weight concentrations.

Figure 2.8.B Surface tension at different molar concentrations.
The presence of NaCl at a fixed temperature lowered the cmc’s of the polybenzoxazine surfactant solutions compared to those evaluated for the salt-free polybenzoxazine surfactant solutions at $23\pm0.1^\circ$C. Figures 2.10.A, B and C show a progressive increase in surface activity for rising polybenzoxazine surfactant concentrations, with the salt containing systems showing a slight reduction in surface tension compared to the salt free systems. Figure 2.11 shows the presence of salt reducing the surface tension and the cmc of the polybenzoxazine surfactant solutions compared to salt free polybenzoxazine surfactant solutions. The minimum values of the $\gamma_{\text{cmc}}$ approached at the 1 wt% of NaCl for the polybenzoxazine surfactant solution. For example, the $\gamma_{\text{cmc}}$ of the poly(4HBA-o-c$\alpha$ Na$^+$) solution was gradually decreased by increasing salinity from 38 mN/m at 0 wt% NaCl to 27 mN/m at 1 wt% NaCl, and then
gradually increased by increasing salinity to 30 mN/m at 3 wt% NaCl. Only slight decreases in $cmc$ values were observed with increasing salinity from 0 to 3 wt% of NaCl for the polybenzoxazine surfactant solution, Table 2.2. The mechanism of surface tension reduction is due to the increase in diffusion of surfactant from bulk to the air-liquid interface by the electrolyte [55]. The effect can be observed at very low polymeric surfactant concentrations, where the pure polymeric surfactant cannot adsorb at the air–water interface. Further, adding salts tend to screen electrostatic repulsions between the head groups of the amphiphiles, and make the amphiphiles effectively more hydrophobic. It then increases hydrophobic interactions among the surfactant monomers and cause them to aggregate at lower concentration, thus the $cmc$ decreases [56].

![Figure 2.10.A](image.png)

**Figure 2.10.A** The effect of salinity on the surface tension of different poly(4HBA-oca$^-$ Na$^+$) solutions.
Figure 2.10.B The effect of salinity on the surface tension of different poly(4HBA-dea\(^-\) Na\(^+\)) solutions.

Figure 2.10.C The effect of salinity on the surface tension of different poly(4HBA-doa\(^-\) Na\(^+\)) solutions
Figure 2.11 The effect of salinity on the *cmc* and the surface tension at *cmc* (*γ_{cmc}* of the solutions of poly(4HBA-oca` Na⁺), poly(4HBA-dea` Na⁺) and poly(4HBA-doa` Na⁺)

The maximum surface excess concentration (*Γ_{max}* ) and minimum surface area per surfactant headgroup (*α_s* ) were calculated, respectively, according to:

\[ Γ_{max} = -\frac{1}{2RT} \left[ \frac{\partial γ}{\partial \ln(m/m_0)} \right]_{P,T} \]  

\[ α_s = \frac{1}{N_A Γ_{max}} \]
where $R$ is the gas constant, $T$ is the absolute temperature, $N_A$ is the Avogadro constant and $m$ is the surfactant molal concentration ($m^o=1 \text{ mol kg}^{-1}$).

$\Gamma_{\text{max}}$ is a useful measure of the effectiveness of adsorption of the surfactant at the air-water interface, and $\alpha_s$ provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule. The cmc, $\gamma_{\text{cmc}}$, $\Gamma_{\text{max}}$ and $\alpha_s$ data as a function of the ionic strength are collected in Table 2.2. With increasing salinity from 0 to 1 wt%; the $\Gamma_{\text{max}}$ and the $\alpha_s$ of poly(4HBA-oca$^+\text{-Na}^+$) and poly(4HBA-doa$^+\text{-Na}^+$) slightly increased and slightly decreased, respectively. The $\Gamma_{\text{max}}$ and the $\alpha_s$ of poly(4HBA-dea$^+\text{-Na}^+$) showed rapid increase and rapid decrease, respectively. The $\Gamma_{\text{max}}$ difference in response to increasing salinity is possibly due to the different molecular weights of (4HBA-oca$^+\text{-Na}^+$), poly(4HBA-doa$^+\text{-Na}^+$) and poly(4HBA-dea$^+\text{-Na}^+$). The poly(4HBA-dea$^+\text{-Na}^+$) with the highest molecular weight showed rapid increase in the $\Gamma_{\text{max}}$. With increasing salinity from 1 to 3 wt%; the $\Gamma_{\text{max}}$ and the $\alpha_s$ tends to decrease and increase, respectively, for (4HBA-oca$^+\text{-Na}^+$), poly(4HBA-doa$^+\text{-Na}^+$) and poly(4HBA-dea$^+\text{-Na}^+$) with different response that may related to their different molecular weights. This trend accompanying the salinity change means that, with increasing salinity, more surfactant molecules are adsorbed when the surface is saturated, resulting in a higher packing density and lower $\gamma_{\text{cmc}}$. Certainly, at high salt concentrations above 1 wt% the salt ions reduce the electrostatic repulsion between the intermolecular head groups, and the electrostatic repulsion become invariable leads the cmc values to become constant [55, 56]. As the concentration of NaCl increases, the electrical double-layer thickness ($1/\kappa$), as measured by the Debye length, decreases sharply. At 1 wt% the $1/\kappa$ was 0.734 nm, and at 3 wt% the $1/\kappa$ was 0.424 nm. The $1/\kappa$ and the forces involving
water structures play a significant role in influencing salinity on $\Gamma_{\text{max}}$. The ions in NaCl affect the structure of water where the $\text{Na}^+$ ions (structure-making ions) promote hydrogen bonding of neighboring waters, and the $\text{Cl}^- \text{ ions}$ (structure-breaking ions) promote electrostatic interaction with the neighboring waters [57]. The structure-making ions tend to flee the air/water interface because they can better organize the water dipoles in bulk water than at the interface. The structure-breaking ions pushed toward the air/water interface by the bulk water because the bulk water molecules can better organize its hydrogen-bond network without the structure breaking ions in order to minimize the system free energy to the lowest values [58]. This trend observed in our experiments when increasing the salinity from 1 to 3 wt%. The diffusion of $\text{Cl}^-$ ions to the air/water interface leads the head groups to become more hydrophilic and decrease the surface excess concentration ($\Gamma_{\text{max}}$) resulting increase in the minimum surface area per surfactant headgroup ($\alpha_s$).
Table 2.2
Influence of NaCl concentration on the cmc, $\gamma_{\text{cmc}}$, $I_{\text{max}}$, and $\alpha_s$ of poly(4HBA-oca`Na$^+$), poly(4HBA-dea`Na$^+$) and poly(4HBA-doa`Na$^+$)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>NaCl (wt%)</th>
<th>cmc (g/L)</th>
<th>$\gamma_{\text{cmc}}$ (mN/m)</th>
<th>$I_{\text{max}}$ (µmol.m$^{-2}$)</th>
<th>$\alpha_s$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(4HBA-oca`Na$^+$)</td>
<td>0</td>
<td>0.120±0.002</td>
<td>38.04±0.24</td>
<td>2.368</td>
<td>0.701</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.118±0.020</td>
<td>27.15±3.46</td>
<td>2.691</td>
<td>0.616</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.116±0.04</td>
<td>30.56±1.73</td>
<td>1.419</td>
<td>1.169</td>
</tr>
<tr>
<td>poly(4HBA-dea`Na$^+$)</td>
<td>0</td>
<td>0.123±0.021</td>
<td>38.07±0.85</td>
<td>1.782</td>
<td>0.931</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.121±0.001</td>
<td>28.70±0.43</td>
<td>2.353</td>
<td>0.705</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.116±0.011</td>
<td>31.56±1.73</td>
<td>1.669</td>
<td>0.994</td>
</tr>
<tr>
<td>poly(4HBA-doa`Na$^+$)</td>
<td>0</td>
<td>0.173±0.004</td>
<td>39.11±0.56</td>
<td>2.439</td>
<td>0.680</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.164±0.005</td>
<td>34.45±0.39</td>
<td>2.457</td>
<td>0.675</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.148±0.004</td>
<td>35.83±0.87</td>
<td>1.640</td>
<td>1.012</td>
</tr>
</tbody>
</table>

The cmc values at 23±0.1 °C obtained in this work are comparable with the values reported for both the low molecular weight surfactants such as sodium dodecylsulfate (SDS) [59], and the high molecular weight surfactants such as carboxymethyl cellulose-based polymeric surfactant (CMC-polymeric surfactant) [60]. Addition of NaCl did not change the surface tension of the CMC-polymeric surfactant solutions, though they have anionic group –COO$. The influence of NaCl on the surface tensions of the polybenzoxazine surfactant solutions was investigated and was reported minima at 1 wt% NaCl. A further comparison between the polybenzoxazine surfactants and some polymeric surfactant reported in literature showed that polybenzoxazine surfactants provided slightly lower $\gamma_{\text{cmc}}$ [8-10, 60].
2.5 Conclusions

The synthesis of novel anionic polymeric surfactants from benzoxazine monomers is reported. The structure of these compounds was determined via FTIR and \(^1\)H NMR spectroscopy. Ring-opened structures were also identified by using FTIR and DSC. The 4HBA-oca, 4HBA-dea and 4HBA-doa showed single exothermic peaks at 184 °C, 187 °C and 190 °C, respectively, which are relatively low due to the effective catalytic nature of the carboxylic acid. TGA showed 45% weight loss around 200 °C for the three benzoxazine polymers, which is attributed to the degradation of linear aliphatic amine. The branched polybenzoxazines have low number average molecular weight (M_n ~ 2200-6000) and high polydispersity (M_w/M_n ~ 1.2-3.3).

Surface tension measurements at the air/water interface clearly show the high surface activity of the anionic polybenzoxazines surfactants. The cmc increases from 0.12 g/L to 0.17 g/L with change in alkyl chain length from C8 to C12. The cmc values at 23±0.1 °C are comparable with literature values reported for polymeric surfactants [8-10, 60]. While surface tension measurements of nonionic polymerizable benzoxazine surfactants have been reported, their cmc values were not determined [36, 37].

The raw materials of these new surfactants are available at low-cost, and the simple purification process ensures high yield and purity. These surfactants have potential applications in many fields including detergency, personal care products such as shampoo, coatings, inks, and for the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsions. A detailed study of the micellization thermodynamics of these surfactants in aqueous media, and the properties and stability of (O/W) emulsion systems made by these surfactants will be the subject of a forthcoming paper.
2.6 References


Chapter 3

3. Anionic Surfactants Based on Comb-like Polybenzoxazine Oligomers: Effect of Salinity and Temperature on Critical Micelle Concentration
3.1 Introduction

Polymeric surfactants attracted considerable attention in recent years for application in personal care product and stabilization of emulsions and suspensions [1]. The characteristic properties of polymeric surfactants originate from the formation of micelle-like aggregates through the association of the hydrophobic alkyl chains in aqueous solution, within a narrow concentration range [2]. Polymeric surfactant micellization process in aqueous media has attracted only little attention as compared to the vast number of extensive studies reported in the literature dealing with monomeric surfactant micellization in aqueous media. The polymeric surfactants may form monomolecular-layer micelles or aggregates of multimolecular-layer micelles of various shapes. As the aggregates are formed, most of the physical and rheological properties of the polymeric surfactant solutions change abruptly. Over a narrow concentration range the critical micelle concentration (cmc), above which micelles are formed in the solutions. The characteristics of these aggregates are easily controlled by the change in the solution conditions such as temperature, concentration and ionic strength, and by the change in the surfactant properties such as chain length, hydrophobic volume and head group area [3-6]. Micellar aggregation can be demonstrated by measurements of physical properties, such as surface tension, against surfactant concentration. As surfactant concentration is increased, surface tension falls to a minimum at the cmc [7]. An important factor that influences cmc is the temperature. The study of cmc versus temperature is reported in the literature for ionic surfactants to probe hydrophobic and head group interactions [8]. The available data indicate that the cmc decreases with
the increase in temperature of the system [9]. The thermodynamic parameters of micellization in aqueous solutions; the standard Gibbs free energy of micellization, $\Delta_{\text{mic}} G^\circ$, the enthalpy of micellization, $\Delta_{\text{mic}} H^\circ$ and the entropy of micellization, $\Delta_{\text{mic}} S^\circ$, can be derived from the temperature dependence of the cmc. They quantify the relative importance of hydrophobic interactions, surfactant-water contact and head-group repulsion. $\Delta_{\text{mic}} G^\circ$ is also the free energy of transfer of one surfactant from the aqueous phase to the micellar pseudophase.

In previous paper [10] we introduced a series of novel anionic polymeric surfactants based on comb-like polybenzoxazine oligomers. In this study experimental values of enthalpy and entropy of micellization in aqueous solutions of these surfactants are calculated and the effects of solution conditions such as concentration, temperature and salinity in the micellization process are reported. The significance of the enthalpy and entropy of micellization of anionic polymeric surfactants and their relation to the theory of micelle formation is considered. These anionic surfactants with univalent counterion are considered 1-1 electrolytes.

### 3.2 EXPERIMENTAL

#### 3.2.1 Chemicals

Three anionic polymeric surfactants, based on Comb-like Polybenzoxazine Oligomers, named; poly(4HBA-oca` Na⁺), poly(4HBA-dea` Na⁺), and poly(4HBA-doa` Na⁺) used during this study were reported somewhere else in the literature [10]. Ions free
water was used as solvent. The salt used in this study was NaCl and this salt was purchased from Fisher Scientific.

3.2.2 Preparation of solutions

Stock solution of poly(4HBA-oca\(^+\) Na\(^+\)), poly(4HBA-dea\(^-\) Na\(^+\)), and poly(4HBA-doa\(^-\) Na\(^+\)) were prepared by dissolving a known amount of these surfactants, either in pure (ion free) water or in the solution of known NaCl concentration. Solutions were kept in identical glass containers and the container wall was kept at a minimum to reduce the effects due to adsorption on the container. Solutions so prepared were used for viscosity, conductance and surface tension measurements.

3.3 Measurements

3.3.1 Surface tension measurements

The surface tension of solutions was determined by means of Wilhelmy platinum plate method and Du Nouy ring platinum (diameter: 19.6 mm, thickness: 0.1 mm) on KRÜSS Tensiometer (K100). The maximum force \(F_{\text{max}}\) exerted on the surface of the lamella is measured as it is removed from the solution just before it breaks. The unit of measurement is given in milliNewton/m (mN/m). Temperature was controlled with a jacket linked to a water circulating system (± 0.1 °C). Reproducibility was checked by frequent determination of the surface tension of de-ionized distilled water. The results show accuracy within ±0.1 mN/m\(^{-1}\). The results were the average of three measurements. The vessel covered with a hole only allowing a small ring (Du Nouy ring) to go through,
to prevent the contamination of the solution from dust in the air during the operation. The whole vessel was placed inside a closed sample chamber of the surface tensiometer. The maximum surface excess concentration, $\Gamma_{\text{max}}$, and the minimum surface area per surfactant headgroup, $a_s$, were calculated, respectively, according to:

$$\Gamma_{\text{max}} = -\frac{1}{2RT} \left[ \frac{\partial \gamma}{\partial \ln \left( \frac{m}{m^o} \right) } \right]_{p,T}$$  \hspace{1cm} (1)

$$a_s = \frac{1}{N_A \Gamma_{\text{max}}}$$  \hspace{1cm} (2)

where $R$ is the gas constant, $T$ is the absolute temperature, $N_A$ is the Avogadro constant and $m$ is the surfactant molal concentration ($m^o=1 \text{ mol kg}^{-1}$).

3.3.2 Viscosity measurements

The viscosity measurements were carried out using an Ubbelohde suspended-level capillary viscometer. The viscometer was suspended vertically in a thermostat used to provide a stable constant temperature of $30\pm0.1^\circ \text{C}$. The viscosity of polymeric surfactant solutions at different concentrations (0.01-1 wt %) was measured. The viscometer was carefully washed, rinsed and dried before use. The flow times for a constant volume of solution through the capillary were measured with a calibrated stopwatch. The viscometer was so selected that the solvent flow time was more than 100 seconds, in order to minimize the contribution of kinematic energy.

3.3.3 Dynamic light scattering

Dynamic light scattering (DLS) measurement performed on a laser light scattering spectrometer with ALV–5000E (ALV–GmbH, Langen, Germany), using He–Ne laser
with wavelength at 632.8 nm. Rayleigh ratio was calibrated with the value for toluene
\((1.3522 \times 10^{-5} \text{ cm}^{-1})\). The sample solution at 0.5 g/L poly(4HBA-o-aca Na+) content was
subjected to measurements after optical clarification with a 0.45-\(\mu\)m Millipore filter into a
clean scintillation vial, and the sample was characterized by DLS at 25 °C and at the
measurement angles 60°, 90° and 130°.

3.3.4 Foaming power measurements

The foam height was measured following a method reported in this paper for the
first time as follows; the method uses a 100 ml graduated cylinder with polypropylene
stopper. The cylinder manufactured from thermally-stable borosilicate glass with the
specifications of; readability: 1 ml, height: 25 cm, diameter of cylinder: 3.1 cm. An
amount of 40 ml from a solution of surfactant (75 ppm or 150 ppm) contained in the
cylinder at a given temperature (25°C). The samples were shaken for 30 seconds by hand
on a standard way, hold the cylinder from the middle and shake it fast by raising your
hand up and down with frequency of one cycle each second. The foam height produced in
the cylindrical was read immediately after all the solution shake had run out of the
cylinder (initial foam height) and again after a given amount of time (generally 1min and
5 min). The experiment repeated 4 times for reliability.

3.3.5 Conductance measurements

Measurements of the electric conductivity \((k)\) were carried out by using a
conductivity meter (Fisher Scientific accumet basic AP65 Portable Conductivity Meter).
The measurements were achieved when the sample solution was carefully adapted to a definite temperature to avoid any disturbance coming from nonequilibrium states that arise from temperature shifts.

3.4 Results and Discussion

The use of polymeric surfactant is widely spread both in industry such as stabilizer of suspensions, and for domestic or personal care purpose [1, 3]. However, their activity as surfactants starts after micellization. Figure 3.1 shows the mechanism of micelle formation as an aggregate. The molecules aggregate to form micelles when the surfactant concentration is above a certain concentration called the critical micelle concentration (cmc). The non-polar chains come close to each other to form a hydrophobic core in such a way that the polar ends point towards the aqueous medium. Due to this aggregation almost all the physical properties change. To investigate the aggregation phenomena, we measured the viscosity and surface tension for the cmc determination.
Figure 3.1 A schematic representation of micelles formation by a polymeric surfactant in aqueous media; unimer-to-aggregate transition.

Figure 3.2 shows the hydrophilic and hydrophobic segments of the structures of the new anionic polymeric surfactants, based on comb-like polybenzoxazine oligomers. The olefin backbone with straight chain alkane is the hydrophobic segments and the carboxylic moieties act as hydrophilic segments distributed throughout the copolymer backbone, both in the form of a comb-polymer. The hydrophobicity of these surfactants depends on the alkyl-chain-length.
The degree of polymerization for the poly(4HBA-oca\(^{-}\) Na\(^{+}\)), poly(4HBA-dea\(^{-}\) Na\(^{+}\)) and poly(4HBA-doa\(^{-}\) Na\(^{+}\)) are: 9, 22, and 16, respectively. The surface tension variation with the concentrations of the anionic polymeric surfactants for the solutions of poly(4HBA-oca\(^{-}\) Na\(^{+}\)), poly(4HBA-dea\(^{-}\) Na\(^{+}\)) and poly(4HBA-doa\(^{-}\) Na\(^{+}\)) was reported recently [10]. A summary of their surface activity properties are presented in Table 1.

**Table 3.1** Summary of the surface activity properties of poly(4HBA-oca\(^{-}\) Na\(^{+}\)), poly(4HBA-dea\(^{-}\) Na\(^{+}\)) and poly(4HBA-doa\(^{-}\) Na\(^{+}\))

<table>
<thead>
<tr>
<th>Property</th>
<th>poly(4HBA-oca(^{-}) Na(^{+}))</th>
<th>poly(4HBA-dea(^{-}) Na(^{+}))</th>
<th>poly(4HBA-doa(^{-}) Na(^{+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>cmc (g/L)</td>
<td>0.120±0.002</td>
<td>0.123±0.021</td>
<td>0.173±0.004</td>
</tr>
<tr>
<td>(\gamma_{\text{cmc}}) (mN/m)</td>
<td>38.04±0.24</td>
<td>38.07±0.85</td>
<td>39.11±0.56</td>
</tr>
</tbody>
</table>
Surface tension variations over time measured with the Wilhelmy Plate are shown in Figure 3.3 for three concentrations of poly(4HBA-doa^−Na^+). The surface tension measuring time period is 60 s. At low viscosity with the 0.01 wt% solution has the lowest viscosity, the liquid film above the meniscus drains fast, and the surface tension is essentially constant over time. On the contrary, the 0.067 wt% solution has higher liquid viscosity drains slowly and reaches equilibrium contact angle after a short period thus the time dependence of the surface tension correlates with the viscosity of the surfactant solution.

Figure 3.3 Surface tension variation over time for the poly(4HBA-doa^−Na^+) solutions with various viscosities.

Figure 3.4 shows the maximum force (F_{max}) exerted on the surface of the lamella as it is removed from the poly(4HBA-oça^−Na^+) solution just before it breaks is measured for different concentrations. However, the higher the poly(4HBA-oça^−Na^+) concentration in
the solution the lower the maximum force ($F_{\text{max}}$) by the liquid on the ring. $F_{\text{max}}$ is directly proportional to the surface tension.

**Figure 3.4** The effect of poly(4HBA-oca $\cdot$ Na$^+$) concentration on both the lamella height and the maximum force at 21+0.1 °C

Viscosity measurements were made using a capillary glass viscometer or Ubbelohde viscometer at 30±0.1°C. Viscosity measurements provide valuable information on the association and conformation behavior of the polymeric surfactant. Figure 3.5 shows the increase in solution viscosity at different surfactant concentrations chosen to represent values below the critical micelle concentration (cmc), in the cmc region, and above the cmc. The variation in viscosity is attributed to the concentration and structural changes in the micelles. The variation of viscosity with concentration changes in the cmc region. The solution viscosity depends upon on the number of polymeric surfactant molecules as well as the
size and number of micelles. The number of monomers is essentially constant while the micelles size and number increase above the cmc. During the viscosity measurement, the micelles may have changed to separated individual molecules and hence it becomes difficult to find the cmc minima. The drastic increase in viscosity with concentration below the cmc may be due to the electroviscous effect rather than the hydrophobic segment interaction of the polymeric surfactants.

Figure 3.5 The viscosities of poly(4HBA-oca⁻ Na⁺), poly(4HBA-dea⁻ Na⁺), and poly(4HBA-doa⁻ Na⁺) solutions at different low concentrations, and constant temperature, 30±0.1 °C.

Figure 3.6 shows the effect of the addition of NaCl on the reduced viscosity (η_red) of poly(4HBA-doa⁻ Na⁺) solution at a concentration of 0.1g/L. The η_red of poly(4HBA-doa⁻ Na⁺) decreases from 0.012 L/g at 0.5 wt% to 0.002 L/g at 4 wt% salt concentration. As expected, the presence of NaCl affects the η_red of the anionic polymeric surfactant solution because of the
reduction in electroviscous effect resulting from the intramolecular repulsive interactions between ionized groups of the anionic polymeric surfactant molecules [11]. The intrinsic viscosity, $[\eta]$, was determined from Huggin’s equation by extrapolation to infinite dilution [12];

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2C \quad (6)$$

$$\eta_{sp} = \eta_r - 1 \quad (7)$$

Where; $\eta_{sp}$ and $\eta_r$ are the specific viscosity and the relative viscosity of the polybenzoxazine surfactant solution, $k$ is the Huggins’ constant, and $C$ is the polybenzoxazine surfactant solution concentration in g/L. The experiments were performed in concentrations of polymeric surfactant solutions lower than the cmc, and the flow time used in all subsequent calculations of $[\eta]$ was the average of at least four readings which agreed to within $\pm0.5$ second. The intrinsic viscosities were found to increase slightly with increasing the alkyl chain lengths of the polybenzoxazine surfactants; $[\eta]$ of poly(4HBA-oca$^-$Na$^+$) =2.8 L/g, $[\eta]$ of poly(4HBA-dec$^-$Na$^+$) =3.1 L/g, and $[\eta]$ of poly(4HBA-doa$^-$Na$^+$) =3.2 L/g, Figure 3.7. Hence, the increase in $[\eta]$ with increasing chain length can be attributed mainly to longer hydrophobic segment due to change in the polymeric surfactant structure. This explains the modest increase of viscosity with the chain length, particularly at high surfactant concentration.
Figure 3.6 Variation of reduced viscosity of 0.1g/L poly(4HBA-doa\textsuperscript{-}Na\textsuperscript{+}) solution with added NaCl.

Figure 3.7 Kraemer plot (intrinsic viscosity = (ln relative viscosity)/concentration vs. concentration) for poly(4HBA-oca\textsuperscript{-}Na\textsuperscript{+}), poly(4HBA-dec\textsuperscript{-}Na\textsuperscript{+}) and poly(4HBA-doa\textsuperscript{-}Na\textsuperscript{+}) solutions at different concentrations and 30±0.1 °C.
The presence of NaCl at a fixed temperature lowered the cmc of the polybenzoxazine surfactant solutions compared to the salt-free solutions at 23±0.1°C. Figure 3.8 illustrates that the presence of salt reducing the surface tension and the cmc of the polybenzoxazine surfactant solutions. The $\gamma_{\text{cmc}}$ approached an asymptotic value 1 wt% in case of poly(4HBA-doa⁻ Na⁺) solution. However, the $\gamma_{\text{cmc}}$ of the poly(4HBA-oca⁻ Na⁺) solution gradually decreased from 37 mN/m without NaCl to 29 mN/m at 3 wt% of NaCl. The decrease in cmc value observed with increasing salinity from zero to 3 wt% of NaCl. The mechanism of surface tension reduction is due to the increase in diffusion of surfactant from bulk to the air-liquid interface by the electrolyte [13]. The effect can be observed at very low polymeric surfactant concentrations. Adding salt tends to screen the electrostatic repulsion between the ionic head groups of the amphiphiles, and make the amphiphiles effectively more hydrophobic. It then increases hydrophobic interactions among the surfactant monomers and cause them to aggregate at lower concentration, thus the cmc decreases [14,15].
Figure 3.8 The effect of salinity on the cmc and the surface tension at cmc ($\gamma_{\text{cmc}}$) of the solutions of poly(4HBA-oca$^-\ Na^+$) (star), poly(4HBA-dea$^-\ Na^+$) (square), and poly(4HBA-doa$^-\ Na^+$) (triangle).
To investigate the effect of temperature, the surface tension was measured as a function of surfactant concentration at three different temperatures, 21, 38, and 48 °C, as shown in Figure 3.9. The cmc values and corresponding surface tension $\gamma_{\text{cmc}}$ are plotted in Figure 3.10. The cmc and $\gamma_{\text{cmc}}$ decreases with increasing temperature for poly(4HBA-oca`Na$^+$). This decrease in cmc due to the reason that the hydrophobic effect increases in strength as the temperature is raised [16], resulting attractive interaction of the nonpolar segments which aggregate to form a hydrophobic core. The same behavior is expected from the other surfactant, poly(4HBA-dea`Na$^+$) and poly(4HBA-doa`Na$^+$).

**Figure 3.9** The variation of surface tension as a function of poly(4HBA-oca`Na$^+$) concentration in aqueous solution at different temperatures (21, 38, and 48 °C).
Figure 3.10 The variation of cmc and $\gamma_{\text{cmc}}$ as a function of temperature for poly(4HBA-oca- Na$^+$).

The Gibbs energy of micellization for univalent ionic surfactants can be calculated from the mass action law model [17] according to:

$$\Delta_{\text{mic}}G^o = (1 + \beta)RT \ln X_{\text{cmc}}$$  \hspace{1cm} (3)

Where $\beta$ is the fraction of charges of micellized univalent surfactant ions neutralized by micelle-bound univalent counterions and $X_{\text{cmc}}$ is the surfactant cmc expressed in mol/dm$^3$ or surfactant molar fraction units.

The variation of the cmc with temperature allows for the determination of the enthalpy of micellization according to:

$$\Delta_{\text{mic}}H^o = (1 + \beta)R \left[ \frac{d \ln X_{\text{cmc}}}{d(1/\tau)} \right]_\rho$$  \hspace{1cm} (4)

and thus the entropy of micellization,

$$\Delta_{\text{mic}}S^o = \frac{\Delta_{\text{mic}}H^o - \Delta_{\text{mic}}G^o}{T}$$  \hspace{1cm} (5)
The mass action law model assumes that micelles comprised of \( n \) surfactant molecules are formed via the reaction

\[
nS + mG = (S^nG^m)^z = M^z
\]

in which \( z \) is the charge or the valence of the micelles.

However,

\[
\beta = \left( \frac{m}{n} - \frac{1}{n} \right)
\]

In this study, the anionic surfactants ions with univalent counterion are considered 1-1 electrolytes. So, \( m=n \) then \( \beta=0 \). Therefore, the values of \( \Delta_{\text{mic}}G^o \) have been calculated using these cmc’s and \( \beta = 0 \).

The thermodynamic parameters of micellization \( \Delta_{\text{mic}}G^o, \Delta_{\text{mic}}H^o \) and \( \Delta_{\text{mic}}S^o \) were determined using Eqs. (3)–(5), and are shown in Figure 3.11. The negative values of standard Gibbs energy change indicate spontaneous micellization; \( \Delta_{\text{mic}}G^o \) remains approximately constant over the studied temperature range. The observed \( \Delta_{\text{mic}}S^o \) values are positive, meaning that the entropy change is favorable to the formation of the micelles. The positive \( \Delta_{\text{mic}}S^o \) values are due to the destruction of ordered hydrogen bonded water structure in the vicinity of the hydrophobic chain [19]. So, the large gain in entropy occurs when water molecules in hydration shells around the hydrophobic parts are released during micellization. In addition, Figure 3.12 shows the micellization of anionic surfactants is endothermic, and in the temperature range of 21- 48°C the \( \Delta_{\text{mic}}H^o> 0 \). This endothermic behavior is a result from the sum of the enthalpy of association between the hydrocarbon tails \( (\Delta H_{\text{ass}} \leq 0) \), their dehydration, \( (\Delta H_{\text{desolvation}} \geq 0) \), and the repulsion between the hydrophilic headgroups, \( (\Delta H_{\text{head}} \geq 0) \), which is of particular importance in the case of charged amphiphiles [20]. Since the sum is positive, the repulsion between the headgroups and
the desolvation of the hydrophobic tails outweigh the exothermic enthalpy of association
between the hydrocarbon tails due to the favourable chain-chain attraction. Moreover, the
enthalpic ($\Delta_{\text{mic}}H^\circ$) and entropic ($-T\Delta_{\text{mic}}S^\circ$) terms, Figure 3.11, indicate that the
micellization is entropically-driven, and the entropy term plays the dominant role in the
negative free energy $\Delta_{\text{mic}}G^\circ$. The entropy change of micellization process is always
positive over the whole temperature range. The increase in entropy of micellization in an
aqueous medium can be attributed to the increase in entropy of the hydrophobic chain of
surfactant molecules when the surfactant molecules are removed from the aqueous
medium to the micelle. The driving force is the tendency of the hydrophobic group of the
surfactant to transfer from aqueous bulk phase to non-aqueous micellar interior.
According to equation (5) the $\Delta_{\text{mic}}H^\circ$ and $\Delta_{\text{mic}}S^\circ$ has an opposite effect on $\Delta_{\text{mic}}G^\circ$. Figure
11 shows enthalpy-entropy compensation in the micellization process at the experimental
temperatures. It is interesting to observe a good linearity in the entropy and enthalpy
compensation plot for thermodynamic measurements [21]. The compensation
phenomenon between $\Delta_{\text{mic}}H^\circ$ and $\Delta_{\text{mic}}S^\circ$ can be described usually as follows:

$$\Delta_{\text{mic}}H^\circ = \Delta_{\text{mic}}H^* - T_c \Delta_{\text{mic}}S^\circ$$

(9)

Where $T_c$ is the slope of $\Delta_{\text{mic}}H^\circ$ vs $\Delta_{\text{mic}}S^\circ$ plot and has a dimension of temperature
which is referred to as the compensation temperature. The compensation temperature is
proposed to be characteristic of solute-solvent interaction [22], which is considered as a
measure of the ‘desolvation’ part, i.e., the dehydration of the hydrocarbon tail of
surfactant molecules, [23]. Figure 12 yields the compensation temperature ($T_c$) of
poly(4HBA-oca Na\(^+\)) is \(\sim 310\) K, which is quite consistent with the compensation temperature \(\sim 315\) K for ionic surfactants in aqueous solution [24]. The intercept \(\Delta_{m,H}^*\) is the measure of solute-solute interaction [24]. From the previous data, a series of valuable surface properties can be evaluated, such as the surface excess concentration at saturation, \(\Gamma_{max}\), and surface area per molecule, \(\alpha_s\), at the air-liquid interface (Table 3.2). \(\Gamma_{max}\), and \(\alpha_s\) were calculated by use of Equations 1 and 2. \(\Gamma_{max}\) is a useful measure of the effectiveness of adsorption of the surfactant at the air-water interface, and \(\alpha_s\) provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule. Table 3.2, shows that \(\Gamma_{max}\) increases with temperature increase while \(\alpha_s\) decreases. This trend indicates that with increasing temperature, more surfactant molecules are adsorbed on the saturated surface, resulting in a higher packing density and lower \(\gamma_{cmc}\).
Figure 3.11 Thermodynamic parameters of micellization for poly(4HBA-oca Na\(^+\)).

Figure 3.12 \(\Delta_{\text{mic}}H^\circ\) vs. \(\Delta_{\text{mic}}S^\circ\) plot for poly(4HBA-oca Na\(^+\)).
Table 3.2 The cmc, $I_{max}$, minimum surface area per molecule, $\Delta_{mic}G^o$ for poly(4HBA-oca`Na+) at different temperatures.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>cmc×10^5/(mol/L)</th>
<th>$I_{max}$/μmol.m^2</th>
<th>$\alpha$/nm^2</th>
<th>$\Delta_{mic}G^o$/KJ.mol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>5.7</td>
<td>2.05</td>
<td>0.81</td>
<td>-23.8</td>
</tr>
<tr>
<td>38</td>
<td>4.0</td>
<td>2.17</td>
<td>0.76</td>
<td>-26.2</td>
</tr>
<tr>
<td>48</td>
<td>3.7</td>
<td>2.57</td>
<td>0.64</td>
<td>-27.2</td>
</tr>
</tbody>
</table>
Figure 3.13 Hydrodynamic diameter intensity of poly(4HBA-oNa) micelles in aqueous solution at 25 °C measured by DLS at concentration of 0.5 g/L, and scattering angles of 60 ° (top), 90 ° (middle) and 130 ° (bottom).
Dynamic light scattering (DLS) techniques are powerful tools for obtaining information on conformation of polymer morphology in a dilute solution [23]. To confirm the spherical shape of poly(4HBA-oca\(^-\) Na\(^+\)) micelles in aqueous solution, the DLS was carried out at different angles to measure the hydrodynamic diameter (D\(_h\)). Figure 3.13 shows the D\(_h\) values of 161.2 nm, 146.0 nm and 161.0 nm at scattering angles of 60\(^\circ\), 90\(^\circ\) and 130\(^\circ\), respectively. The micelles are generally spherical and their average diameters are around 156 nm, the average value of the D\(_h\) values. The width of the D\(_h\) distribution indicates that more than one oligomer species is present in solution. Figure 3.14 shows the hydrodynamic diameter distribution \(f(D_h)\) of poly(4HBA-oca\(^-\) Na\(^+\)) micelles at 25\(^\circ\)C measured by DLS at concentration of 0.5 g/L and scattering angle of 90\(^\circ\) in the D\(_h\) range from 50 nm to 500 nm. The D\(_h\) of poly(4HBA-oca\(^-\) Na\(^+\)) micelles detected at two D\(_h\) values (116 nm and 289 nm). These two peaks with different intensity indicate the present of two assemblies. Here, the polydispersity index of the poly(4HBA-oca\(^-\) Na\(^+\)) is slightly high, 3.3, reported somewhere else [10]. However, the presence of poly(4HBA-oca\(^-\) Na\(^+\)) oligomers with different degree of polymerization confirmed by the surface tension plots that exhibit a shallow minimum attributed to the effect of polydispersity (Figure 2.8). The poly(4HBA-oca`Na\(^+\)) of high degree of polymerization aggregated and produce micelles larger in size.
Figure 3.14 Hydrodynamic diameter distributions $f(D_h)$ of poly(4HBA-oca$^-$ Na$^+$) micelles in aqueous solution at 25 °C measured by DLS at concentration of 0.5 g/L, and scattering angle of 90 °C.

The surfactants present in the aqueous solution adsorbed at the gas/liquid interface and lower the surface tension. The presence of the surfactant facilitates the dispersion of gas bubbles in a surfactant solution and reduces the bubble size [24]. The experimental systems used to study the stability of foams made with aqueous surfactant solutions against coalescence and characterized by the variation of the foam height with time or the rate of foam decay. The foam produced with the anionic surfactant sodium dodecylsulfate (SDS) depends on the SDS concentration, the maximum foam produced when the SDS micelles are less stable [25]. The stability of foams made with 75 ppm (0.075 g/L) and 150 ppm (0.15 g/L) anionic polymeric surfactants solutions were studied at 25 °C by measuring of foam volume decrease during 1min and 5min. The dependence of the foam volume ratios on time shown by:
Foam volume ratio = \frac{Foam volume at time=0}{Foam volume at time=t} ........................................ (10)

Figure 3.15 shows the foam volume ratio as measured by the ratio of the height of the foam initially produced to the foam height measured after 1 min and 5 min. The foam volume ratios increase with an increase in the chain length. The rate of foam decay calculated from the following equation:

\[ \text{Decay rate} = \frac{dl}{dt} \] ........................................ (11)

Where,

I= Property (Foam volume ratio) and
t=time (minute)

Figure 3.16 shows the rate of foam decay increases as the surfactants chain increase, and shows that the foam stability measurements are consistent with that of cmc measurement. For example, the rate of foam decay increases from 0.19, 0.21 and 0.25 at concentrations 75 ppm to 0.21, 0.40 and 0.46 at concentration 150 ppm for poly(4HBA-oca` Na⁺), poly(4HBA-dea` Na⁺) and poly(4HBA-doa` Na⁺), respectively.
Figure 3.15 The dependence of the foam volume ratios on time, 150 ppm (left) and 75 ppm (right).
Figure 3.16 The decay rate plot (top) and the surfactants solution foams (bottom) after 1 min, a-poly(4HBA-oca- Na+) , b- poly(4HBA-dea- Na+) and c- poly(4HBA-doa- Na+).

It can be concluded that, the surfactant system of low surface tension is more efficient against coalescence of bubbles and foam collapse, which has the highest foam height and the lowest foam decay rate.

Determination of the Krafft point, K.P., otherwise known as critical micelle temperature relies on the measurement of electrical conductivity (κ). The concentration of
polybenzoxazine surfactant solutions were 0.05 wt % (0.5 g/L) which is above the cmc of all the polybenzoxazine surfactants, and in this system, all components are different only in hydrocarbon chain length and are completely soluble in water. The temperature dependences of \( \kappa \) is shown in Figure 3.17, which shows that the Kraft Point increases with alkyl chain length of the polymeric surfactant, as reported in the literature [28]. Thermodynamically, at the Kraft Point, the hydrated solid surfactants, monomers, and liquid micelles are in equilibrium and the hydrated solid surfactants dissolve into monomers and transform into liquid micelles. Then, the Kraft Point is known as the melting temperature of a hydrated solid surfactant [29]. From Figure 3.17, at low-temperature region, rather low values of \( \kappa \) are observed due to partial dissolution of the surfactant species. At a certain temperature, illustrated by an arrow in Figure 3.17, the amount of the dissolved species increases resulting in a sudden change in \( \kappa \), as shown by the abrupt rise of the curves. This region of sharp rise in \( \kappa \) designates the Kraft Point of the surfactant. The values of the Kraft Point for poly(4HBA-oct-Na\(^+\)), poly(4HBA-dec-Na\(^+\)) and poly(4HBA-doc-Na\(^+\)) are 4\(^\circ\), 6\(^\circ\) and 8\(^\circ\)C respectively. Above this point the polymeric surfactant associates to form liquid micelles, and the conductivity of the micellar solution increases with temperature depending on the chain length which affects the size, charge and mobility of the micelles [30].
Figure 3.17 Temperature dependence of $\kappa$ in the systems of polymeric surfactant solutions, 0.05 wt% (poly(4HBA-oca- Na$^+$), poly(4HBA-dea- Na$^+$) and poly(4HBA-doa- Na$^+$)). A sharp rise of $\kappa$ with temperature is due to the Krafft phenomenon, and shows the Krafft point of the polymeric surfactant species.
3.5 Conclusion

In this work, we have investigated the aqueous micellization behavior of the solutions of three anionic polymeric surfactants based on comb-like polybenzoxaizne oligomers; poly(4HBA-oca− Na⁺), poly(4HBA-dea− Na⁺), and poly(4HBA-doa− Na⁺). Upon salt (NaCl) addition, the cmc initially decreases slightly and remains constant at 3wt% NaCl. The chain expansion due to changes in polymeric surfactant structure was mainly affected on the values of the intrinsic viscosities. However, the electroviscous effect was investigated by addition of an electrolyte, NaCl. The existence of electrolyte can suppress the electroviscous effect. The temperature-dependence studies have shown a linear fall in cmc i.e. as temperature increases cmc decreases of poly(4HBA-oca− Na⁺), in the studied temperature range. poly(4HBA-oca− Na⁺) shows an enthalpy−entropy compensation, and the micellization is entropically-driven. The Krafft temperature increases with alkyl chain length of the polymeric surfactant molecule.
3.6 References


Chapter 4

4. Gemini (dimeric) benzoxazine surfactants: Synthesis, characterizations and molecular dynamics simulation of self assembly
4.1 Introduction

Dimeric surfactants, also known as gemini surfactants consist of two hydrophilic segments connected by a spacer and two hydrophobic tails [1,2]. The properties of dimeric surfactants differ from conventional surfactants that consist of a hydrophilic head group and a hydrophobic tail. The dimeric surfactants have lower critical micelle concentration, cmc, and are more to reduce the surface tension of water to values lower than conventional surfactant. In addition, they exhibit interesting rheological properties [3]. However, it is believed that the spacer plays an important role in the micellization behavior. The spacer length and flexibility are essential parameters for determining the shape of the surfactant aggregate, where the spacer reduces the intramolecular electrostatic repulsion between head groups, and this leads to micelle formation at low cmc values in gemini surfactants [4], in this work a new class of anionic dimeric surfactants based on benzoxazine chemistry developed. The synthesized anionic dimeric surfactants consist of a linear hydrophobic tail opposing two hydrophilic polar head-groups. The two polar head groups that containing carboxylic show unique feature when compared to regular dimeric surfactants. The polar head groups are benzene rings with a negatively charged carboxylate group and a hydroxyl group, connected to amine group via methylene bridge. The hydrophobic tail connected to the nitrogen atom results in a symmetric dimer structure [scheme 1]. The spacer consists of the amine and the methylene bridge known as Mannich bridge. Formation of the Mannich bridge structure is due to the cationic ring opening polymerization of benzoxazine [5]. Recently, benzoxazine chemistry has gained immense interest because of the capability of the benzoxazine to have a great deal of molecular design flexibility compared with ordinary
phenolic resins [6]. Hence, it is our interest to originally propose the inclusion property of an original structure of anionic dimeric surfactant derived from benzoxazine is proposed and validated in this work. Though several researchers have synthesized amphiphiles with unique head group topology (e.g., two carboxylates rigidly held on a dibenzobarrelane skeleton) [7] and examined the relationship between amphiphile structure and aggregate morphology [8], not enough studies in the literature provide a molecular level picture of the surfactant aggregates and the self-assembly of these molecules. It is important to understand the role of the spacer on the dimer benzoxazine flexibility. The dynamics of polymer backbones can be investigated in great detail on nanosecond time scales theoretically by all-atom molecular dynamics (MD) simulations [9]. MD is a powerful technique for studying the micellization behavior [10] and surface phenomena [11] at the molecular level. In the present study, experimental and computational studies are done to investigate the amphiphilic nature of the anionic dimeric benzoxazine surfactant, di(4CaP-oca`Na+). Experimentally, surface tension measurements are used to investigate the surface activity of di(4CaP-oca`Na+) at the air/water interface, and to show its ability to form micellar aggregates. Computationally, atomistic level molecular dynamics (MD) simulations are performed to study the di(4CaP-oca`Na+) adsorption at air/water interface and to investigate the aggregation behavior of the di(4CaP-oca`Na+) in aqueous media. So, this paper describes the synthesis and characterization of di(4CaP-oca`Na+) its surface activity investigated by experiments and MD simulations.
4.2 Experimental method

4.2.1 Materials

3-octyl-3, 4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-oca) was prepared as described in the literature [12], and 4-hydroxybenzoic acid (abbreviated as HBA-COOH) (99%) was used as received from Sigma-Aldrich.

4.2.2 Preparation of 3,3’-(octylazanediyl)bis(methylene)bis(4-hydroxybenzoic acid), or, [4-carboxylphenol-based benzoxazine dimer] [abbreviated as di(4CaP-oca) ]

The model dimer for benzoxazine was reported elsewhere in the literature [13] and the synthesis was done by following the same procedure. The 4HBA-oca and 4-Hydroxybenzoic acid were used as starting monomers. Briefly, in a 100 mL flask were mixed together 4HBA-oca (10 mmol, 2.43 g) and 4-hydroxybenzoic acid (10 mmol, 1.38 g), 1:1 mol ratio, and heated at 140 °C and solvent-less reaction for 3 hrs. The yellowish product was removed and used without any further purification.

4.2.3 Ionization of di(4CaP-oca) into di(4CaP-oca’ Na+) “Salt formation”

1.0 Gram of dimeric benzoxazine, abbreviated as di(4CaP-oca), was weighed into 50 mL beaker. The designated amount of NaOH (to neutralize all carboxylic acid groups) was dissolved in 20 mL of deionized water, and then added into the 50 mL beaker of dimeric benzoxazine. The beaker containing dimeric benzoxazine sample and base solution was placed in an ultrasonic bath until the solids were dissolved. The solution was then filtered using a filter paper and cooled to room temperature. The resulting dimer salt was dried overnight at 60°C in an air circulating oven to a constant weight.
4.3 Measurements.

Fourier transform infrared (FTIR) spectroscopic analysis was carried out on a Bomem Michelson MB100 Spectrophotometer with a deuterated triglycine sulfate detector. After casting a thin film onto a KBr plate and purging with dry air, coadded spectra of 64 scans were recorded at a spectral resolution of 4 cm\(^{-1}\). Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC Model 2920 at a heating rate of 10 °C/min from 25 to 300 °C and nitrogen flow rate of 62 mL/min; 2mg samples were sealed between aluminum hermetic pans and lids for all tests. Thermogravimetric analysis (TGA) was performed with a TA Instruments High Resolution 2950 Thermogravimetric Analyzer at a heating rate of 10 °C/min from 25 to 800 °C and with nitrogen purge at a flow rate of 40 mL/min; 5 mg samples were placed in an open platinum crucible for all tests. Surface tension measurements of aqueous solutions were carried out using a KRÜSS Tensiometer (K100) using the Wilhelmy platinum plate method. All measurements were performed at 24±0.1 °C. Reproducibility was checked by frequent determination of the surface tension of de-ionized distilled water (72–73 mN/m).

4.4 Computational Methods

Molecular dynamics (MD) simulation track the motion of atoms by estimating the atomic trajectory over time in response to the inter-intra molecular forces. It was used to elucidate the behavior of dimeric benzoxazine in aqueous media. MD simulations can provide us with detailed information about a system, such as the structure and dynamic
properties. In particular, every atom was explicitly. The simulations were carried out with
the Gromacs software package [14]. The input topology file was generated by the server
TopolGen version 1.1 [15], and was carefully adjusted before using for MD. The
TopolGen is a reliable tool for quickly obtaining topologies using the empirical all-atom
optimized potentials for liquid simulations, OPLS-AA, force field [16]. The SPC/E water
model [17] and the OPLS-AA force field were used to describe the water and the organic
molecules, respectively. Energy minimizations were carried out using steepest descent
algorithm until the maximum force in the system becomes less than 0.001 N/mol (1000
kJ/mol/nm). Using the NVT ensemble (constant number of particles, N, and constant
volume of the system, V, at well defined temperature, T) and the NPT ensemble (constant
number of particles, N, and constant pressure of the system, P, at well defined
temperature, T) the MD simulations were sequentially carried out to equilibrate the
system. First, the simulations were carried out at constant temperature (T=298 K) and constant
volume where the MD trajectories were generated in the NVT ensemble using the Berendsen
thermostat [18]. The NVT MD simulation was performed for 200 ps at 298 K with time
step of 1 fs. Then the pressure was coupled to a semi-isotropic Parinello-Rahman pressure
coupling [19] in other continuous simulations conducted under the NPT ensemble at a
constant pressure of 1 bar. The NPT MD simulations were performed for 200 ps at 1 bar
with time step of 1 fs. Finally, the MD simulations were carried out under conditions that
best mimic the experimental conditions. During the MD simulations; the energies and
other statistical data (coordinates, velocities and forces) are stored every 2000 steps. In
addition, the time step of 1 fs is taken to be constant for all the simulations of this study.
Periodic boundary conditions were applied, in all three directions for all the trajectories,
to generate a quasi-infinite solution. A 1.0 nm-cutoff was used for the short-range interactions. Long-range electrostatic interactions were treated using the particle mesh Ewald (PME) summation method with a spaced grid of 0.12 nm, and fourth-order B-spline interpolation. For the organic molecules, the bonds containing hydrogen atoms were constrained by the LINCS algorithm [20] and for water molecules, they were kept rigid by the SETTLE algorithm [21]. The equations of motion were integrated with a time step of 1 fs using the Verlet (leapfrog) algorithm. The VMD 1.9.1 [22] viewer was used to analyze the MD trajectories and inspect the arrangement of surfactant molecules, both in the bulk water and on the water surface, by capturing images throughout the trajectories.

### 4.5 Simulation details:

To simulate the self-assembly of Gemini benzoxazine surfactant an initial simulation box structure was generated using the Gromacs utility “genbox”. Comparing the effect of the hydrocarbon spacer length ((CH₂)n) and the chain length (m) on the average aggregation number (N) of a micelle of dimeric surfactant, the Mannich bridge is assumed to be equivalent to a hydrocarbon spacer of n=4. Therefore, the number of di(4CaP-oçaNa⁺) molecules to be simulated was chosen to be 31. This is compatible with the average aggregation number N=30 for a micelle of dimeric surfactant of n=4 and m=10 [23]. 31 di(4CaP-oçaNa⁺) molecules were positioned or inserted randomly into a cubic simulation box of 10×10×10 nm³, and then solvated by adding 32384 SPC/E water molecules into the box. The simulated di(4CaP-oçaNa⁺) concentration, 22.006 g/L (0.046 M), is higher
than the predicted cmc, 0.270 g/L (5.71×10⁻⁴ M), in order to avoid simulations over large domains that result by extending the box size 200 times to reach the predicted cmc. In addition, 62 water molecules were randomly replaced by Na⁺ counterions for system neutralization by using the Gromacs utility “genion”. In this case the spontaneous self-assembly into a single spherical micelle was observed after 10 ns of simulation. The simulation was extended for another 10 ns, after the system had reached an equilibrium state based on the self-assembly and the RDFs, to allow the micelle to relax toward its equilibrium structure. The last 5 ns of simulation were chosen for analysis. To simulate the behavior of di(4CaP-oca’Na⁺) molecules at the air/water interface, a thin water layer (10×10×4 nm³) was sandwiched between two layers (10×10×2 nm³) containing 20 di(4CaP-oca’Na⁺) molecules in each layer. The surfactant molecules were initially placed randomly at the sandwiched water. Further simulations were carried out to investigate the nature of the hydrophilic segments affected by the electrostatic interactions between the charged head groups of each di(4CaP-oca’Na⁺). For example, simulations carried out in vacuum were compared with the simulations performed in aqueous media to study how the electrostatic interactions might occur. In other words, the repulsion between the charged head groups of each di(4CaP-oca’Na⁺) molecule may either increase the distance or increase the plane angle between the carboxylate groups in each molecule.
4.6 Results and discussions

4.6.1 Synthesis and characterizations

Benzoxazines are typically hydrophobic materials and show limited water solubility. In this work, the application of benzoxazine chemistry to the field of anionic Gemini surfactant was studied by observing the surface tension change of water versus surfactant concentration. The dimeric benzoxazine contain a hydrophobic olefin backbone with straight chain alkane as the hydrophobic segments and carboxylic moieties as hydrophilic segments distributed throughout the dimer backbone. These anionic dimeric surfactant molecules introduced here have an affinity for interfaces, and are able to reduce the water/air surface tension and form micelles. The benzoxazine dimer is shown in Scheme 1, and its synthesis followed the published procedure [13].

\[ \begin{align*}
\text{COOH} & \quad \text{CH}_3 \\
\text{OH} & \quad \text{COOH}
\end{align*} \]

Scheme 4.1 Synthesis of dimeric benzoxazine 4CaP-oca.

The FTIR spectra of 4CaP-oca at room temperature as illustrated in Figure 1 shows the characteristic absorption bands of benzoxazine structure at 1240 cm\(^{-1}\) due to the stretching of C–O–C and at 940 cm\(^{-1}\) due to the out-of plane bending vibration of the
benzene ring attached to the oxazine ring [24]. Figure 1 also shows the weakening of the characteristic bands of benzoxazine at 1240, and 940 cm\(^{-1}\). Disappearance of these bands after polymerizing at 140 °C for 1 hr to 3 hrs indicates ring-opening of benzoxazine moieties and the formation of benzoxazine dimer.

Figure 4.1 FTIR spectra of 4HBA-oca+HBZ-COOH (1:1) at 25 °C/0 hr, 140 °C/1 hr and 140 °C/ 3 hrs.

It is well-known that thermally accelerated ring-opening polymerization of 1,3-benzoxazines is an autocatalytic, exothermic process having maximum around 200 to 270 °C depending on the functionalities of the benzoxazines [25]. The ring-opening behavior of the monomer was examined by DSC. Figure 2 shows the exotherm observed for the
di(4CaP-oca) corresponding to the ring opening polymerization. 4HBA-oca showed an exotherm with an onset at 130 °C and a maximum peak at 184 °C, corresponding to the polymerization of benzoxazine with a heat of polymerization, ΔH, of 75 J/g. This exotherm temperature is unusually low in comparison to ordinary benzoxazine monomers [25] due to the effective catalytic nature of carboxylic acid towards benzoxazine polymerization [26]. After each heating cycle of 4HBA-oca+HBA-COOH, the exotherm corresponding to benzoxazine polymerization decreased constantly and almost disappeared after 3 hrs at 140 °C. Figure 2 shows the DSC thermograms of 4HBA-oca+HBA-COOH at different thermal treatments; the heat of polymerization decreased from 75 J/g to 0 J/g due to heating for 3 hrs at 140 °C, indicating the disappearance of benzoxazine structure. The endotherm around 218°C is due to the degradative evaporation of the amine moiety, as discussed in later.
Figure 4.2 Dynamic DSC plots for (4HBA-oca) at 25°C, and for (4HBA-oca + HBZ_COOH) at 140°C after heating for 1 hr and 3 hrs.

The thermal stability of benzoxazine dimer di(4CaP-oca) was analyzed by TGA as shown in Figure 3. The first weight loss of about 45% observed around 200°C for the benzoxazine dimer, is attributed to the degradation of linear aliphatic amine as reported in the literature [12]. The carboxylic acid group of the benzoxazine dimer was neutralized by adding required amount of NaOH as shown in Scheme 2, and converted to anionic dimeric benzoxazine surfactant di(4CaP-oca`Na`).
Figure 4.3 TGA curves of di(4CaP-oca)

4.6.2 Surface tension experiments

Scheme 4.2 shows the ionized form of the Gemini surfactant and Figure 4.4 illustrates the hydrophilic and the hydrophobic segments of the proposed structure. The surface tension variation with the concentrations of the anionic dimeric surfactant for the di(4CaP-oca⁻ Na⁺) solutions is shown in Figure 4.5. The effect of the dimeric surfactant on the surface tension can be observed at very low surfactant concentration, where dimeric surfactant adsorbs at the air–water interface. Least squares regression analysis was performed to find the best equation for each of the linear portion below the cmc value (the pre-cmc line) and the portion above the cmc value (the post-cmc line). The surface activity properties of this anionic dimeric surfactant are summarized in Table 4.1. However, these values are shown for general comparison only; there are significant
differences in the surface tension values below the cmc. This anionic Gemini surfactant shows better surface activity than sodium dodecylsulfate (SDS); the cmc is an order of magnitude lower for the dimeric surfactant.

Scheme 4.2 The proposed dimeric benzoxazine structure of di(4CaP-oca) and its ionization into the ionized form, di(4CaP-oca Na⁺).

Figure 4.4 Representative structure of the anionic Gemini surfactant, represented by CPK model using VMD.
Table 4.1 Summary of the surface activity properties of di(4CaP-oca Na+) compared with values for anionic monomeric surfactant, SDS, from the literature.

<table>
<thead>
<tr>
<th>Property</th>
<th>di(4CaP-oca Na+)</th>
<th>SDSa</th>
</tr>
</thead>
<tbody>
<tr>
<td>cmc (g/L)</td>
<td>0.27</td>
<td>2.36</td>
</tr>
<tr>
<td>$\gamma_{cmc}$ (mN/m)</td>
<td>37</td>
<td>39.5</td>
</tr>
</tbody>
</table>

a reference 27

Figure 4.5 Surface tension at different weight concentrations of di(4CaP-oca Na+) in water.
4.6.3 Simulation analysis

4.6.3.1 Bulk behavior of dimeric benzoxazine surfactant

4.6.3.1.1 Aggregation into spherical micelles Knowing the dynamics of self-assembled surfactant leads to understanding the aggregation mechanism, and associated interactions between the surfactant molecules. The spontaneous aggregation of the di(4CaP-oca`Na+) molecules in aqueous media is illustrated in Figure 4.6. The micelle formation is identified via direct visual examination using VMD software, which is used to animate and analyze the trajectory of the MD simulation. Micelles are identified as clusters of neighboring di(4CaP-oca`Na+) molecules. The simulations were initiated by placing the system molecules randomly in the simulation box. To avoid the exposure of the hydrophobic region to the aqueous surrounding, the molecules tend to rapidly aggregate into unstable small micelles, observed in 2 ns that coalesce to form a large micelle, observed in 10 ns. The hydrophobic segment of the di(4CaP-oca`Na+) molecules points toward the center of the hydrophobic micellar interior, whereas its hydrophilic segments faces the aqueous phase. The self-assembly is opposed by electrostatic repulsions between the charged head groups as they come closer to each other [28]. The aggregation process may be divided into three periods; first period (0-3 ns) for single surfactants and small clusters, second period (3-10 ns) for intermediate and large loose clusters, and finally the third period (10-16 ns) for compact micelles.
Figure 4.6 Spontaneous aggregation of di(4CaP-oca’Na+) into a micelle. Snapshots of the simulation at the start (t=0 ns), intermediate (t=3-10 ns), micelle and single molecule stage (t=10-16 ns), and micelle (16-20 ns) are shown. Water molecules are omitted for clarity and the black points represents the Na ions.

4.6.3.1.2 Radial distribution function (RDF) analysis The radial distribution function (RDF) provides more intimate understanding of the packing as it measures how the density of some material varies as the distance from another species increases.
\[ g_{AB}(r) = \frac{\langle \rho_B(r) \rangle}{\langle \rho_B \rangle_{\text{local}}} \]

\( g_{AB}(r) \) represents the probability of finding particle B within the range \( r + dr \) around particle A, where \( \langle \rho_B(r) \rangle \) is the density of B at a distance \( r \) around A, and \( \langle \rho_B \rangle_{\text{local}} \) is density of B averaged over all sphere around A with radius \( r_{\text{max}} \).

Figure 4.7 shows the RDF between the water molecules (W) and each of the spacer (N), the polar head-groups (COO) and the hydroxyl functional groups (OH) of the dimeric benzoxazine surfactant at the simulation period from 15ns to 20ns. The system achieved equilibrium after 15 ns, and the simulation results for analysis at the last 5 nm are credible. However, the negatively charged polar heads are the carboxylate group, essentially COO\(^{-}\). To demonstrate the possible artifacts due to truncating electrostatic interactions between these charged groups, RDFs between the water molecules and the carbon atoms in the carboxylate groups were examined [29]. From Figure 4.7, the calculated RDFs show two peaks, representing two water shells around the spacer [W-N], polar head [W-COO], and the carboxylate group [W-OH], at radial distances of (0.550 and 0.814 nm), (0.256 and 0.356 nm), and (0.186 and 0.286 nm), respectively. The strong peaks around 0.256 and 0.356 nm for the [W-COO] correspond to the first and second solvation shells of the head-groups composed of hydrogen bonded water molecules. Both the [W-N] and the [W-OH] curves show two small but well-defined peaks, which are the signature of the solvation shells for the head-groups. Further, the sharp peaks of [W-COO] and [W-OH] are attributed to a close interaction between water molecules and each of polar heads, and carboxyl groups, Figure 4.7. The water distribution around the polar head-groups is generally of low intensity and suggests that water molecules...
penetrate the polar head-groups and tend to reduce the repulsion between hydrophilic groups and lead to eliminate the polar heads interaction. From the Figures 4.6 and 4.7, it can be concluded that the dimeric surfactants orient themselves with the polar head-groups spread out to form the surface facing the water shells.

**Figure 4.7** Radial distribution functions of water relative to the polar heads (W-Co), spacer (W-N), and carboxylic groups (W-OH) calculated from the MD simulations were carried out at 298K.

To obtain more insight into the structure of dimeric surfactants, the RDFs of a polar head group with the surrounding polar head groups [COO-COO] and a spacer with the surrounding spacers [N-N] were calculated and presented in Figure 4.8a. The [COO-COO] curve shows a small first peak located at 0.526 nm, a prominent second peak at 1.00 nm, and a broad third peak at 1.846 nm. Peaks can be specified knowing the RDF
between neighboring head groups [COO-COO] for each di(4CaP-ocaNa\(^{+}\)). Figure 4.8b shows the RDFs between neighboring head groups [COO-COO] for each di(4CaP-oca\(^{-}\)Na\(^{+}\)) in aqueous media and in gas phase. In case of aqueous media, the [COO-COO] curve shows a small first peak located at 0.520 nm, and a prominent second peak at 1.00 nm, the peaks suggest two different conformations, as will be explained later.

**Figure 4.8** The RDFs between the charged head groups represented by the carbon atoms in the carboxylate groups [COO-COO] and between the spacers [N-N] (a). The RDFs
between neighboring head groups [COO-COO] for each di(4CaP-oca′Na+) in aqueous media and in vacuum (b).

4.6.3.1.3 Conformational analysis: Conformational analysis and the surfactant conformation give detailed information about the inner structure of surfactant. The spacer of di(4CaP-oca′Na+) is treated as a chain, including the dihedral angles ($\theta_1$, $\theta_2$) between C-C bonds, and the dihedral angles ($\beta_1$, $\beta_2$) between C-N bonds, that are arranged symmetrically as shown in Figure 4.9a. Each bond may take one of three rotational states (trans, gauche⁺, and gauche⁻). Figure 4.9b shows the analysis of the dihedral angle distribution of spacer in di(4CaP-oca′Na⁺). In case of aqueous system, the analysis showed the predominance of gauche conformation around both the C-C bonds and the C-N bonds, and the results are summarized in Table 4.1. Table 4.1 presents the fraction of the three conformers, calculated from the area of each Gaussian with respect to the total area (Figure 4.9b). The gauche (+,-) conformer has an occurrence of 75.3 %, whereas 24.7 % trans is supposed to be present. This means that 23 di(4CaP-oca′Na⁺) out of the total 31 di(4CaP-oca′Na⁺) in the system favor gauche conformation. Overall, this suggests that, the dihedral angles $\beta_1$ and $\beta_2$ for C-N bonds play a major role in defining a conformational propensity than the dihedral angles $\theta_1$ and $\theta_2$ for C-C bonds. This is attributed to the considerable probability that the dihedral angles $\beta_1$ and $\beta_2$ exist in trans conformation, and the change causes difference in energy, while the dihedral angles $\theta_1$ and $\theta_2$ are fixed at gauche conformation. The distribution of dihedral angles of the alkyl chain shown in Figure 4.10 indicates that the tail has relatively larger trans fractions and are more extended.
In order to recognize the effects of intermolecular hydrogen bonding of water molecules in the high percentage of gauche and electrostatic attraction or repulsion between neighboring polar heads, MD simulations were carried out in vacuum, comprising di(4CaP-ocaNa\(^+\)), and compared with the simulation results of an aqueous system, comprising di(4CaP-oca\(\text{Na}^+\)), as shown in Figure 4.9b. Comparison of the dihedral angle distribution of the two systems gives the extent of match, and this suggests, according to the [COO-COO] vacuum curve in Figure 4.8b, the existence of a strong specific intramolecular interaction between the binary head-groups in vacuum. The first small peak located at 0.774 nm confirms the existence of electrostatic repulsion in case of the vacuum system, and the same peak shifted to 0.520 nm in case of aqueous medium, and the low intensity of these peaks represent the low existence of trans
conformation. The same figure (Figure 4.8b) shows that water molecules can reduce the electrostatic repulsion compared to vacuum. The hydration shell created around the polar heads allows the polar groups to come closer to each other up to 0.520 nm, represented by the first small peak of the [COO-COO] aqueous curve. In summary, the distribution of dihedral angles \((\beta_1, \beta_2, \theta_1, \theta_2)\) in the di(4CaP-oca'Na') structure is well explained by macroscopic analysis of data obtained from atomic molecular simulation. The observed sharp peaks represent the dominant guauche conformation of the spacer structure; the sharpness is due to the high energy barriers between the trans and gauche conformations that translates into the high peak found in the dihedral angle distribution. Thus there is no need to invoke additional interactions to explain the spacer conformations of the dimeric benzoxazine surfactants.
Figure 4.9.B Distribution of the gauche and trans dihedral-angles for the spacer at vacuum system (left) and in aqueous media (right) obtained by various deidral angle sampling methods.

Table 4.2 The fractions of the guache and trans spacer conformers in aqueuos media.

<table>
<thead>
<tr>
<th></th>
<th>gauche⁺</th>
<th>trans</th>
<th>gauche⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>β1</td>
<td>5.84</td>
<td>42.73</td>
<td>51.44</td>
</tr>
<tr>
<td>β2</td>
<td>55.83</td>
<td>36.77</td>
<td>7.40</td>
</tr>
<tr>
<td>θ1</td>
<td>36.49</td>
<td>9.68</td>
<td>53.83</td>
</tr>
<tr>
<td>θ2</td>
<td>54.72</td>
<td>9.19</td>
<td>36.09</td>
</tr>
<tr>
<td>Average</td>
<td>38.14</td>
<td>24.67</td>
<td>37.19</td>
</tr>
</tbody>
</table>
Figure 4.10 Distribution of the dihedral angle for the alkyl chain produced by the various dihedral angle sampling methods

4.6.3.2 Behavior of dimeric benzoxazine surfactant at air/water interface

4.6.3.2.1 Density Profiles: Figure 4.11 shows the calculated mass density profiles, along the Z axis of the box, for the system investigated by MD simulation. The density distributions profile of the surfactant molecules (two layers) and water (middle layer) in the system are symmetric, and the traces correspond to the center of mass position of each group. The calculated bulk density of water is 1008 kg/m$^3$ agree with the experimental value of 997 kg/m$^3$ for water [30]. The density profile of water shows a flat region of bulk water in the middle, approximately from -1.00 nm to 1.00 nm. At the water/air interfaces, the water density increased slightly up to a maximum value at around $Z \approx \pm 1.5$ nm, before gradually decreased from its maximum value to zero at around $Z \approx \pm 2.5$ nm. The small increase in density is attributed to water molecules attracted to the charged head groups and their counterions [31]. The density distribution of the surfactant
molecules show a uniform distribution of surfactant at the interfaces that confirm the well adsorption of surfactant molecules along the air/water interface resulting in a stable monolayer [32].

![Figure 4.11](image)

**Figure 4.11** Density profiles of water and di(4CaP-oca`Na+) along the Z axis.

### 4.6.3.2.2 The geometric shape.

In order to obtain a quantitative view on how the anionic head groups and the alkyl chain of di(4CaP-oca`Na+) are arranged at the air/water interface, the topology was analyzed during MD trajectories by reporting the average values of the tilt angles and the spacer bend angle. Figure 4.12.a shows the time dependencies of the tilt angles of one di(4CaP-oca`Na+) that is depicted in Figure 4.12.b over a period of 10 ns. The tilt angles \( \alpha_1, \alpha_2 \) and \( \alpha_3 \) are defined as the angles between the Z axis and the vectors that are connecting; the N atom and the methyl carbon atom in the surfactant tail, the N atom and the carbon atom that connected one ring to the spacer, the
N atom and the carbon atom that connected the other ring to the spacer, respectively. In addition, $\phi$ measures the degree to which spacer bend. Although tilt angles of the spacer are observed to fluctuate, the tilt angle of the alkyl chain ($\alpha_1$) appears to show low fluctuation and yield nearly constant angles around $46^\circ \pm 5.5^\circ$. The tilt angles of the spacer ($\alpha_2, \alpha_3$) are around $(84^\circ \pm 8.4^\circ, 112^\circ \pm 10.2^\circ)$, respectively. Their high fluctuation are possibly resulted by breaking and forming intramolecular hydrogen bonds between the N atom and the hydrogen atoms (H1, H2) of the hydroxyl groups as shown in Figure 4.12.b. $\phi$ is around $118^\circ \pm 1.2^\circ$ and shows small fluctuation, this is probably due to the rigidity of the benzene ring. Figure 4.12.c shows the RDF between N and H of the hydroxyl groups in each individual di(4CaP-oca$\cdot$Na$^+$) molecule, the hydrogen atoms were observed at distance of $d(N\cdots HO) = 0.22 \pm 0.01$ nm from the spacer (N), and the existence of an intramolecular hydrogen bond of type N$\cdots$HO was considered. The observed N$\cdots$HO distance is significantly higher than the reported N$\cdots$HO distance for crystal structure of benzoxazine dimer which is about 0.098 nm by x-ray diffraction of a benzoxazine dimer [33], although solid-state 1H-NMR analysis reported closer value of $0.196 \pm 0.005$ nm [34]. Overall, the knowledge obtained from density profile and tilt angle distributions provides a clearer picture of the di(4CaP-oca$\cdot$Na$^+$) in the air/water interface, where the dimer polar heads lie approximately parallel to each other in the planes of the benzene rings, as shown in Figure 4.12.d.

In summary, the first measurements of the molecular structure; distance, orientation, bending, and conformational dynamics of anionic dimeric benzoxazine surfactant molecules are reported. The results provide a detailed picture of the aggregation of these molecules in aqueous bulk media, the theoretical predictions of the
conformational order of the alkyl chain and the spacer in the polar headgroup, and the orientation of these molecules at the air/water interface. This study demonstrates the feasibility and value of future investigations in the design of benzoxazine based surfactants for understanding their behavior in aqueous media and at air/water interface.

**Figure 4.12** The average values of the tilt angles and the spacer bend angle (a) that characterizes the geometric shape of the surfactant at air/water interface (b). The RDF between N and H of the hydroxyl groups in each individual di(4CaP-oca’Na⁺) molecule (C). Equilibrium MD simulation snapshot (d) showing a dimeric benzoxazine molecule at
the air/water interface, Color legend: dark, di(4CaP-oca'Na⁺) molecule; gray, water molecule.
4.7 Conclusion

In this study, the synthesis and the surface activity characterizations of Gemini benzoxazine surfactants have been investigated by experiments and molecular dynamics (MD) simulations. The chemical structure was determined via FT-IR. Ring-opened structures were also identified. Surface tension measurements clearly show the surface activity of the dimeric benzoxazine surfactant and micelle formation above the cmc. A spontaneous self-assembly of the dimeric benzoxazine surfactant in aqueous media was observed by using MD simulations. The micelles have a randomly distributed configuration. Detailed results on the structures and dynamics of the aggregates are analyzed. Two thin shells of water are detected around the hydrophilic segments. There are mainly two conformations: gauche and trans, present in vacuum and aqueous phases; the aqueous environment strongly favors the gauche conformation. This investigation may provide a fundamental approach to predict the behavior of benzoxazine and other surfactant molecules.
4.8 References


Chapter 5

Molecular dynamic simulations of self-assembly of amphiphilic comb-like anionic polybenzoxazines
5.1 Introduction

Amphiphilic macromolecules have been a recent focus of both applied science as well as basic research. When polymeric amphiphiles are dissolved in water, the molecules spontaneously self-assemble into micelle structures whose geometry and size depend on the structure [1] and concentration [2] of the amphiphilic molecule, as well as solution temperature [3], pH [4], ionic strength [4], and other physicochemical parameters. Many studies have been devoted to the elucidation of micelle structures important for diverse fundamental and technological applications [5-7]. Various experimental techniques, such as surface tension, light scattering, and density measurements, have been employed to characterize the structure, dynamic behavior, and thermodynamic properties of micellar systems [8]. More recently, molecular dynamics (MD) simulation studies have generated valuable information complementary to the experimental results, at the Angstrom level and at time scales in the nanosecond-microsecond range.

Many simulation studies have been carried out in relation to the self-assembly of amphiphilic molecules [9-19]. Smit et al. [9, 10] reported MD simulations of the spontaneous aggregation of surfactants and analyzed the structure of a water/oil interface in the presence of micelles. Maillet et al. [11] performed large-scale MD simulations to investigate the structural and dynamical properties of self-assembled cationic surfactants in aqueous solution. Goetz et al. [12, 13] carried out MD simulations of coarse-grained amphiphilic molecules in aqueous solution to investigate the spontaneous self-assembly into spherical micelles, cylindrical micelles, and bilayers. Khurana et al. [14] studied the behavior of a series of Gemini surfactants at the air/water interface. Several recent
investigations have focused the dynamics of surfactants between micelles, and the fusion and fission of small micelles [15-17], as well as the sphere-to-rod transition in micellar structures [18, 19].

In this paper, amphiphilic polybenzoxazines are investigated via molecular dynamics simulation. The amphiphilic polybenzoxazines contain alkyl chains as hydrophobic segments, carboxylic moieties attached to phenolic rings as hydrophilic segments, with the rings connected by Mannich bridges as the backbone. Formation of the Mannich bridge structure is due to the ring-opening of benzoxazine [20]. Previously, the surface tension of high-repeat-unit polybenzoxazines (with 9, 18 and 22 repeat units) was measured by Mahfud et al. [21] as a function of the surfactant concentration. The amphiphilic polybenzoxazines offer several interesting physiochemical properties, such low surface tension and low critical micelle concentrations [21, 22]. Our particular interest is to investigate the self-assembly processes of the amphiphilic polybenzoxazine molecules and how the micellar shape that develops depends on the molecular size and concentration.

5.2 Computational Methods

Molecular dynamics (MD) simulation, a method to track the atomic trajectory over time in response to the inter- and intra-molecular forces, was used to study systems that consist of amphiphilic polybenzoxazines in aqueous solution. In this study, the amphiphilic polybenzoxazines are abbreviated as iBnXz, where i represents the number of repeat units: trimer (i=3), tetramer (i=4), hexamer (i=6), octamer (i=8) and decamer
benzoxazine (i=10); these molecules are shown in Table 5.1. Different concentrations of iBnXz were simulated to examine the effects of both the number of repeat units and the molecular concentrations on the micellar morphology. The simulated concentrations are higher than the critical micelle concentrations (cmc’s) (see [21] for the cmc of the i=9 molecule and [23] for the cmc of the i=2 molecule), to allow manageable system sizes to be examined (for concentrations closer to the cmc, the box size would need to be 200 times larger). The MD simulations provide us with detailed information about a system, such as the structure and dynamic properties.

Every atom was explicitly represented (including all hydrogen atoms). The simulations used an all-atom force field for organic molecules, the OPLS-AA force field [24]. The OPLS-AA force field describes the bonded (bond stretching, bond angle and dihedral angle) and non-bonded (Lennard-Jones and Columbic) interactions in the system. The SPC/E water model [25] was used to describe the water molecules.

The simulations were carried out with the Gromacs software package [26]. The input topology files were generated by TopolGen version 1.1 [27], and carefully adjusted before use for MD. A specific number (between 5 and 90) of iBnXz molecules were positioned or inserted randomly into a cubic simulation box of 10×10×10 nm³, and then solvated by adding specific SPC/E water molecules into the box; all simulations began with a random distribution of the molecules in a cubic periodic box, generated with the Gromacs utility “genbox”. In addition, a specific number of water molecules were randomly replaced by Na⁺ counterions for system neutralization, using the Gromacs utility “genion”. As a first step, energy minimizations were carried out using the steepest
descent algorithm until the maximum force in the system becomes less than 0.001 N/mol (1000 kJ/mol/nm). Then, MD simulations in the NVT ensemble (constant number of particles N, volume V, and temperature, T) and the NPT ensemble (constant N, pressure, P, and T) were sequentially carried out for 200 ps each to equilibrate the system at T=298 K and P=1 bar. Finally, a 20 ns MD production run was carried out under T=298 K and P=1 bar, and the last 5 ns of this run were used for analysis.

The simulation details are as follows. The simulations use the Berendsen thermostat [28] and the semi-isotropic Parinello-Rahman pressure coupling [29]. The energies and other statistical data (coordinates, velocities and forces) were stored every 2000 steps during the simulation. The time step of 1 fs was used for all the simulations. Periodic boundary conditions were applied in all three directions to generate a quasi-infinite solution. A 1.0 nm-cutoff was used for the short-range Lennard-Jones and non-bonded interactions. Long-range electrostatic interactions were treated using the particle mesh Ewald (PME) summation method with a grid spacing of 0.12 nm, and a fourth-order B-spline interpolation. For the organic molecules, the bonds containing hydrogen atoms were constrained by the LINCS algorithm [30] and the water molecules were kept rigid by the SETTLE algorithm [31]. The equations of motion were integrated with the Verlet (leapfrog) algorithm. The viewer VMD 1.9.1 [32] was used to analyze the MD trajectories and inspect the arrangement of surfactant molecules in bulk water, by capturing images throughout the trajectories. The simulations were performed in parallel on an Ohio Supercomputer Center (OSC) achieving a rate of 60 CPU hours/ns using 8 nodes.
Table 5.1  The chemical structures and the snapshots of the used amphiphilic polybenzoxazines: The first column shows the abbreviated names, the second column shows the chemical structures using ChemDraw, and the third column shows the snapshots of the molecules at the minimum energy using VMD molecular viewer.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>VMD snapshot</th>
</tr>
</thead>
<tbody>
<tr>
<td>3BnXz</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Snapshot" /></td>
</tr>
<tr>
<td>4BnXz</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Snapshot" /></td>
</tr>
<tr>
<td>6BnXz</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Snapshot" /></td>
</tr>
<tr>
<td>8BnXz</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Snapshot" /></td>
</tr>
<tr>
<td>10BnXz</td>
<td><img src="image" alt="Chemical structure" /></td>
<td><img src="image" alt="Snapshot" /></td>
</tr>
</tbody>
</table>
5.3 Results and discussions

As reported in our previous work (Mahfud et al. 2013) the anionic dimeric benzoxazines are surface-active molecules that aggregate in aqueous media. Simulations were carried out at a concentration much higher than the experimental cmc, which is 0.27 g/L for i=2 and 0.12 g/L for i=9, so that micelles would be expected to form. The simulations began from random initial structures and the spontaneous aggregation of the amphiphilic polybenzoxazine molecules was observed, forming either spherical or cylindrical micelles depending on the molecular concentration and size.

5.3.1 Simulations Analysis

Figure 5.1 shows a series of snapshots illustrating the spontaneous aggregation process at various times (t=0, 1, 2, 4, 8, 16 and 20 ns). The number of the iBnXz molecules was 30 in each case, corresponding to a concentration of 49.8×10⁻³ M. The water molecules are not depicted in Figure 5.1 in order to more clearly show the micelles. Initially, the configurations of the iBnXz molecules are random and almost all the iBnXz molecules are isolated. At t=1 ns, small micelle-like clusters have formed in several positions. As time continues, small micelle-like clusters coalesce into larger structures, such as spherical micelles for 3BnXz and 4BnXz, and cylindrical micelles for 6BnXz, 8BnXz and 10BnXz. Figure 5.1 shows that the micellar shape depends on the molecule size (number of repeat units) at constant molarity. This behavior is attributed to the dependence of the micellar shape on the intensity of the molecular interactions [33], and in particular the short-range forces [34].

129
<table>
<thead>
<tr>
<th>time</th>
<th>3BnXz</th>
<th>4BnXz</th>
<th>6BnXz</th>
<th>8BnXz</th>
<th>10BnXz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ns</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>1 ns</td>
<td><img src="image6" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
</tr>
<tr>
<td>2 ns</td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
</tr>
<tr>
<td>4 ns</td>
<td><img src="image16" alt="Image" /></td>
<td><img src="image17" alt="Image" /></td>
<td><img src="image18" alt="Image" /></td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
</tr>
<tr>
<td>8 ns</td>
<td><img src="image21" alt="Image" /></td>
<td><img src="image22" alt="Image" /></td>
<td><img src="image23" alt="Image" /></td>
<td><img src="image24" alt="Image" /></td>
<td><img src="image25" alt="Image" /></td>
</tr>
<tr>
<td>16 ns</td>
<td><img src="image26" alt="Image" /></td>
<td><img src="image27" alt="Image" /></td>
<td><img src="image28" alt="Image" /></td>
<td><img src="image29" alt="Image" /></td>
<td><img src="image30" alt="Image" /></td>
</tr>
<tr>
<td>20 ns</td>
<td><img src="image31" alt="Image" /></td>
<td><img src="image32" alt="Image" /></td>
<td><img src="image33" alt="Image" /></td>
<td><img src="image34" alt="Image" /></td>
<td><img src="image35" alt="Image" /></td>
</tr>
</tbody>
</table>
**Figure 5.1** Snapshots represent the spontaneous aggregation of the amphiphilic polybenzoxazines (at a concentration of 49.8×10⁻³ M) into spherical and cylindrical micelles. Water molecules are omitted for clarity and the black points represents the Na ions.

The changes in energy during the micellization process were probed. The iBnXz-iBnXz and the iBnXz-H₂O intermolecular potentials are composed of the Coulomb electrostatic and van der Waals (vdW) contributions. Figures 5.2.a and 5.2.b show the changes in iBnXz-iBnXz interaction energy that accompany the micellization process. The changes in the electrostatic interaction are much stronger than the vdw interaction, and therefore electrostatic interactions play a dominant role in the micelle formation. Figures 5.3.a and 5.3.b show the iBnXz-H₂O interaction energy, where the electrostatic interactions is again dominant. In addition, Figures 5.2 (a-b) and 5.3 (a-b) show that electrostatic and vdw interactions are enhanced by increasing the molecule size, mainly due to the increase of interactions between the hydrocarbon chains.
Figure 5.2.a: iBnXz-iBnXz (Atom_Atom) electrostatic short-range interactions (Coul-SR).

Figure 5.2.b: iBnXz-iBnXz (Atom_Atom) van der Waals short-range interactions (LJ-SR).
Figure 5.3.a: iBnXz-H$_2$O (Atom_Atom) electrostatic short-range interactions (Coul-SR).

Figure 5.3.b: iBnXz-H$_2$O (Atom_Atom) van der Waals short-range interactions (LJ-SR).
The cluster size distribution during the simulations was analyzed. Figure 5.4(a and b) shows the number of clusters and the maximum cluster size through the entire simulation. It is assumed that two molecules belong to the same cluster if the distance between their centers of mass is shorter than a cutoff. The clustering algorithm applied to the MD trajectories was developed by Daura et al. [35]. As previously mentioned, the iBnXz molecules are initially randomly distributed in the cubic box and unaggregated, (each molecule is a “cluster”). As the micellization proceeds, the number of clusters within the simulation box decreases in time. The 6BnXz, 8BnXz and 10BnXz clusters show high stability compared to the 3BnXz and 4BnXz clusters, as shown in Figure 5.4.a. This higher stability may be attributed to the fact that molecular interaction increases as the molecule size increased, as shown in Figures 5.2 and 5.3. In addition, the cluster size increases with increase in molecule size. The cluster tripled in size when the molecule size increased from 3BnXz to 10BnXz, as shown in Figure 5.4.b.
Figure 5.4: The number of clusters as a function of time (a), and the relative clusters sizes during the simulations for all the iBnXz molecules based on 3BnXz cluster (b). The analysis was performed by using 1.2 nm cutoffs to define the interaction between iBnXz molecules.

The shape of the iBnXz micelles was investigated by the snapshots of typical configurations, as shown in Figure 5.1. Furthermore, a quantitative analysis, reported by Salina et al [36], was used to describe the geometrical shape of the micelles. This analysis is based on the principal moments of inertia of the micelles. Of particular relevance is $I_{\text{max}}/I_{\text{min}}$ and the eccentricity $e = 1 - \frac{I_{\text{min}}}{I_{\text{avg}}}$ where $I_{\text{min}}$ is the smallest moment of inertia, $I_{\text{max}}$ is the largest moment of inertia, and $I_{\text{avg}}$ is the average value over
all three axes. A micelle with $I_{\text{max}}/I_{\text{min}}=1$ and $e=0$ has a perfect spherical shape, whereas $I_{\text{max}}/I_{\text{min}}>1$ and $e\to1$ for a cylindrical shape. In Table 5.2, the shape parameters for all the simulated aggregates are reported. The 3BnXz and 4BnXz micelles are nearly spherical with small fluctuations [36], and as $I_{\text{max}}/I_{\text{min}}$ gets larger the micelles become less spherical.

**Table 5.2:** Structural Properties of the iBnXz clusters formed in the 49.8 mM simulation systems

<table>
<thead>
<tr>
<th>iBnXz</th>
<th>$I_{\text{max}}/I_{\text{min}}$</th>
<th>$I_{\text{avg}}/(\text{a.m.u.}/(\text{nm}^2))$</th>
<th>$e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3BnXz</td>
<td>1.66±0.24</td>
<td>5.7E10±4.8E10</td>
<td>0.23±0.06</td>
</tr>
<tr>
<td>4BnXz</td>
<td>1.38±0.16</td>
<td>2.8E10±7.7E10</td>
<td>0.17±0.06</td>
</tr>
<tr>
<td>6BnXz</td>
<td>2.69±0.19</td>
<td>1.2E10±4.3E10</td>
<td>0.48±0.03</td>
</tr>
<tr>
<td>8BnXz</td>
<td>4.47±0.57</td>
<td>2.0E10±8.0E10</td>
<td>0.68±0.05</td>
</tr>
<tr>
<td>10BnXz</td>
<td>8.76±0.73</td>
<td>2.3E10±1.3E10</td>
<td>0.83±0.01</td>
</tr>
</tbody>
</table>

Figure 5.5 shows the eccentricity as a function of simulation time for the final 5 ns of the production run. Increasing the molecule size from 3 to 10 repeating units leads to an increase in the eccentricity from 0.23±0.06 to 0.83±0.01, corresponding to a change from spherical to cylindrical shape. Visual inspections of snapshots, as shown in Figure 5.1, confirm this result.
5.3.2 Surfactant Concentration and Micelle Structure

Micellar growth is influenced by many factors, including the alkyl chain length, temperature, counter ion, and surfactant concentration [37]. To study the effect of the iBnXz concentrations on micelle formation kinetics and structure, the concentration was systematically varied from 8.3 mM to 149.4 mM for each of the molecules studied, as shown in Figure 6. More specifically, simulations were performed for same size systems (10 nm$^3$) but with different numbers of molecules. Figure 5.6 shows snapshots from the simulations. All pictures confirm that the hydrophobic alkyl chains point to the center of the micelle and the hydrophilic groups arrange to coat the outside, shielding the hydrophobic core from the surrounding water molecules. It is clear from these results that larger molecules and higher concentrations act to make cylindrical micelles stable.
relative to spherical micelles. Figure 5.7(a-b) summarizes the systematic dependence of
the micelle shape on the concentration of the systems. At concentrations below the
dashed line the most efficient packing geometry is a spherical shape. However, at
concentrations above this line the molecules arrange into cylindrical shaped micelles.
Note (from Figure 5.6) that the spherical micelles are not perfect spheres, but more or
less elliptical, and the cylindrical micelles are not perfectly straight, but have diameters
that vary significantly along their axes.
Figure 5.6 Overview of simulations performed: The snapshots at t= 20 ns represent the effect of both the molecule size and the molecules concentration on the micellization morphology. The letters in the first row define the systems. The numbers between the brackets represent the following: 1- milli-molarity (mM), 2- iBnXz molecules, 3- water molecules, 4- Na ions, 5- wt% of amphiphile. The micelles in the center of the cell represented as van der Waals spheres; Red spots represent the oxygen atoms, cyan color represents the carbon and hydrogen atoms, and the nitrogen atoms are blue.
Figure 5.7 Plots of repeating units, i, in the iBnXz molecules vs. iBnXz concentration (mM)(a) and iBnXz wt% (b). The snapshots of micellar shape in the iBnXz system after 20 ns represent the spherical and the cylindrical regions. The dashed blue line represents the micelles shape transfer zone of iBnXz molecules and indicates the maximum available iBnXz concentrations for spherical micellar shape. The color legend is as described before.
Figure 5.7.a shows that much lower concentrations are needed for the sphere-to-cylinder transition as the number of repeat units in the molecule increase. For example, the transition occurs at ≈ 130 mM for 3BnXz, but at less than 20 mM for 10BnXz. One reason for this is that the molecules with more repeat units are larger in size. Therefore, the concentration by weight percent would be a more effective quantity to describe this transition than molarity (concentration by number of molecules). In Figure 5.7.b the results are shown in terms of weight percent, and the variation is the spherical-to-cylindrical transition point is indeed smaller: a factor of 3 difference between the transition concentrations for 3BnXz and 10BnXz, rather than a factor of more than 6.

But even when weight percent is used for the concentration, there remains a dependence of the transition concentration on the number of repeat units in the molecule. We believe this dependence may be explained by the relative flexibility of the molecules. The flexibility of the iBnXz molecules was assessed through the end-to-end distance. The molecule is considered dynamically flexible if its end-to-end distance varies significantly with time. Figure 5.8.a shows the end-to-end distance of each molecule over the simulation time (20 ns). It is clear that the small molecules (3BnXz and 4BnXz) are less flexible than the larger molecules (6BnXz, 8BnXz and 10BnXz). The distributions of the end-to-end distances have one peak and are approximately Gaussian, as shown in figure 5.8.b. The distributions of the end-to-end distances of the large molecules are broader than those of the small molecules, because the large molecules are much more flexible.

We believe these flexibility results can help explain the dependence of the spherical-to-cylindrical transition on molecular size. Molecules with greater flexibility have greater size fluctuations – the large fluctuations prevent other molecules from
coming close, and thus the more flexible molecules effectively take up more space. Thus the molecules with more repeat units are thus effectively larger than indicated by their molecular weight. For this reason a lower concentration is needed for the spherical-to-cylindrical transition for larger molecules, as found in our results (Figure 5.7.b).

**Figure 5.8:** (a) the end-to-end distances of the iBnXz backbones (left). The measured distances represented by the black lines (right). (b) The end-to-end distance distribution.
5.4 Conclusion:

Molecular dynamics simulations of amphiphilic polybenzoxazine molecules (iBnXz) in water have been carried using the OPLS-AA force-field for the iBnXz molecules and the SPC/E force field for water, where $i$ is the number of repeat units in the molecule. The study is carried out for trimers, tetramers, hexamers, octamers and decamers. Simulations begin with random iBnXz placement, but as the simulation proceeds the iBnXz molecules self-assemble into micelles; the self-assembly process is monitored through changes in the intermolecular energy. At a concentration of 49.8 mM, increasing the molecular size causes the preference of a cylindrical shape over a spherical shape for the micelles; the shape is identified visually as well as quantitatively based on the eccentricity ($e$), which varies from $e=0.23$ for 3BnXz to $e=0.83$ for 10BnXz. The effect of the iBnXz concentrations on micelle shape were studied by systematically varying the concentration of iBnXz from 8.3 mM to 149.4 mM, and the phase diagram was obtained that shows where the spherical and cylindrical shaped micelles are stable. Spherical micelles are stable at lower concentrations, and cylindrical micelles are stable at higher concentrations. The transition point depends on the molecular size – smaller molecules have a higher transition concentration than larger molecules. The effective molecule size depends not only on the molecule’s physical size (related to molecular weight), but there is also an entropic component related to the flexibility of the molecule (the more flexible molecule will require more space).
5.5 References


Chapter 6

6. Conclusions and Future Work
6. Conclusions and Future work

This chapter is split into three main sections. The first part focuses on the synthesis of a novel series of anionic polymeric surfactants via benzoxazine ring opening polymerization, and the influence of the structure, salinity and temperature change on the surface activity. The second part summarizes the conclusions drawn from the MD simulations, highlights their micellization morphology and reviews the predicted behavior of a newly designed family of anionic polybenzoxazine surfactants. The third part of this chapter suggests some promising directions for future research that this thesis has opened.

6.1 Surface active anionic polybenzoxazines

This dissertation focused on the synthesis of novel anionic polymeric surfactants from benzoxazine monomers and correlating the enhancements of surface activity to their chain length change. In the case of poly(4HBA-ocaNa+) surfactant, octylamine (chain length C8) reacted with 4-hydroxybenzoic acid and paraformaldehyde to produce 4HBA-oca. The 4HBA-oca monomer was thermally polymerized via ring-opening of benzoxazine to form poly(4HBA-oca). The poly(4HBA-oca) was ionized by using NaOH to yield poly(4HBA-ocaNa+). The poly(4HBA-deaNa+) and poly(4HBA-doaNa+) were synthesized by using decylamine (chain length C10) and dodecylamine (chain length C12), respectively. The structure of these compounds was determined via FTIR and 1H NMR spectroscopy. Ring-opened structures were also identified by using FTIR and DSC. The 4HBA-oca, 4HBA-dea and 4HBA-doa showed single exothermic peaks at 184 °C, 187 °C and 190 °C, respectively, which are relatively low due to the effective catalytic
nature of the carboxylic acid. TGA showed 45% weight loss around 200 °C for the three benzoxazine polymers, which is attributed to the degradation of linear aliphatic amine. The branched polybenzoxazines have low number average molecular weight \((M_n \sim 2200-6000)\) and high polydispersity \((M_w/M_n \sim 1.2-3.3)\). The surfactant chain length affected the surface activity of anionic polybenzoxazines in the aqueous media and the overall micellization process. The surface tension measurements revealed transition points corresponding to the critical micelle concentrations of the polymeric surfactants. The cmc increases from 0.12 g/L to 0.17 g/L with change in alkyl chain length from C8 to C12. The cmc values at 23±0.1 °C are comparable with literature values reported for polymeric surfactants.

The effects of electrolyte and temperature change on the properties of anionic polybenzoxazine surfactants are important specially at low surfactant concentrations. Upon salt (NaCl) addition, the cmc initially decreases slightly and becomes constant at 3wt% NaCl. The minimum values of the \(\gamma_{\text{cmc}}\) were obtained 1 wt% NaCl for the polybenzoxazine surfactant solution. For example, the \(\gamma_{\text{cmc}}\) of the poly(4HBA-octa-Na\(^+\)) solution gradually decreased from 38 mN/m at 0 wt% NaCl to 27 mN/m at 1 wt% NaCl, and then gradually increased to 30 mN/m at 3 wt% NaCl. Only slight decrease in cmc value was observed with increasing salinity from 0 to 3 wt% of NaCl for the polybenzoxazine surfactant. The mechanism of surface tension reduction is due to the increase in diffusion of the surfactant from bulk to the air-liquid interface by the electrolyte. The temperature-dependence studies of poly(4HBA-octa-Na\(^+\)) show a linear fall in cmc, i.e. as temperature increases cmc decreases in the temperature range 21 to 48 °C. Poly(4HBA-octa-Na\(^+\)) shows an enthalpy–entropy compensation, and the
micellization is entropically-driven. The Krafft temperature increases with alkyl chain length of the polymeric surfactant molecule; the values for poly(4HBA-oca- Na+) poly(4HBA-dea- Na+) and poly(4HBA-doa- Na+) are 4°, 6° and 8°C, respectively.

6.2 MD simulations of surfactants

This thesis also focuses on using MD simulation methods to investigate the structural and dynamical behavior of the low and the high molecular weight anionic benzoxazine surfactants in bulk water phase or at the water/air interface. All MD simulations were carried out by using the OPLS-AA force-field. Due to the complexity of simulating large size molecules, a small size molecule of an anionic dimeric benzoxazine surfactant, di(4CaP-oca- Na+), was synthesized and studied by means of MD simulations in order to understand the main forces and conformational transitions which govern their self-assembly. Furthermore, five amphiphilic anionic polybenzoxazines (iBnXz; where the repeating unit i=3, 4, 6, 8 and 10) were investigated via MD simulations. This study is directly relevant to the experimental work on synthesized anionic amphiphilic polybenzoxazines.

6.2.1 MD simulations of anionic dimeric benzoxazine

The synthesis and the surface activity characterization of dimeric anionic benzoxazine surfactant were investigated experimentally and supplemented by MD simulations. The chemical structure was determined via FT-IR. Ring-opened structures were also identified. Surface tension measurements clearly show the surface activity of the dimeric benzoxazine surfactant and micelle formation above the cmc. A spontaneous
aggregation of the dimeric benzoxazine surfactant in aqueous media was reported by using MD simulations, which form a randomly distributed configuration. Detailed results on the structures and dynamics of the aggregates are analyzed. Two thin shells of water are detected around the hydrophilic segments. There are mainly two conformations: gauche and trans, present in the gas and aqueous phases, the aqueous environment strongly favors the gauche conformation. This investigation provides a theoretical approach to predict the behavior of di(4CaP-ocaNa⁺) molecules. In summary, this thesis presents the first analysis of the molecular structure: distance, orientation, bending, and conformational dynamics of the anionic dimeric benzoxazine surfactant molecules. The results provide a detailed picture of: the self-assembly of these molecules in aqueous bulk media, the predictions on the conformational order of the alkyl chain, the spacer and the polar head-groups, and the orientation of these molecules at the air/water interface. This study demonstrates the feasibility and potential value of future investigations in the design of polymeric surfactants for understanding their behavior in aqueous media and at air/water interface.

6.2.2 MD simulations of anionic polybenzoxazines

MD simulations of the iBnXz molecules were begun with random iBnXz placement. At a concentration of 49.8 mM, iBnXz simulation results show that increasing the molecule size causes a spherical to cylindrical shape transition. The change in micelle shape is related to an increase in the eccentricity (e); the value of e is equal to 0.23 and 0.83 for 3BnXz and 10BnXz, respectively. The iBnXz surfactants are shown to be Gaussian with respect to their end-to-end distance, where the 6, 8 and 10BnXz are much
more flexible than the 3 and 4BnXz molecules. The 6, 8 and 10BnXz molecules tend to exhibit larger van der Waals and electrostatic inter/intra-molecular interactions compared to the 3, 4BnXz molecules; increasing molecule size enhances the hydrophobic interactions between the hydrocarbon chains, and the larger molecules experience larger attractive force. The effect of iBnXz concentration on micelle morphology was studied by systematically varying the concentration of 3, 4, 6, 8 and 10BnXz from 8.3 mM to 149.4 mM, and the regions of spherical and cylindrical shape micelles were defined. The theoretical physical radius of the 9BnXz micelle was 1.356 nm, complementary to the experimental data, 1.364 nm.

6.3 Future Work

A comparison of the cmc and $\gamma_{\text{cmc}}$ of the new anionic polymeric surfactants with literature values for both low and high molecular weight surfactants are made to justify that the polybenzoxazines offer a superior alternative to conventional surfactants. Furthermore, the polymeric surfactants reported herein are thermally stable up to about 170 °C and do not contain sulfur, and therefore are more ecofriendly than many commercial surfactants. So, the focus for future research should be on controlling the repeating units of the amphiphilic anionic polybenzoxazines because it plays a crucial role in surface activities. Moreover, the head groups can be anionic, cationic, zwitterionic, or nonionic. The negatively charged group can be carboxylate, $-\text{CO}_2^-$, sulfate, $\text{SO}_4^{2-}$ or sulfonate, $-\text{SO}_3^-$. The carboxylic head group can be replaced by sulfate head group by using 4-Hydroxyphenyl hydrogen sulfate instead of 4-Hydroxybenzoic acid, in order to examine the effect of increasing the hydrophilicity of the charged head.
groups. If the produced surfactant is more efficient in decreasing the surface tension and reducing the cmc, then the sulfate based surfactant provides another opportunity for fundamental research. However, this work clearly demonstrates that variation in the alkyl chain length of the anionic polybenzoxazine surfactants has a significant effect on reducing the water/air surface tension and decreasing the cmc.

Potential avenues for future research based on this study are extensive. The possible ideas presented here are greatly enriched by suggestion, but by no means are fairly exhaustive. All-atom MD simulations can performed to explore many aspects of self-assembly in detail. This work shows clearly the usefulness of using MD simulations at an all-atom level, as it provided detailed information about the micelle morphology, the structural and conformational analysis, the inter/intra-molecular interactions, etc. Research points to possible new route to modify the surfactants based benzoxazine might have some capability to suggest the surfactant structure. The illustration of the energetic and structural determinants of amphiphilic polybenzoxazine aggregation poses an essential challenge to synthesis and physical studies of macromolecular compounds and still needs to rely on the study of simplified model systems. Although the OPLS-AA model still remains simple, it presents a model that will lead to the determination of reliable structural models for amphiphilic polybenzoxazines. Moreover, concepts and insight from theoretical and simulation studies help to describe and understand polymeric surfactant behavior at a molecular level.
Appendix

i. The Molecular Dynamics Algorithm

The molecular systems are described by the Optimized Potentials for Liquid Simulations- All Atom (OPLS-AA) force field [1]. This force field contains terms for the following interactions:

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

\[ V_{\text{bonded}} = V_{\text{bonds}} + V_{\text{angles}} + V_{\text{dihedrals}} \]

\[ V_{\text{bonds}} = \sum_{\text{bonds}} K_r (r - r_0)^2 \]

\[ V_{\text{angles}} = \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 \]

Here the subscripts 0 are used to denote the equilibrium values of the bond length \( r \) and angle \( \theta \).

\[ V_{\text{dihedrals}} = \sum_{l} \left( \frac{V_1^l}{2} [1 + \cos(\phi_l - f_{1l})] + \frac{V_2^l}{2} [1 - \cos2(\phi_l - f_{2l})] \right. \\
\left. + \frac{V_3^l}{2} [1 + \cos3(\phi_l - f_{3l})] \right) \]

Where \( \phi_l \) is the dihedral angle, \( V_1, V_2, \) and \( V_3 \) are the coefficients in the Fourier series, and \( f_{1l}, f_{2l}, \) and \( f_{3l} \) are phase angles.

\[ V_{\text{nonbonded}} = \sum_{l} \sum_{j} \left[ \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left( \frac{a_{ij}^{12}}{r_{ij}^{12}} - \frac{a_{ij}^{6}}{r_{ij}^{6}} \right) \right] f_{ij} \]
The non bonded interactions between two molecules \(a\) and \(b\) are represented by the
Coulomb's and Lennard-Jones where: \(r_{ij}\) is atom \(i\)-atom \(j\) distance; \(\sigma_{ij} = \left(\frac{\sigma_{ii}}{\sigma_{jj}}\right)^{1/2}\) and
\(\epsilon_{ij} = \left(\frac{\epsilon_{ii}}{\epsilon_{jj}}\right)^{1/2}\), \(\sigma_{ij}\) is the arithmetic mean
for the unlike size parameter motivated by collisions of hard spheres (atom \(i\) and atom \(j\)), and \(\epsilon_{ij}\) is the geometric mean for the unlike energy parameter.

The same expression is used for intramolecular non bonded interactions between all pairs
of atoms \((i < j)\) separated by three or more bonds; 1,4 interactions are scaled down by the "fudge factor" \(f_{ij}=0.5\), otherwise \(f_{ij}=1.0\). All the interaction sites are centered on the atoms; there are no "lone pairs". The OPLS-AA parameters are supported by GROMACS [2].

ii. Integrating the equations of motion

The integration in GROMACS is performed using the leap-frog algorithm [3] and can be summarized in the following scheme;

\[
V(t + \frac{\Delta t}{2}) = V(t - \frac{\Delta t}{2}) + \frac{F(t)}{m} \Delta t
\]

\[
r(t + \frac{\Delta t}{2}) = r(t) + V(t + \frac{\Delta t}{2}) \Delta t
\]

Here \(\Delta t\) denotes time step, \(r(t)\) the particles coordinate vector, and \(V(t)\) respective velocities.
iii. Berendsen temperature and pressure coupling

To maintain the temperature, the system is coupled to an external heat bath with fixed Temperature $T_0$ [4]. The temperature of the system is corrected such that the deviation exponentially decays with some time constant, $\tau$;

$$\frac{dT(t)}{dt} = \frac{1}{\tau}(T_o - T(t))$$

$$\Delta T = \frac{\delta t}{\tau} (T_o - T(t))$$

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left\{ \frac{T_o}{\left(T(t - \frac{\delta t}{2})\right)} - 1 \right\}, \text{ where } \lambda^2 \text{ is the scaling factor for the velocities.}$$

To maintain the pressure, the system is made to obey the equation of motion at the beginning of each time step [4];

$$\frac{dP(t)}{dt} = \frac{1}{\tau}(P_o - P(t))$$

Where $P(t)$ is the instantaneous pressure, $P_o$ is the desired pressure, and $\tau$ is the barostat relaxation time constant.

At each time step the MD cell volume and the cell vector are scaled by $\eta$ and $\eta^{1/3}$, respectively.

$$\eta(t) = 1 - \frac{\Delta t}{\tau} \gamma (P_o - P(t))$$

Where $\gamma$ is the isothermal compressibility of the system.
iv. **Trajectory Analysis**

The trajectory files were analyzed through `g_rdf`, `g_angle`, `g_dist`, `g_gyrate`, `g_rms` and `g_energy` GROMACS utilities in order to obtain the radial distribution function (RDF), dihedral angle analysis, atom-atom distance, radius of gyration, root mean square deviation (RMSD) and interaction energies, respectively. Furthermore, the VMD (Visual Molecular Dynamics) was used to animate and analyze the trajectory of MD simulations, by displaying and animating the molecules undergoing simulation on a remote computer.

v. **References**

Chapter 7

7. Bibliography
7. Bibliography


Dynamics Simulation of Liquid Benzene and Naphthalene." Molecular
Physics 70: 53–63.
Simulations: Techniques and Approaches In: "Molecular Liquids - Dynamics
and Interactions" (Eds: A.J. Barnes et al.) NATO ASI Series C135, (Reidel,
Dordrecht) 475-500.
[18] Bogusz, S., R.M. Venable, et al. (2000) “Molecular Dynamics Simulations of
Octyl Glucoside Micelles: Structural Properties” The Journal of Physical
Chemistry B 104(23): 5462-5470.
Advances in Polymer Science 143: 113-194.
and biopolymers.” Advances in Polymer Science 48: 1–124.
Branching from Combined Quasi-Elastic and Intergrated Scattering”
Macromolecules 13(5) 1265-1272.
poly(methacrylic acid) Diblock Copolymers: Self-Assembly in Aqueous
with Low Interfacial Tension by Ultrasonic Method” Polymer Journal 31(11-
1): 920-923.
surfactants” European Polymer Journal 38(7): 1457-1463.
behavior of polymeric surfactants in aqueous solution.” Journal of Applied
Polymer Science 98(3): 945-949.
model wastewater by using polybenzoxazine aerogel.” Desalination 256(1-3):
108-114.
polybenzoxazines formed by polymerization with argon, oxygen, and
hydrogen plasmas.” The Journal of Polymer Science Part B: Polymer Physics
42(22): 4063-4074.
concentration of polyoxyethyleneated non-ionic surfactants.” Colloids and


Journal of the American Chemical Society 64(11): 2716-2718.


Polymer 36(26): 3151–3158.


Journal of the American Chemical Society 118(45): 11225-11236.


Publications, Inc.


[107] Mahfud, R., H. Ishida, and S. Qutubuddin. Anionic Surfactants Based on Comb-like Polybenzoxazine Oligomers: Effect of Salinity and Temperature on Critical Micelle Concentration. ‘prepared to be submitted’

[108] Mahfud, R., D. Lacks, H. Ishida, and S. Qutubuddin, Molecular Dynamics Simulations of iBnXz. ‘Submitted’


