

**School of Chemical and Petroleum Engineering  
Department of Chemical Engineering**

**Adsorption and Ionization of Carboxylic Acids at the Air/Water  
Interface**

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**This thesis is presented for the degree of  
Master of Philosophy (Chemical Engineering)  
Of  
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## DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Date: 22 May 2017

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## Publications with materials produced in this study

1. Shiva Badban, Anita E. Hyde and Chi M. Phan, Hydrophilicity of nonanoic Acid and its Conjugate Base at the Air/Water Interface, ACS Omega Journal. August 2017. (Accepted and published)
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## ABSTRACT

Surface active agents or surfactants are widely used in different industries. They can be found in essential application in our daily life: pharmaceuticals, soap, detergents and washing products. They also have crucial role in industries such as petroleum, foaming, wetting, printing and biotechnology. Their importance comes from their special behaviour when existing in small amounts at an interface (boundary between two immiscible medium). Surfactants adsorb at interfaces of a system and change the amount of work required to expand the surface and alter interfacial behaviours. Despite of thousands years of applications, some fundamental aspects of surfactants remain unknown. Specifically, the ionization of surfactants at the air/water interface is still unquantified.

This study focuses on ionic surfactants performance at air/water interface. Carboxylic acids of  $C_9$  and  $C_{10}$  were investigated experimentally and theoretically. Experiments on these surfactants were carried out in two conditions: one was acid only and the other one was constant sodium hydroxide concentration. In first case, fatty acids solutions were prepared by mixing small amounts of acids in water, measuring surface tension (pendant bubble method) and  $pH$  while diluting the solution with increasing amount of water. In second section of experiments, acids were dissolved in water by adding 10 mole percent extra of sodium hydroxide. Then surface tension was measured using Wilhelmy plate method. These two sets of experimental data were considered in order to validate the theoretical model.

In modelling part, a general adsorption model based on the dissociation constant was developed for ionic surfactants. The well-known Gibbs equation was applied to quantify the adsorbed concentration. The model was applied to the two experimental conditions simultaneously.

It was found that the adsorption constant for the neutralized species is much higher than that of the ionized species. Finally, adsorption parameters such as adsorption constants and surface concentrations, dissociation constant  $pK_a$  and  $CMC$  of acids used in this work were compared. The results shed important insights into ionization of fatty acids at the air/water interface.

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## LIST OF ABBREVIATIONS AND SYMBOLS

A	Surface Area - mathematical constant	m <sup>2</sup>
B	Mathematical constant	
CMC	Critical Micelle Concentration	M
C <sub>b</sub>	Bulk Concentration	M
C <sub>i</sub>	Concentration of component i	M
DST	Dynamic Surface Tension	mN/m
G	Surface Free Energy	mJ/m <sup>2</sup>
IFT	Interfacial Tension	mN/m
k <sub>a</sub>	Acid Ionization or Dissociation Constant	M
k <sub>b</sub>	Base Ionization or Dissociation Constant	M
K <sub>A</sub> , K <sub>AH</sub>	Adsorption Constants for ionized and neutralized acid	M <sup>-1</sup>
K <sub>H</sub>	Henry Adsorption Constant	M <sup>-1</sup>
K <sub>L</sub>	Langmuir Adsorption Constant	M <sup>-1</sup>
m	Mass of the Wilhelmy plate	kg
n	Number of moles of a component - pre factor/ number of carbon atoms	
ρ	Perimeter of the Wilhelmy plate	m
pk <sub>w</sub>	Ionic product of water	
pk <sub>a</sub>	Acid strength constant	
Δp	Pressure difference	atm
r	Radius of the drop	m
R <sub>1</sub> , R <sub>2</sub>	Radii of Curvature	m
R	Gas Constant	
S	Surface area of the drop - entropy	m <sup>2</sup> - J/K
ST	Surface Tension	mN/m
T	Temperature	°C
V	Volume of the drop	m <sup>3</sup>
W	Work	J

## Greek Symbols

$\alpha$	Degree of ionization	M
$\gamma$	Surface tension	mN/m
$\gamma_0$	Solvent surface tension	mN/m
$\gamma_{eq}$	Equilibrium surface tension	mN/m
$\Gamma$	Surface Excess Concentration	mole/m <sup>2</sup>
$\Gamma_{eq}$	Equilibrium Surface Excess Concentration	mole/m <sup>2</sup>
$\Gamma_m$	Maximum Surface Excess Concentration	mole/m <sup>2</sup>
$\Gamma_v$	Number of Vacant Sites	mole/m <sup>2</sup>
$\chi$	Adsorption Constant	M <sup>-1</sup>
$\mu_i$	Chemical Potential	J/mole
$\Lambda_0$	Limiting conductance	S
$\Lambda_c$	Equivalent conductance	S

## GLOSSARY OF THE TERMS

<b>Adhesion</b>	The tendency of dissimilar particles or surfaces to cling to one another.
<b>Adsorption</b>	The adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface.
<b>Aliphatic compounds</b>	Organic compounds in which carbon atoms form open chains (as in the alkanes), not aromatic rings.
<b>Amphiphilic</b>	Of a compound (such as a surfactant) consisting of molecules having a polar water-soluble group attached to a water-insoluble hydrocarbon chain.
<b>Anion</b>	A negatively charged ion.
<b>Aqueous Solubility</b>	The ability of chemical substances, called solute, to dissolve in a water solution.
<b>Biodegradation</b>	The disintegration of materials by bacteria, fungi, or other biological means.
<b>Bulk phase</b>	The majority of the solid or liquid in a large mass compared to the surface phase.
<b>Cation</b>	A positively charged ion.
<b>Capillary action</b>	The ability of a liquid to flow in narrow spaces without the assistance of, or even in opposition to, external forces like gravity.
<b>Chemical potential</b>	A thermodynamic function expressing the ability of an uncharged atom or molecule in a chemical system to perform physical work.
<b>Cohesion</b>	The tendency of similar or identical particles/surfaces to cling to one another.
<b>Conductivity</b>	A measure of an electrolyte solution ability to conduct

	electricity.
<b>Contact angle</b>	One of the common ways to measure the wettability of a surface or material.
<b>Diffusion</b>	The process of a substance spreading out to evenly fill its container or environment.
<b>Dissociation</b>	A general process in which molecules (or ionic compounds such as salts, or complexes) separate or split into smaller particles such as atoms, ions or radicals, usually in a reversible manner.
<b>Dissociation constant</b>	Any constant used to measure acids and bases strength.
<b>Double electrical layer</b>	A region existing at the boundary of two phases and assumed to consist of two oppositely charged layers (such as a layer of negative ions adsorbed on colloidal particles that attracts a layer of positive ions in the surrounding electrolytic solution) called also Helmholtz double layer.
<b>Dynamic surface tension</b>	The value of the SFT or IFT referred to a particular surface age or interface age. In the case of liquids with surface-active substances (surfactants), this can differ from the equilibrium value.
<b>Electrolyte</b>	A chemical compound that conducts electricity by changing into ions when melted or dissolved into a solution.
<b>Chemical Equilibrium</b>	The point at which the concentrations of reactants and products do not change with time. It appears as though the reaction has stopped but in fact the rates of the forward and reverse reactions are equal so reactants and products are being created at the same rate.
<b>Fatty acid</b>	A carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Most naturally occurring fatty

acids have an unbranched chain of an even number of carbon atoms. The general formula of a fatty acid is R-COOH, with R referring to the rest of the molecule.

<b>Hydrophilicity</b>	The tendency of a molecule to be solvated by water.
<b>Hydrophobicity</b>	The physical property of a molecule that is seemingly repelled from a mass of water.
<b>Interface</b>	A term used for a boundary between different phases.
<b>Interfacial tension</b>	The force that holds the surface of a particular phase together and is defined to the interface of two immiscible liquids.
<b>Ionization</b>	Any process by which electrically neutral atoms or molecules are converted to electrically charged atoms or molecules (ions).
<b>Krafft point</b>	The minimum temperature at which surfactants form micelles.
<b>Lipophilicity</b>	The ability of a chemical compound to dissolve in fats, oils, lipids, and non-polar solvents such as hexane or toluene.
<b>Micelle</b>	Micelles are aggregates of surfactants in aqueous solutions. The formation of a micelle is a response to the amphipathic nature of surfactants, meaning that they contain both hydrophilic regions (polar head groups) as well as hydrophobic regions (the long hydrophobic chain). Normally, micelles have a spherical shape.
<b>Monolayer</b>	A single, closely packed layer of atoms, molecules, or cells. In some cases it is referred to as a self-assembled monolayer.
<b>Neutralization</b>	The opposite process of ionization, in which an acid and a base react quantitatively with each other.



<b>Natural Soap</b>	The product from the saponification of triglycerides. Historically, it can be obtained by mixing oils, alkali and water.
<b>Surface activity</b>	The property possessed by certain solid substances to influence the surface tension of liquids or the strong adsorption of such materials at surfaces or interfaces in the form of an orientated monomolecular layer (or monolayer).
<b>Surface excess concentration</b>	The area-related concentration of a surfactant at the surface or interface. It has the unit of mol/m <sup>2</sup> .
<b>Surface free energy</b>	The work per unit area done by the force that creates the new surface.
<b>Surface tension</b>	The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension. The molecules at the surface do not have other like molecules on all sides of them and consequently they cohere more strongly to those directly associated with them on the surface. It is defined to a single liquid surface
<b>Surfactant</b>	Surface active agents that lower the surface tension (or interfacial tension).
<b>Turbidity</b>	Cloudiness or haziness of a fluid caused by large numbers of individual particles that are generally invisible to the naked eye, similar to smoke in air.
<b>Van der Waals force</b>	Weak, short-range electrostatic attractive forces between uncharged molecules, arising from the interaction of permanent or transient electric dipole moments.
<b>Wettability</b>	The tendency of one fluid to spread on, or adhere to, a solid surface in the presence of other immiscible fluids.

# 1 INTRODUCTION

## 1.1 BACKGROUND

Adsorption of surfactants at interfaces plays an important role in different industries from foaming and coating to petroleum, from pharmaceutical and cosmetics to waste water treatment and from agricultural to detergent industry.<sup>1, 2</sup> Special behaviour of surfactants results from their characteristic structure. These surface active agents consist of two parts; one with tendency toward polar groups which includes heteroatoms such as *O*, *S*, *P*, or *N* in their functional groups; and the other part with affinity to nonpolar groups which is in general a hydrocarbon chain.<sup>3, 4</sup> When surfactants exist in interfaces such as air/water, they orient to place their hydrophilic head into water and their hydrophobic tail into air in order to get adsorbed on to the interface. Therefore, the adsorption causes reduction in surface tension.<sup>5, 6</sup>

Two common surfactant based products are soaps and detergents. Soaps are fatty acid salts with at least eight carbon atoms. Detergents are surfactants, or surfactant mixtures with cleaning properties.<sup>1, 7</sup>

The study combines experimental and theoretical frameworks to verify the adsorption of two types of fatty acids at air/water interface. For weak electrolytes such as carboxylic acids, it has been proposed that the surfactant has different ionic states<sup>8</sup>: ionized species dominate the bulk while neutralized species dominate the interface. The adsorption of ionic states is simultaneously controlled by both interfacial adsorption and reaction equilibria.<sup>9</sup> Hence, an appropriate adsorption model has to include the reaction equilibrium. The model can reveal important insights. For instance, the thickness and the ionic nature of the interfacial zone can be properly quantified.<sup>10</sup> The adsorption constants of ionized and neutralized species can be also quantitatively described.

This study focuses on the adsorption of weak electrolytes, decanoic acid and nonanoic acid. The acids were selected for several reasons. First, they are partially

dissociated at normal conditions. Hence, both ionized and non-ionized species exist, at significant percentages in the bulk. Second, the dissociation constant can be routinely determined by *pH* measurements. The effective modelling can describe the ionic status of the adsorbed acid as well as the physical characteristic of the interfacial zone. Finally, the carboxylic acid remains an important and economical surfactant for commercial soaps and detergents.

This study demonstrates the effects of carboxylic length on adsorption and interfacial properties at air/water interface.

## 1.2 OBJECTIVES OF THE THESIS

Although adsorption of surface active agents has been studied in last decades, the nature of these surfactants at the air/water interface remains poorly described. The main objective of this thesis is to address anionic surfactants adsorption behaviour at air/water interface by:

1. An adsorption model based on the dissociation constant developed for ionic surfactants;
2. Applying the model to the adsorption of decanoic acid and nonanoic acid at the air/water interface;
3. Considering two limiting cases for experimental verification: acid only and acid with a constant and high  $Na^+$  concentration. (The model was applied at both conditions simultaneously).

## 1.3 SCOPE OF WORKS

The study consists of experimental works and theoretical modelling in order to achieve adsorption parameters at the interface. Experimentally, we had to measure surface tension and *pH* of carboxylic acids, more specifically fatty acids as surfactants at air/water interface. Then experimental data were fitted into the proposed model to obtain surface excess concentration and adsorption constants.

Ultimately, achieved data for all surfactants were compared with each other in graphical descriptions.

## 1.4 FORMAT OF THE THESIS

### CHAPTER1:

General introduction to the research including the methodology toward understanding the proposed ionic surfactants adsorption performance at air/water interface is given in this chapter.

### CHAPTER2:

A review of wide range of studies toward understanding the adsorption phenomena, adsorption isotherms, interfacial tension phenomena, surface tension measurement methods, surfactants types and their adsorption behaviour are carried out in this chapter.

### CHAPTER3:

All the chemicals used for this work are presented in this chapter. The applied apparatus and measurement methods are also described which include equilibrium and dynamic surface tension measurement along with *pH* and density.

### CHAPTER4:

The experimental results, proposed theoretical model and modelling results for decanoic acid adsorption at air/water interface are discussed in this chapter. The theoretical modelling (section 4.2) is applicable to all fatty acids, including nonanoic acid in chapter 5.

### CHAPTER 5:

The experimental results of nonanoic acid adsorption at air/water interface are presented in this chapter. Theoretical model introduced in chapter 4 is applicable to this chapter. Therefore, theory section is briefly described in chapter 5. Furthermore, experimental and theoretical results for adsorption of nonanoic acid and decanoic acid (from chapter 4) are compared here.

Finally, interesting conclusions are achieved from comparing both acids physical and adsorption data.

#### CHAPTER6:

Summary of the procedures, unique measurement methods and novel theoretical framework are described here. Recommendations for further research toward fully understanding the behaviour of anionic surfactants at air/water interface are also provided.

## 2 LITERATURE REVIEW

This section includes previous research studies investigating the phenomena applied in adsorption of surfactants at air/water interface. Interfacial phenomena, surface tension measurement methods, surfactants classification, ionization process and adsorption fundamentals are introduced. Although much of the research up to now has been descriptive in nature of surfactants adsorption at interfaces, adsorption behaviour of anionic surfactants at air/water interface is inadequately described.

### 2.1 INTERFACIAL PHENOMENA

Interfacial tension between air-liquid or liquid-liquid systems has been major phenomena in nature and our daily life. Interfacial tension allows an insect to float on water surface and it is also responsible for the shape of liquid droplets.<sup>11</sup>

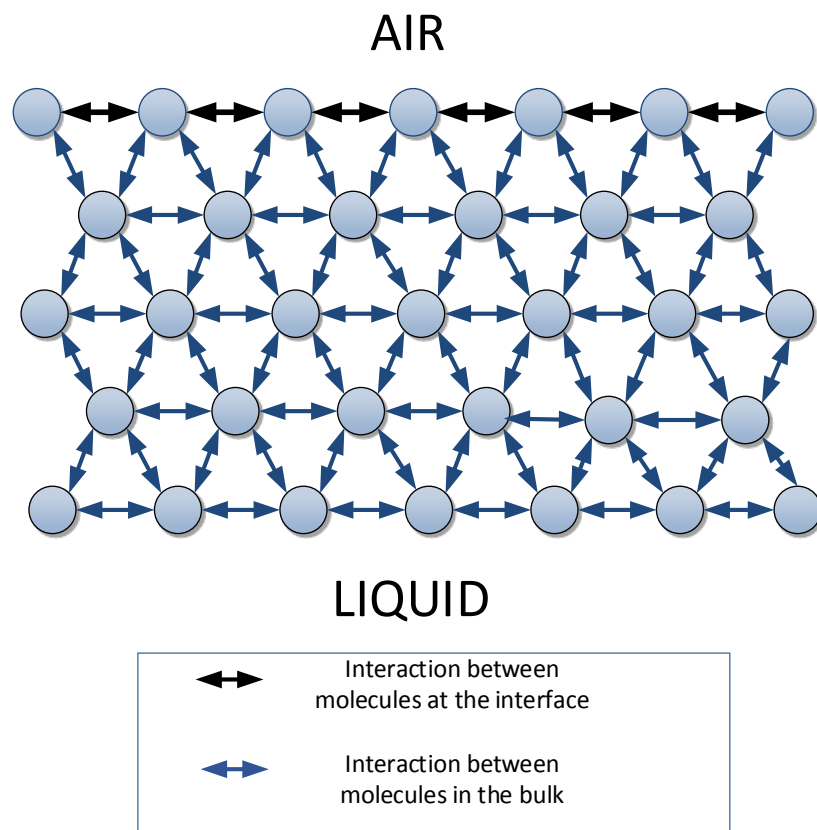
To investigate interfacial properties of liquids, some measuring factors such as surface tension, interfacial tension and critical micelle concentration play crucial role in understanding the phenomena. These data give necessary information in the measurement of adhesion, material solubility, biocompatibility and lubricity of solid surfaces as well as wetting, washability, spreading, and adsorption of liquids.<sup>12, 13</sup>

Interfacial phenomena play a significant role in systems affected by interfacial processes. In these systems, phase boundaries show unusual and different behaviour than the whole bulk solution. It is necessary to understand the roots of this abnormal behaviour and the factors influencing it. So that we will be able to control such a system and the parameters affecting it.<sup>12, 14</sup> There is a growing interest in understanding properties of surfaces and interfaces in past years that requires more research to be done in this area.<sup>15</sup>

## 2.2 INTERFACIAL TENSION

Surface tension is a measurement of the cohesive energy present at an interface. All molecules in the bulk of a liquid tend to absorb each other in a way that equal forces attract them in all directions. However, interfacial molecules feel a different force as indicated in Figure 2-1. Surface free energy is the excess energy present at the surface and can be quantified as a measurement of energy per area. The above mentioned experience for molecules at the surface is described as having a line tension or a surface tension which is quantified as a force per length measurement. The most common units for surface tension are *dynes/cm* or *mN/m* which are equivalent.<sup>16, 17, 18</sup>

The surface typically refers to a boundary between two fluids (the denser and the less dense phase). The boundary might be between solid and liquids as solids also have surface free energy at their interfaces but measurement method at this condition is not possible through the techniques used for liquids.<sup>19</sup>

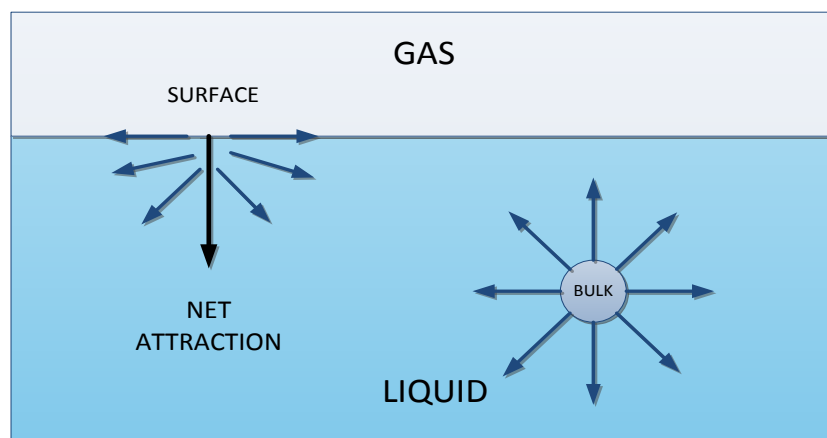


**Figure 2-1. Intermolecular forces around molecules at interface and in the bulk**

Interface is a term used for a boundary between different phases. The liquid-liquid interface is that between two immiscible liquids and the air-liquid interface is that between air and liquid.

Excess free energy or lateral stress is initiated from density and composition difference across the interface. This excess energy is called interfacial tension.<sup>20</sup> Interfacial tension can be viewed in two ways; thermodynamics and mechanical points of view. Thermodynamically, it is free excess energy per unit area. In interfacial region density is lower than bulk phase. Accordingly, molecules average distances are greater. Since molecules attract each other, additional energy per molecule is needed to separate them which is known as interfacial tension. From mechanical point of view, tension is a force per unit length parallel to the interface which is also two dimensional counterpart of pressure in a bulk fluid.<sup>14, 21</sup>

The required work to bring molecules to the interface or change a surface area can be given as  $\partial W = \gamma dA$  where  $W$  is work,  $A$  is surface area and  $\gamma$  is surface or interfacial tension.<sup>22</sup>



**Figure 2-2. Unequal forces around molecules at a gas/liquid interface**

Consequently, in a medium like a liquid, all molecules feel the same van der Waals forces except the ones in the interfacial region and this unequal force that pulls the interfacial molecules inwards is called surface tension. (Figure 2-2)<sup>23, 24</sup> The interfacial energy can be derived based on the Laplace equation and modelled as a ratio of the excess Gibbs interfacial energy<sup>25</sup> which will be described in the following sections.



### 2.2.1 GIBBS LAW

Interfacial region between two phases usually has a thickness with properties that are different from the two bulk phases. A substance will be more soluble in the surface than it is in the liquid whenever its presence in the surface decreases the free surface energy. To obtain the definition of surface tension, Gibbs model is applied. This model assumes an interfacial region between two phases which has different thermodynamic properties than the phases. Gibbs-Deuhem equation applies to this region:

$$dG = -SdT + Ad\gamma + \sum n_i d\mu_i \quad [1]$$

Where  $G$  is the surface free energy,  $S$  is the entropy,  $A$  is the area of the interface, and  $n_i$  is the number of moles of component  $i$  with chemical potential  $\mu_i$  at the interface. At constant temperature and composition of the interface:

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T, n_i} \quad [2]$$

The surface tension is force per unit length tangentially to the surface measured in units of  $mN/m$  or energy per unit area measured in  $mJ/m^2$ .<sup>16, 26</sup>

### 2.2.2 LAPLACE LAW

Let us consider a drop of liquid which is in equilibrium with a large amount of vapour around it. At equilibrium phase, small amount of vapour condenses into the drop and changes its radius about  $\delta r$ . Considering  $\Delta p$  as difference between pressure in the drop and vapour,  $V$  and  $S$  as volume and surface area of the drop, according to Gibbs law, pressure difference can be described as:

$$\Delta p = \gamma \frac{\delta S}{\delta V} \quad [3]$$

For a spherical drop, substitution of  $\Delta S = 8\pi r \delta r$  and  $\delta V = 4\pi r^2 \delta r$  in above equation, results in Laplace Law:

$$\Delta p = \frac{2\gamma}{r} \quad [4]$$

Where  $r$  is radius of a drop,  $\Delta p$  is pressure difference between neighbouring phases and  $\gamma$  is surface tension.<sup>27</sup>

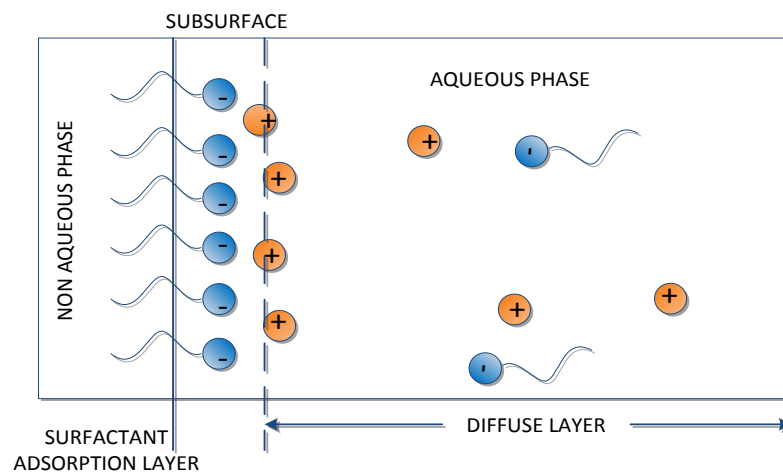
Interfacial tension is responsible for the shape of fluid interfaces. For instance, droplets of liquid and bubbles of gas tend to adopt a spherical shape since it reduces the surface free energy.<sup>28</sup>

### 2.2.3 EQUILIBRIUM VERSUS DYNAMIC SURFACE TENSION

While the above theories are applicable to surfactant solutions, these are often applied to equilibrium condition only. In practice, the surface tension of a certain system may take some time to reach equilibrium. The transient values during the equilibration is called dynamic surface tension. This is often due to the diffusion of surfactant from the bulk into the interface.

Dynamic surface tension data have wide applications in coating and photographic industry as the coating process is highly dynamic and involves generation and extension of surfaces.<sup>29</sup> In a surfactant solution, changes in surface, forces the system to restore equilibrium by a flux of surfactant between subsurface layer and the surface. This process involves two stages:

- Exchange of surfactant from the bulk solution to the subsurface layer;
- Flux of surfactant from subsurface to the adsorption layer.<sup>1, 30</sup>



**Figure 2-3. Adsorption layer of a surfactant**

At a newly formed interface of a surfactant, surface tension  $\gamma$  is close to solvent surface tension  $\gamma_0$ . After a while,  $\gamma$  reaches to  $\gamma_{eq}$  which is equilibrium surface tension. This period of dynamic adsorption lasts from milliseconds to a few days depending on surfactant concentration and type. When the surface is fresh, there is

a flux of surfactant from the bulk into the interface. Therefore, surface tension changes from  $\gamma_0$  to  $\gamma_{eq}$  and interfacial concentration also reaches the equilibrium value.<sup>31</sup> Dynamic surface tension, *DST* or  $\gamma(t)$  is very important in biological processes, photographic, coating, agricultural, oil recovery, foaming, metal, textile, paper, pharmaceutical and many more industries.<sup>32</sup> There are different ways to measure *DST*, however the most common ones are maximum bubble pressure, drop volume and inclined plate flow cell.<sup>31</sup> The applicability of each method depends on the time scales of dynamic steps. For example, the max bubble pressure method can measure surface tension from 10 ms to 10 s only.

## 2.3 METHODS OF MEASURING INTERFACIAL TENSION

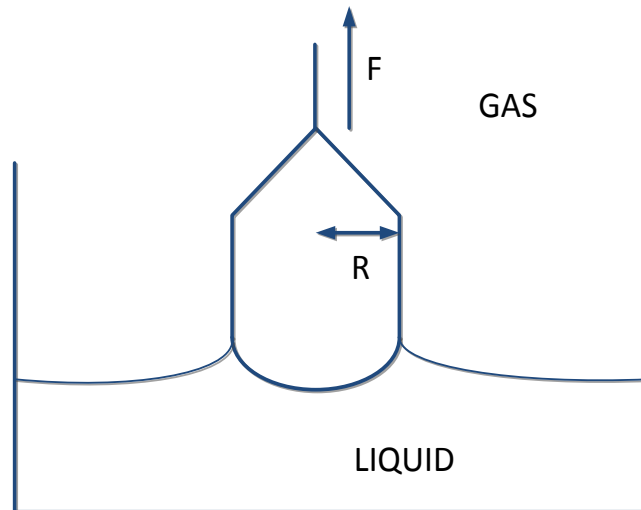
There are many methods developed for measuring equilibrium surface tensions which can be classified as bellow categories:

- Force based methods - Du Nouy ring and Wilhelmy plate;
- Shape base methods - Sessile drop, pendant drop, and spinning drop;
- Pressure methods - Small bubble surfactometer;
- Other methods.<sup>33</sup>

Amongst these methods, shape based ones are the most versatile. They can be used at different conditions such as high temperature and pressure.<sup>18, 24</sup>

### 2.3.1 DU NOUY RING METHOD

In this method, the capillary force on a platinum ring at the gas-liquid surface is measured. When the ring is pulled upward, the capillary force is the highest amount. This force is in proportion to the surface tension, the cosine of the contact angle, and the wetted perimeter. Depending on the ring dimensions, a correction factor is usually needed. The method is suitable for measuring equilibrium tensions of systems which reach equilibrium quickly.<sup>34</sup>



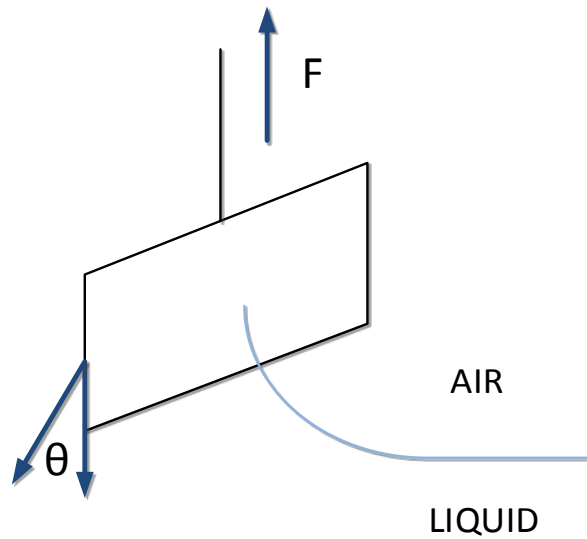
**Figure 2-4. Surface tension measurement applying Du Nouy ring method**

### 2.3.2 WILHELMY PLATE METHOD

This method is similar to the Du Nouy method except that it gives more reliable results. However, it needs some conditions to be considered in order to get precise results; the plate should be kept steady as the tension is measured and the force needs to be measured continuously with a sensitive electro balance. This method has been widely used to quantify dynamic and equilibrium surface properties. Total force on the plate can be given by following equation: <sup>21</sup>

$$f = mg + \gamma P \quad [5]$$

Where  $m$  is mass of the plate and  $P$  is perimeter of the plate. Interfacial tension  $\gamma$  will be easily calculated as all quantities in above equation can be measured.



**Figure 2-5. Surface tension measurement using Wilhelmy plate method**

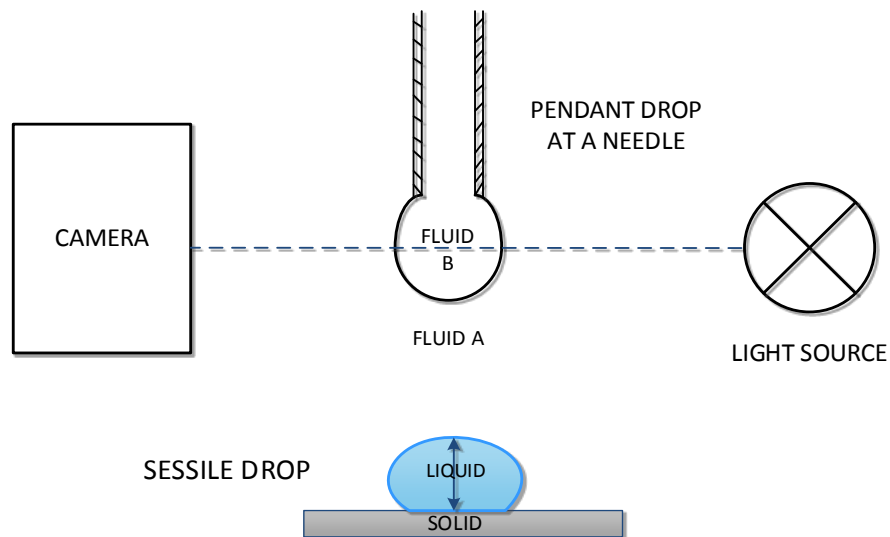
### 2.3.3 PENDANT AND SESSILE DROP METHOD

In these methods, drop of the denser phase is suspended from a capillary tube. In case of a less dense phase, pendant and sessile bubbles can be used instead of drops and the whole apparatus will be upside down. The shape of the drop results from the relationship between the surface tension and gravity. Drop shape changes are monitored during the process and image analysis techniques are used to calculate surface tension. As the tension decreases, the drop deforms further and expands more effectively which makes the equilibrium process slower. Both methods are applicable in gas-liquid and liquid-liquid systems. The accuracy and precision of the shape methods make them quite reliable.<sup>14, 32</sup>

The shape of pendant and sessile drops are governed by Young-Laplace equation<sup>35</sup>:

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad [6]$$

Where  $\Delta p$  is pressure difference across the interface,  $R_1$  and  $R_2$  are radii of curvature.<sup>36</sup>

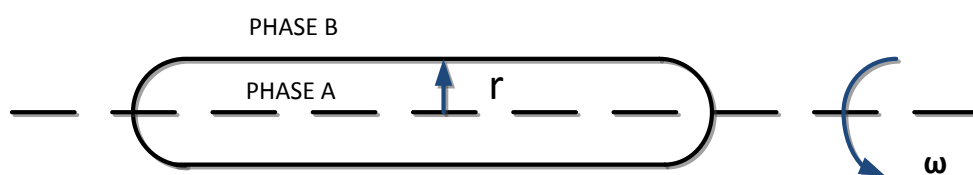


**Figure 2-6. Surface tension measurement by Pendant drop or Sessile drop experiment**

One of the significant features of pendant drop/bubble method is that there is no mechanical or electrical forces involved. Gravity is the major driving force that leads to surface tension measurement. The other characteristic of this method is that it can be used for both equilibrium and dynamic measurements specifically for the slow dynamic step (from minutes to hours) such as polymers/proteins.<sup>37, 38</sup>

### 2.3.4 SPINNING DROP METHOD

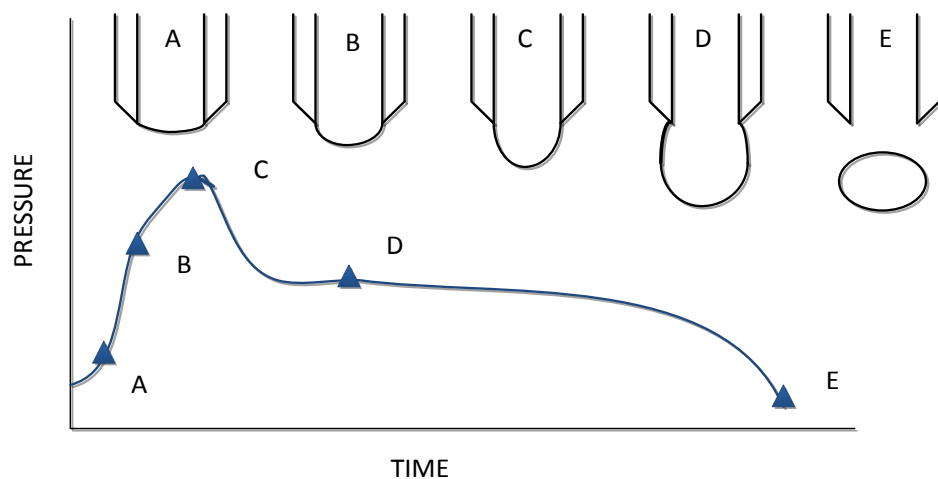
In this method, drop of a less dense liquid is injected into a denser phase inside a horizontal tube. Then the tube is rotated along the horizontal axis. As the tube rotates, droplet grows and since surface area extends, surface tension can be calculated. The drop shape relies on the density difference between phases, surface tension and rotation speed. This method is suitable for equilibrium surface tension measurements, especially when the tension is very low. Spinning drop method is most popular for liquid/liquid interfacial tension.<sup>14</sup>



**Figure 2-7. Surface tension measurement using Spinning drop method**

### 2.3.5 MAXIMUM BUBBLE PRESSURE METHOD

The maximum bubble pressure method has been mostly used to measure dynamic surface tension of surfactant solutions. In this method the maximum pressure needed to blow a bubble in a liquid from the tip of a capillary is measured. Both pressure and lifetime of each individual bubble are measured. This method can be used to monitor the development of surface tension for time scales from 0.1 seconds to minutes. Due to the dynamic nature of the process and since the lifetime of each bubble does not allow equilibrium to be achieved, this method is utilized for dynamic measurement rather than equilibrium.<sup>39</sup>



**Figure 2-8. Surface tension measurement applying maximum bubble pressure method**

### 2.3.6 OSCILLATING JET METHOD

This method is mostly used for dynamic surface tension measurement of fresh surfaces when kinetic mechanisms of adsorption are to be investigated. The oscillating jet method is done in a way that the solution is ejected through an orifice under constant pressure. The instability of the jet leads to non-uniform pressure inside the liquid. The effect of surface tension acts as a restoring force on the liquid of the jet produced.<sup>32</sup>

### 2.3.7 INCLINED PLATE METHOD

In this method a thin layer of a surfactant solution flows over an inclined glass plate, so the new interface develops at the inlet and surfactants adsorb at the interface with increasing distance. Therefore, by raising distance from the inlet, surface tension drops gradually and can be measured by Wilhelmy plate method at different locations.<sup>32</sup>

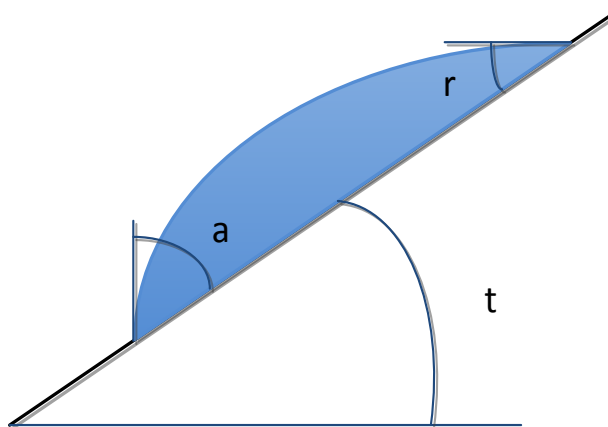


Figure 2-9. Surface tension measurement using tilting plate method

### 2.3.8 DROP WEIGHT OR VOLUME METHOD

In this method, size of a hanging drop attached to the tip of a capillary tube is slowly increased until it reaches its largest amount. In this case, interfacial tension is the proportion of drop volume, density difference between phases, gravity and capillary tube radius.<sup>14</sup>

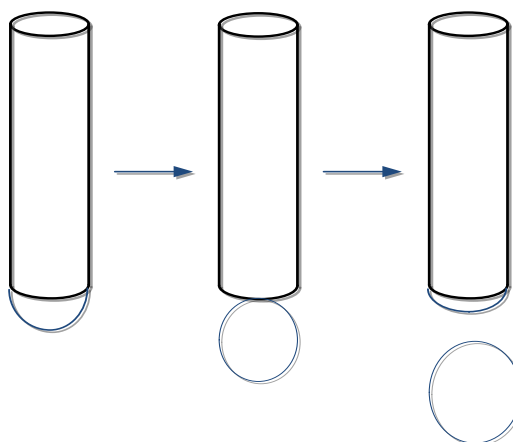


Figure 2-10. Surface tension measurement by drop weight method



As described above, various methods have been developed and introduced to measure surface tension. However, advantages of using the Drop shape methods are explained here:

- Drop shape methods can be used when long time measurement (even hours) is required;
- They can be applied to both air/liquid and liquid/liquid interfaces;
- They have vast ranges of application to various situations, such as high temperature and pressure.<sup>40</sup>

Surface tension measurement applying a drop shape method usually involves four steps:

- The image of a liquid drop or a gas bubble is provided using a photographic device;
- The profile of the drop or the bubble is extracted from the raw image using an edge detection operation;
- The data related to drops (or bubbles) geometry such as height and the diameter of the drop are given into a calculation scheme to compute surface tension.<sup>41</sup>

In this study, pendant bubble method is used for one part of experimental measurement to obtain equilibrium surface tension data at low surfactant concentration (acid-only) condition. The main underlying reason for this selection is that the chemical reaction may take some time and can disturb the interface temporarily. On the other hand, the Wilhelmy plate method is applied for surface tension measurement at higher surfactant concentration case in order to obtain more concentrations automatically and accurately. And finally, maximum bubble pressure was used for dynamic measurement of surface tension.

## 2.4 SURFACTANTS

Surfactants are very diverse products used in everyday life from motor oil in cars to pharmaceutical and detergents for cleaning.<sup>42</sup> Since surfactants have significant

effects on surfaces and interfaces properties, they have large number of applications in petroleum industry from producing to transportation of oil. <sup>24, 43</sup>

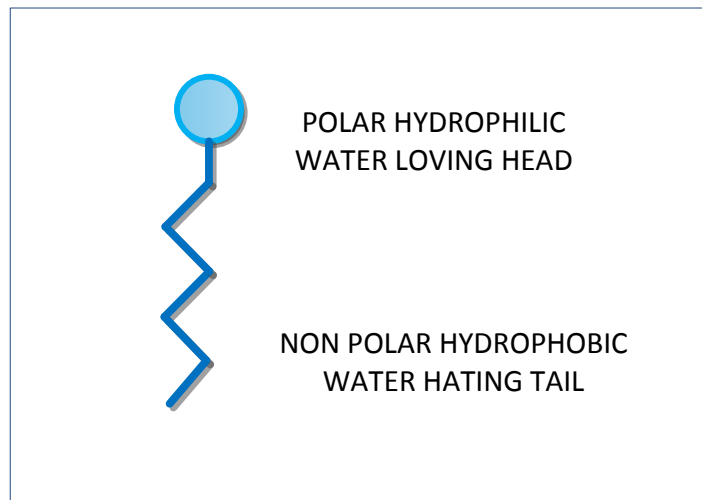
As a general law, at the surface of a liquid, molecules orient in a way that the part with less activity or polarity locates closest to the vapour phase. This molecular orientation causes a double electrical layer at the surface. In a solution with water as solvent, solutes which are less polar than water, adsorb in the surface. Also the less polar part of solutes turn toward air. <sup>44, 45</sup>

A surface active agent or a surfactant is a substance that adsorbs onto the surfaces or interfaces of a system. These molecules consist of two structural groups; the hydrophobic group that has little attraction to the solvent and hydrophilic part which is more solvent friendly (Figure 2-11). This is known as amphiphilic structure. <sup>46, 42</sup>

When a surfactant dissolves in an aqueous solution, it is adsorbed to the interface of the system. To minimize contact with water molecules, surfactants are oriented in a way that their hydrophobic groups are toward the air. Since air molecules and hydrophobic groups are both nonpolar and similar to each other, this leads to a drop in the surface tension of the water. On the other hand, the hydrophilic group keeps the surfactant close to the solvent. According to thermodynamic laws, happening of any process in the interface decreases free energy and surface tension. <sup>47</sup>

So the amphiphilic structure of a surfactant results in:

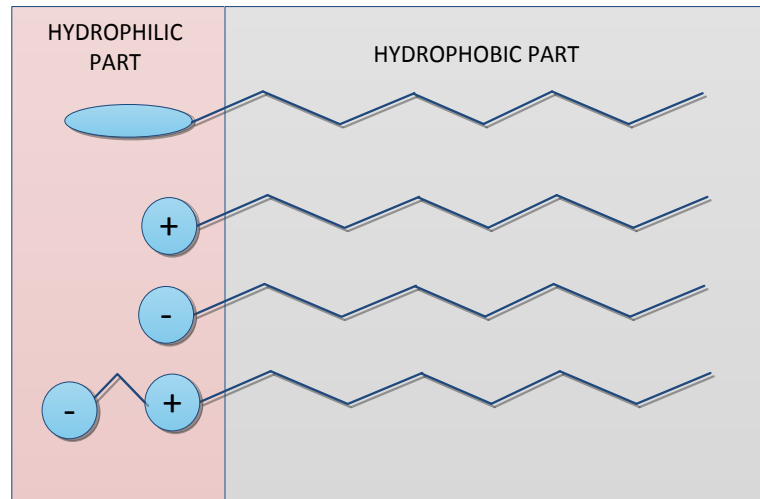
- Surfactant concentration at the surface;
- Surface tension reduction of water;
- Orientation of surfactant molecule at the surface with its hydrophobic group away from the aqueous phase and its hydrophilic group in the aqueous phase. <sup>42</sup>



**Figure 2-11. Surfactant molecule structure**

### 2.4.1 SURFACTANT CLASSIFICATION

Surfactants are classified based on their dissociation in water. <sup>47</sup> Figure 2-12 describes common surfactant types according to the composition of their head groups.



**Figure 2-12. Surfactant classification based on the composition of heads:**

**Non-ionic, Cationic, Anionic, Amphoteric**

#### 2.4.1.1 Anionic Surfactants

These types of surfactants when dissociated in water form an amphiphilic anion and a cation. The surface-active part of the molecule contains a

negative charge. They include alkyl benzene sulfonates (detergents), fatty acid (soaps), lauryl sulphate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants), carboxylates, phosphates, etc. <sup>48</sup>

#### *2.4.1.2 Non-ionic Surfactants*

They do not ionize in aqueous solution, because their hydrophilic group is not dissociated in aqueous medium. The surface-active portion of these molecules bears no apparent ionic charge. They consist of alcohols, ethoxylated acids, phenol, ether, ester, ethoxylated amines, alkanolamides or amine oxides. <sup>49, 50</sup>

#### *2.4.1.3 Cationic Surfactants*

Dissolving these surfactants in water results in an amphiphilic cation and an anion. The surface-active portion of the molecules carries a positive charge. The common example of this class is nitrogen compounds such as fatty amine salts and quaternary ammonium salts. <sup>39</sup>

#### *2.4.1.4 Amphoteric or Zwitterionic*

For this kind of surfactant, dissociation produces portions with positive and negative charges. They include synthetic products such as carboxybetaines or sulfobetaines and natural substances like amino acids and phospholipids. <sup>32</sup>

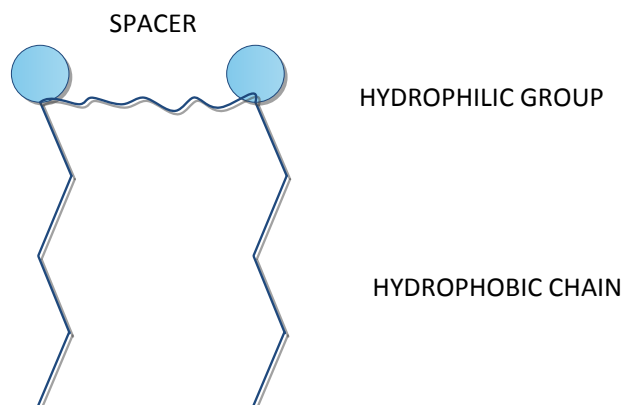
#### *2.4.1.5 Polymeric surfactants or surface active polymers*

The polymeric surfactants are products of the association of one or several macromolecular structures and show hydrophilic and lipophilic characters. They are now very commonly used in formulating products such as cosmetics, paints, foodstuffs, and petroleum production additives. <sup>51, 24, 42, 48, 52</sup>

#### *2.4.1.6 Gemini Surfactants*

These relatively new type of surfactants have a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail. Gemini surfactants are also called bis-surfactants and are more surface-

active than conventional surfactants. Geminis show specific characteristics. They have lower *CMC* values (by about an order of magnitude), increased surface activity and lower surface tension at the *CMC*. They also exhibit enhanced solution properties such as hard-water tolerance, superior wetting times and lower Krafft points. Structure of these surfactants is presented in Figure 2-13.<sup>53, 54</sup>



**Figure 2-13. Gemini surfactant structure**

The focus of this study is on a group of anionic surfactants called fatty acids. Fatty acids are carboxylic acids with a long aliphatic chain. (As classified in section 2.4.1.1)

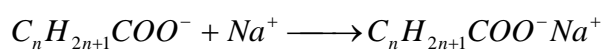
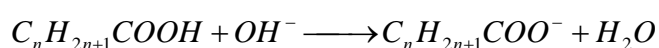
At air/water interface, fatty acids behave as a monolayer and turn to soaps with raising *pH*.<sup>55</sup> They are considered as weakly ionisable surfactants which exist in a solution with different molecular species. At lower *pH*, their existence is mostly in the form of un-dissociated species,  $RCOOH$ . At higher *pH*,  $RCOO^-$  mostly occupies the bulk and interface.<sup>56</sup> Long chain fatty acids when dissolving in water undergo an ionization reaction between *pH* 4 to 10 and in this *pH* range there are different chemical compounds in the system: ionized carboxylate ( $RCOO^-$ ), unionized fatty acid ( $RCOOH$ ) and fatty acid salts ( $RCOONa$ ).<sup>57</sup>

One of the most important characteristics of fatty acids is the ionization process. The process can change the fundamental properties and interfacial effects.

## 2.4.2 IONIZATION CONSTANT

When fatty acids are dissolved in water, their physical behaviour is influenced by ionization process.<sup>58</sup> Ionization constant or dissociation constant is any constant used to measure acids and bases strength. It shows the percentage an ionic species is ionized. Neutralization is the opposite process of ionization, in which an acid and a base react quantitatively with each other. The reaction consumes the excessive hydronium/hydroxide ions in the solution.

Fatty acids in *pH*-dependant systems are the mixture of two species: the un-dissociated form (*RCOOH*), which acts as a hydrophobic non-ionic surfactant, and the ionized form (*RCOO<sup>-</sup>*), which is hydrophilic.<sup>59</sup> The *RCOO<sup>-</sup>* groups of the molecules face the aqueous phase. Hence, the *RCOOH* groups of the fatty acid have a favourable orientation for interacting with the hydroxide ions to form carboxylate anions. Carboxylate ions also pair with *Na<sup>+</sup>* ions.<sup>60, 61</sup>



The behaviour of fatty acid monolayer changes by changing *pH* of the solution.<sup>62</sup> The ionization/neutralization equilibrium for acids is given by:



Where *HA* represents a weak acid and *A<sup>-</sup>* stands for the acid's anion.

And ionization constant, *k<sub>a</sub>* is:

$$k_a = \frac{[H_3O^+][A^-]}{[HA]} \quad [7]$$

Where [] shows the concentration of each ionic species in *mol/lit*. To avoid negative powers of ten, the term *pk<sub>a</sub>* is used which is defined here:

$$pk_a = pH + \log[HA]/[A^-] \quad [8]$$

The stronger the acid, the lower its *pk<sub>a</sub>*.

Values of *k<sub>b</sub>* for bases can also be determined at a specific temperature from *pk<sub>a</sub>* values, since:

$$pk_a + pk_b = pk_w \quad [9]$$

Where  $pk_w$  is ionic product of water,  $pk_a$  and  $pk_b$  show acid and base strength.

Ionization constant can be obtained from different methods. By measuring the conductivity of the solution,  $k_a$  will be determined by:

$$k_a = \frac{\alpha^2 c}{1 - \alpha} \quad [10]$$

Where  $k_a$  is the acidic ionization constant,  $\alpha$  is the degree of ionization ( $\alpha = \Lambda_c / \Lambda_0$ ),  $\Lambda_c$  is the equivalent conductance and  $\Lambda_0$  is the limiting conductance. However a conductometric determination of  $pk_a$  cannot be widely used for bases and also conductivity values are very sensitive to temperature changes. In addition, this method has significant results at great dilution which is not achieved for carboxylic acids solutions in water. <sup>63, 64, 65</sup>

Studies on measuring  $pk_a$  at different  $pH$  values show that at lower  $pH$  range (~1-2) fatty acid molecules which are unionized, accumulate at the interface in a way that their carboxyl group is toward water. At  $pH$  around  $pk_a$  (when half of the molecules are ionized), there is a strong interaction between molecules so they are packed closest together. When the  $pH$  is high (~9-10), ionic repulsion happens between the carboxylate ions that causes the molecules stay away from each other. When all the fatty acid molecules become ionized, repulsion between polar groups results in an expansion of the monolayer at high  $pH$  which leads to a weak monolayer. <sup>66, 56</sup>

### 2.4.3 CHAIN LENGTH EFFECTS ON PKA

Electronic effects between molecules in a fatty acid are not felt beyond two to three carbons in the chain and intramolecular interactions decrease beyond four carbons in the alkyl chain. Therefore, when the chain length is increased beyond about four carbons, the  $pk_a$  does not change much. On the other hand for fatty acids ranging from  $C_8$  to  $C_{18}$ , increasing chain length, makes  $pk_a$  of the solution higher. <sup>56, 57</sup>

Values of  $pk_a$  for carboxylic acids from  $C_3$  to  $C_{18}$  are presented in Table 2-1.

**Table 2-1. Values of bulk dissociation constants for saturated fatty acids**

Carboxylic Acid Name	Structural Formula	Carbon Numbers	$pK_a$
Propionic or Propanoic acid	$CH_3CH_2COOH$	3	4.779 <sup>67</sup> , 4.87 <sup>56</sup>
Butyric or Butanoic acid	$CH_3(CH_2)_2COOH$	4	4.82 <sup>67, 68, 69</sup>
Valeric or Pentanoic acid	$CH_3(CH_2)_3COOH$	5	4.82 <sup>66</sup> 4.8 <sup>70</sup>
Caproic or Hexanoic acid	$CH_3(CH_2)_4COOH$	6	4.63 <sup>67, 71</sup> 4.83 <sup>57</sup>
Enanthic or Heptanoic acid	$CH_3(CH_2)_5COOH$	7	4.90 <sup>63</sup>
Caprylic or Octanoic acid	$CH_3(CH_2)_6COOH$	8	4.8 <sup>69</sup> , 4.93 <sup>67</sup> , 6.5 <sup>56</sup>
Pelargonic or Nonanoic acid	$CH_3(CH_2)_7COOH$	9	4.96 <sup>72, 73</sup> , 6.8 <sup>66</sup>
Capric or Decanoic acid	$CH_3(CH_2)_8COOH$	10	4.9 <sup>74</sup> , 6.8 <sup>69</sup> , 7.2 <sup>56</sup>
Undecylic or Undecanoic acid	$CH_3(CH_2)_9COOH$	11	7.4 <sup>56</sup>
Lauric acid or Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	12	7.5 <sup>56</sup> , 7.5 <sup>57</sup>
Tridecylic or Tridecanoic acid	$CH_3(CH_2)_{11}COOH$	13	7.9 <sup>56</sup>
Myristic or Tetradecanoic acid	$CH_3(CH_2)_{12}COOH$	14	8.1 <sup>56</sup>
Pentadecylic or Pentadecanoic acid	$CH_3(CH_2)_{13}COOH$	15	8.5 <sup>56</sup>
Palmitic or Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	16	8.7 <sup>56</sup>
Margaric or Heptadecanoic acid	$CH_3(CH_2)_{15}COOH$	17	9.2 <sup>56</sup>
Stearic acid or Octadecanoic acid	$CH_3(CH_2)_{16}COOH$	18	10.15 <sup>66</sup> , 10 <sup>56</sup>

As shown above, observed dissociation constant of long chain carboxylic acids rises by increasing carbon chain length. However, increasing chain length for short fatty acids does not change their  $pK_a$  much.<sup>56</sup> Although the  $pK_a$  values for short fatty acids in water are typically 4.8, for medium and long chain carboxylic acids, higher  $pK_a$  values are observed. These observations stem from association of fatty acids into lamellar or crystalline aggregates resulting in lower proton activity in the bulk.

75

The above values can be obtained from well-known processes in the bulk and the ionization of the bulk solution can be routinely quantified by  $pH$  measurement.



However, the ionization at the interface remains unknown. There is no experimental method to directly measure the  $pH$  at the interface. The  $pH$  of the pure water surface is a hotly debated topic in the literature.<sup>76, 77</sup> For instance, Beattie et al. has come to the conclusion that the surface of neat water in air is basic, not acidic.<sup>78</sup> While Buch et al. have shown that based on molecular computational and experimental evidences, the surface of neat water is acidic.<sup>79</sup>

## 2.5 CRITICAL MICELLE CONCENTRATION

When highly surface-active materials dissolve in solutions, they mostly show unusual physical properties. In dilute solutions, these molecules behave as normal solutes (and in the case of ionic surfactants, normal electrolyte behaviour is observed). However, at higher concentrations, sudden changes in physical properties such as osmotic pressure, turbidity, electrical conductance and surface tension are observed. This abnormal reaction is the result of micelle formation in the solution.<sup>46</sup>

The specific concentration above which micelle formation will be seen is called the critical micelle concentration ( $CMC$ ). Micellisation is therefore, an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution might decrease. To determine the value of critical micelle concentration micelle-influenced physical properties can be measured as a function of concentration. Measuring surface tension and electrical conductivity are the most popular ones.<sup>80, 81</sup>  $CMC$  is an important factor in industry because it is a point that near which adsorption of surfactants onto the surfaces is saturated.<sup>24</sup>

Above critical micelle concentration the surface tension is almost independent from the bulk concentration, because all additional surfactant virtually form micelles.<sup>58</sup>

A determination of  $CMC$  gives a first basis in understanding the intermolecular interactions in aqueous solutions of surfactants.<sup>82</sup> Above the  $CMC$ , the equilibrium tensions of the solutions remain essentially constant, because only the monomeric form of the surfactant contributes to the surfactant activity or chemical potential, and hence to the tension reduction.<sup>32</sup> Chain length of a surfactant which is the

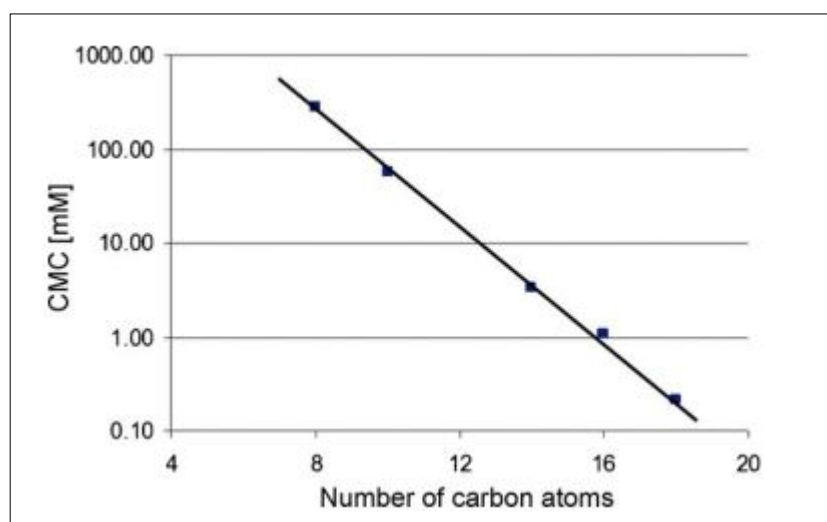
surfactant hydrophobic group has direct effects on its properties. Longer hydrophobic group makes the surfactant less soluble in water. It also raises the concentration of surfactant at the interface because it increases the affinity of surface active agents to adsorb into the interface. Therefore, their tendency to form aggregates and micelles become higher.<sup>12</sup>

The *CMC* follows the empirical Stauff–Klevens rule, which is a universal rule of the surfactant length and *CMC* for ionic surfactants and indicates a logarithmic relationship between *CMC* and the number of carbon atoms.<sup>83</sup> This such relationship has been well-established for single branch surfactants:  $\log(\text{CMC})$  increases linearly with increasing carbon number.<sup>42</sup> The linear relationship is given as:

$$\log \text{CMC} = A + Bn \quad [11]$$

Where  $A$ ,  $B$  are mathematical constants for a particular homologous series and  $n$  is number of carbon atoms in the hydrocarbon chain. The above relationship is universally applicable to all anionic and cationic surfactants.<sup>42</sup>

For instance, relationship between *CMC* and chain length is presented by Christian et al. in Figure 2-14.<sup>83</sup>



**Figure 2-14. CMC and chain length relationship for carboxylic acids**-Reprinted with permission from Elsevier

## 2.6 QUANTIFICATION OF ADSORPTION

When a new surface is created, the surface excess concentration,  $\Gamma$  is lower than equilibrium concentration,  $\Gamma_{eq}$ . Therefore, there is a flux of surfactant molecules from the bulk phase to the interface in order to fulfil equilibrium. Usually an imaginary subsurface is considered a few molecular diameters below the interfacial zone and is assumed that surfactant molecules diffuse from the bulk to the subsurface and then adsorb at the interface. The amount of surfactant adsorbed per unit area of interface can be obtained by surface tension measurement and use of adsorption isotherms.<sup>31, 30</sup>

Several models for predicting the equilibrium surface tension, surface density, and adsorption parameters of an aqueous surfactant have been developed.<sup>84</sup> The most commonly used equations are described here.

### 2.6.1 THE GIBBS ADSORPTION ISOTHERM

The most general form of Gibbs adsorption equation is:

$$d\gamma = -\sum_i \Gamma_i d\mu_i \quad [12]$$

Where  $d\gamma$  is change in surface tension,  $\Gamma_i$  is surface excess concentration of any component,  $d\mu_i$  is chemical potential of any component in the system.

At equilibrium,  $d\mu_i = RT d \ln (a_i)$ ; where  $a_i$  is activity of any component in the bulk phase,  $R$  is Gas constant and  $T$  is absolute temperature. Thus, following equation is applied:

$$d\gamma = -RT \sum \Gamma_i d \ln a_i \quad [13]$$

For dilute system containing solvent and one solute and activity being shown by molar concentration, above equation changes to:

$$d\gamma = -nRT \Gamma d \ln C_b \quad [14]$$

$$\text{Or} \quad \Gamma = -\frac{1}{nRT} \left( \frac{d\gamma}{d \ln C} \right)_T \quad [15]$$

Where  $n$  is the number of solute in the system,  $\Gamma$  is surface excess concentration of surfactant ( $\text{mol}/\text{m}^2$ ),  $C_b$  is the bulk concentration of the surfactant ( $M$ ) and  $\gamma$  is interfacial tension ( $\text{mN}/\text{m}$ ). Pre-factor  $n$  depends on the ionic nature of the surfactant. For instance,  $n$  equals 1 and 2 for non-ionic and ionic surfactants, respectively.<sup>24, 42, 32</sup>

### 2.6.2 HENRY'S LAW ISOTHERM

The simplest equation used for single component systems is Henry isotherm which can be shown as:

$$\Gamma = K_H C_b \quad [16]$$

Where  $K_H$  is Henry adsorption constant,  $\Gamma$  is surface concentration and  $C_b$  is the bulk concentration of the surfactant. Henry isotherm is valid for low surface concentrations.<sup>32</sup>

### 2.6.3 LANGMUIR ADSORPTION ISOTHERM

Langmuir isotherm is a non-linear isotherm which is broadly used and can be described as below<sup>42</sup>:

$$\Gamma = \Gamma_m \frac{K_L C_b}{1 + K_L C_b} \quad [17]$$

Where  $\Gamma_m$  is the maximum surface concentration,  $K_L$  is Langmuir adsorption constant and  $C_b$  is the bulk concentration of the surfactant.

Langmuir isotherm can be applied to the system of surfactant mixtures if surface interactions are insignificant. For two component system it can be stated as bellow equations:

$$\Gamma_i = \Gamma_m \frac{K_{L,i} C_i}{1 + K_{L,i} C_i + K_{L,j} C_j} \quad [18]$$

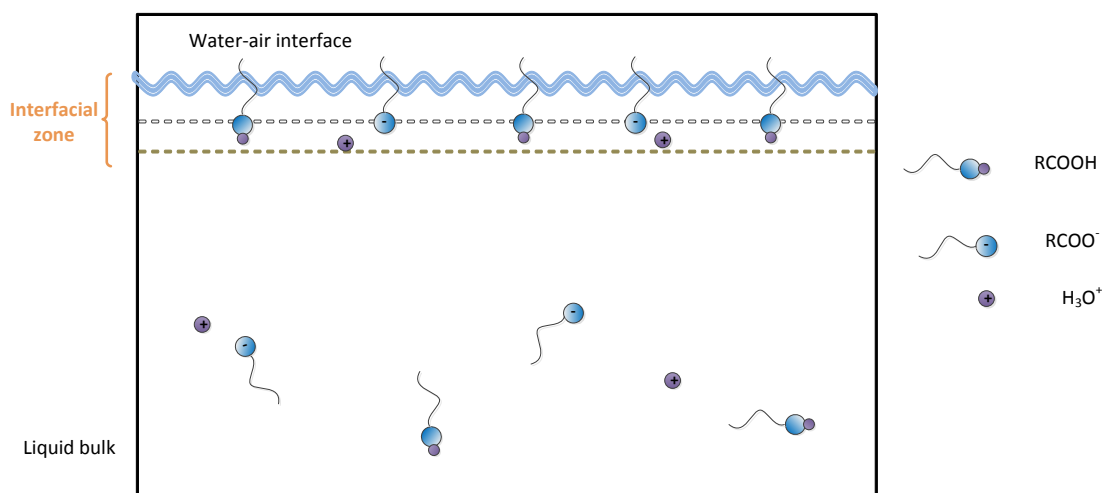
$$\Gamma_j = \Gamma_m \frac{K_{L,j} C_j}{1 + K_{L,i} C_i + K_{L,j} C_j} \quad [19]$$

Where  $C_{ij}$  refers to concentration of each species in the bulk solution,  $\Gamma_{ij}$  is the species concentration at the interface and  $K_{L,ij}$  is their related adsorption constant.

Adsorption isotherms described above are originally derived for a non-ionic surfactant system except the Gibbs isotherm that can be applied to the system including ionization reaction.<sup>86</sup>

## 2.7 GAP OF KNOWLEDGE

As shown in Figure 2-15, carboxylic acids when in aqueous phase at an interface, show different ionization behaviour than in the bulk. Yet, there is no quantitative information about it. The acids exist in the system in form of ionized and unionized species. Neutralized species intend to accumulate more in the interface rather than in the bulk. Assessing ionization in the bulk solution has been reported in the literature, however there is no direct method to measure these qualities at the interface.



**Figure 2-15. Adsorption of an ionic surfactant onto air/water interface at ionization equilibrium**

This thesis develops the methods to obtain ionization and adsorption data of the surfactants at the air/water interface and addresses the deficits in the knowledge by experimentally and theoretically investigation of two carboxylic acids.

The effects of hydrocarbon chain length on adsorption parameters are also investigated extensively in this work. Two acids were selected for this study; decanoic acid and nonanoic acid which are fatty acids of 10 and 9 carbons in their

carboxylic chain respectively. These fatty acids are classified as anionic surfactants and ionization reaction is the governing process in their adsorption at the interface.

In experimental section, their interfacial tension was measured by pendant bubble and Wilhelmy plate methods. Surface concentration and adsorption constants were then calculated. The  $pH$  data were also measured to quantify ionization constant at the interface. Two common methods for surface tension measurement were applied in order to achieve accurate data based on proposed conditions.

In theoretical part, Gibbs adsorption isotherm was applied to the system of ionized and unionized species as starting equation. Extended equations were then developed to precisely measure adsorption parameters. Finally, adsorption and ionization data of two acids are compared with each other.

The main goal of the current study is to determine adsorption parameters in the interface while ionization reaction is the governing process and it was fulfilled by successfully modelling of ionic surfactants adsorption behaviour at air/water interface.

Ultimately, the study aims to quantify the influence of Hydrocarbon length on the ionization process and adsorption at the air/water interface. The new insights provide fundamental understandings for industrial processes.

### 3 METHODOLOGY

#### 3.1 MATERIALS

In this work carboxylic acids of  $C_{10}$  and  $C_9$  were used as anionic surfactants at air/water interface. One reason to choose fatty acids as surfactants for this study was their biodegradability and low toxicity. The acids can be obtained from plants or animals fat. These qualities make them more environmentally friendly type of surfactants.<sup>87</sup> Fatty acids used in this study are listed in Table 3-1.

**Table 3-1. List of fatty acids used in this work**

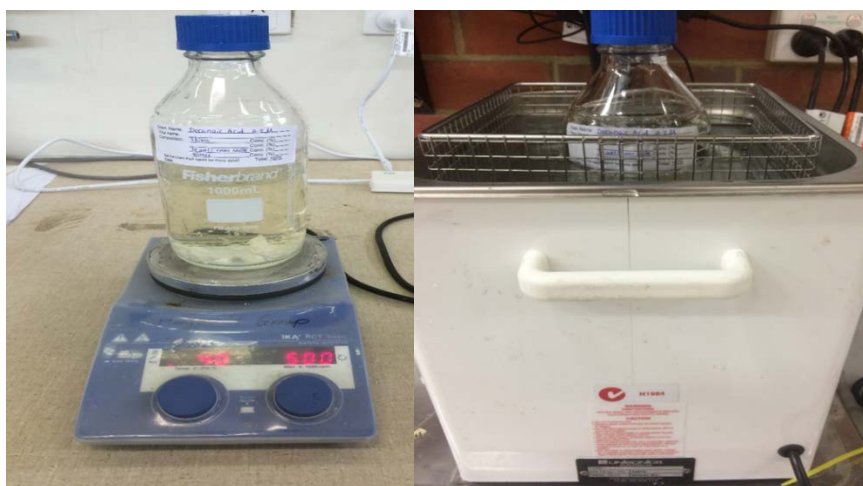
Chemical Name	Other names	Molecular Weight	Formula
Nonanoic acid	Pelargonic acid	158.24	$\text{CH}_3(\text{CH}_2)_7\text{COOH}$
Decanoic acid	Capric acid	172.26	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$

The first sets of experiments were done on decanoic acid. The acid was selected because a few of its interfacial properties had been studied before. Thus, it was easier to compare some of the results obtained in this study with the ones in literature. The comparison was necessary in order to make sure the experiment and modelling done in this thesis were consistent with previous work, the methodology and model were novel though. Then, to confirm the results obtained for decanoic acid and see the effects of hydrocarbon chain length on adsorption and interfacial data, a second acid was required. Initially, undecanoic acid was applied. However, the solubility was too low to have an effective measurement. Consequently, only decanoic and nonanoic acids were used for this study. These acids are partially dissociated in water at normal conditions, and thus suitable for experimental investigation. Therefore, both ionized and non-ionized species exist, at significant percentages, in the bulk and the dissociation constant can be routinely determined by  $pH$  measurements. The effective modelling can describe the ionic status of the adsorbed acid as well as the physical characteristic of the interfacial zone.

Decanoic acid also known as capric acid or decylic acid is a saturated fatty acid. Neutralization of decanoic acid with sodium hydroxide gives sodium decanoate which is a major component of some types of soaps. Nonanoic acid also called pelargonic acid is a fatty acid used in the preparation of plasticizers and lacquers.

Decanoic acid was supplied by Sigma Aldrich Chemical Company. Its purity was specified as  $\geq 98.0\%$  and was used without further modification. Nonanoic acid and undecanoic acid with  $\geq 97.0\%$  purity were also obtained from Sigma Aldrich Company.

Sodium Hydroxide solution was purchased from Sigma Aldrich Company with 50% concentration in  $H_2O$ . Hydrochloric acid solution was provided from AJAX FINECHEM Pty Ltd with 32% concentration. Water for preparing solutions was pure water purified by Ibis ultrapure system and its conductivity was  $>17.5\text{ M}\Omega\cdot\text{cm}$ .



**Figure 3-1. Decanoic acid solution preparation using magnetic stirrer**





Figure 3-2. Nonanoic acid preparation using balance and magnetic stirrer



Figure 3-3. Chemicals used in the study

## 3.2 MEASUREMENT METHODS AND APPARATUS

### 3.2.1 EQUILIBRIUM SURFACE TENSION

Two measurement methods of Wilhelmy plate and pendant bubble were applied in this study. The reason to use two methods for surface tension measurement is the advantages and applications of each method for each condition.

In acid-only case, solubility and acid precipitation on the platinum plate was a problem which made me apply pendant bubble method at this condition. Although

it was a time consuming method, acid solid formation did not affect the experiment results. On the other hand, Wilhelmy plate method was selected for measurement in case of high  $pH$ . This method was applicable since acid was completely dissolved in water and there was no residue on the plate. Another advantage of Wilhelmy plate method was to achieve more measurement points accurately by automatic dilution.

#### *3.2.1.1 WILHELMY PLATE METHOD*

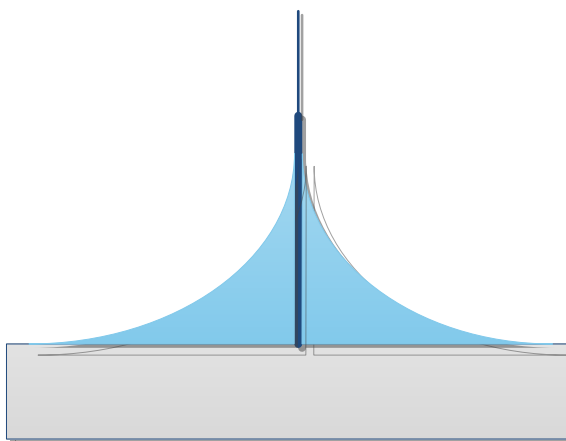
Equilibrium surface tension values for high concentration solutions were measured using tensiometer KSV Sigma 700 applying Wilhelmy plate method. The instrument consisted of a measuring unit, Auto dispensing equipment and required glassware. Figure 3-5 shows the whole setup for Wilhelmy plate measurement. Dispenser used here was a TITRONIC universal model provided from SCHOTT instruments GmbH Company. The Sigma 700 calculates surface or interfacial tension based on force measurements. The probe used in this method was a platinum plate which interacts at the boundary between solution and air. The obtained results from the device is surface tension if the boundary is between liquid and gas phases and the data are interfacial tension values if the fluids are both liquid. The measurement starts by hanging a probe from a balance. Then probe is lowered from lighter phase to the interface until it is a certain depth in the liquid. Surface tension is finally calculated from probe movement and resulting force changes on the probe. The forces depend on the following factors:

- Size and shape of probe;
- Contact angle between the liquid and the probe;
- The surface tension of the liquid.<sup>88</sup>

Overall, the weight of the liquid lifted when a plate is withdrawn through the surface is measured. When plate is completely wetted by the liquid, the maximum weight is achieved. In order to ensure the complete wetting, the plate is usually made of micro-roughened platinum.<sup>21</sup> A schematic of the plate during experiment is shown in Figure 3-4. The platinum micro-roughened Wilhelmy plate was cleaned regularly after use. It was roasted in flame before and after each experiment to remove contaminants from its surface and the whole system including sample

container and tubes were drained with pure water and air to ensure the cleanliness of the system. For instance, for decanoic acid in higher concentration case, the normal Wilhelmy plate method was applied. The starting solution contained 0.88%  $\text{NaOH}$  by weight (0.22 M of  $\text{Na}^+$ ) with an initial  $\text{pH}$  of 14.45. The stock solution was prepared by adding decanoic acid into the above solution to make 0.2 M solution. The mixture was then pumped gradually onto the measurement beaker. As a result, the surface tension at acid concentrations ranging from 0.0003 M to 0.182 M was obtained at a constant concentration of  $\text{Na}^+$ .

The same solution of sodium hydroxide used as additional solution to dilute initial solution was applied to prepare stock solution. Therefore, we can assume the concentration of  $\text{Na}^+$  was kept constant during the experiment.



**Figure 3-4. Platinum plate moving inside the solution**



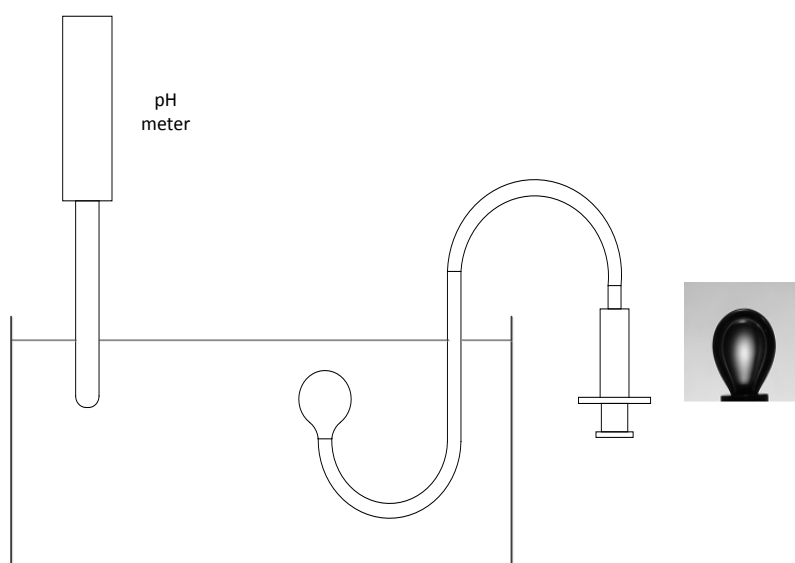
**Figure 3-5. Equilibrium surface tension measurement using Wilhelmy plate method**

### 3.2.1.2 PENDANT BUBBLE METHOD

Another method applied here to measure surface tension was pendant bubble/drop shape analysis method. Pendant bubble method apparatus consisted of video camera, optical rail for proper alignment, light source, syringe, needle, plastic cuvette, *pH* meter (Aqua-pH from TPS Instruments Ltd.) and an electrode.

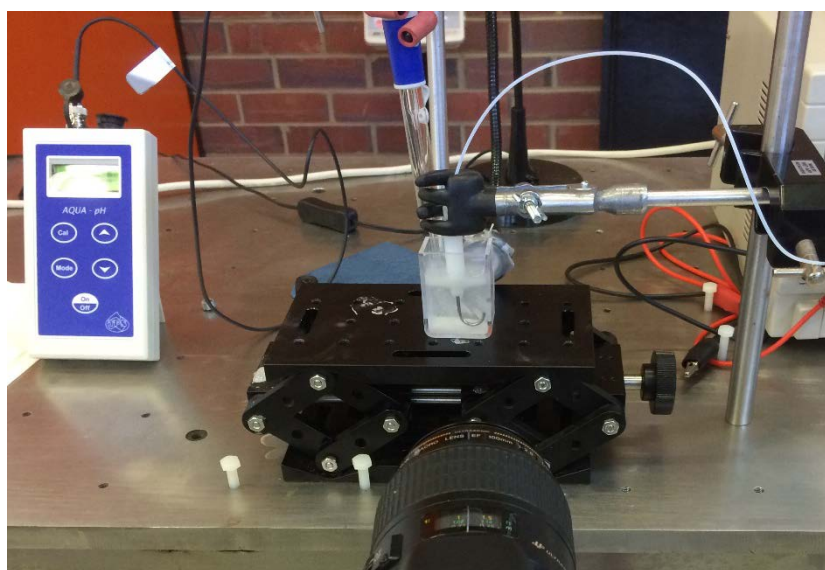
In the pendant bubble method, interfacial tension is calculated from the image of a pendant drop or bubble using shape analysis methods. An increased pressure is produced inside the bubble as a result of the interfacial tension between inner and outer phase. Finally, the correlation between the pressure difference ( $\Delta p$ ), the radii of curvature of the surface and the interfacial tension is explained by the Young-Laplace equation. A schematic of the experiment setup is shown in Figure 3-6.

For decanoic acid, the starting concentration was 1 *mM* which was acquired by adding 0.0172 *gr* decanoic acid into 100 *ml* (99.98 *gr*) water, stirring and heating up the solution until solid particles disappear. Then the solution was cooled down at room temperature (25 °C). After cooling, specified amount of solution was put into a transparent cuvette and an air bubble was formed at the tip of a needle submerged into the solution. Further dilution was obtained by adding a controlled quantity of water to the initial solution and stirring. After stirring, a new pendant bubble was formed in the solution. In this procedure, any excessive and non-soluble acid stays on the water surface, not on the surface of the newly-formed bubble.



**Figure 3-6. Experimental setup for un-adjusted pH measurement**

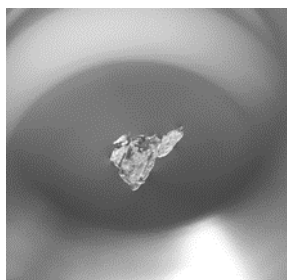
A stainless steel needle with a nominal outer diameter of 1.8 *mm* attached to a syringe, was used. A *pH* sensor was also submerged inside the solution. Several air bubbles were formed at each concentration. Furthermore, multiple images were taken from each air bubble for analysis. Finally, surface tension was calculated using a MATLAB code. The average values and standard deviations were obtained for all images (more than 20 images) at each concentration. A picture of the whole setup is given in Figure 3-7.



**Figure 3-7. Pendant bubble method setup**

The problem with applying Wilhelmy plate method for acid only case was solubility issue. In decanoic acid experiment when solutions of  $> 1$  *mM* were cooled down, solid appeared on top as a result of solubility depression. A picture of the solid formation on top of decanoic acid solution is shown in Figure 3-8. In nonanoic acid experiment the insoluble acid accumulate on top in liquid form. By applying the Wilhelmy plate for acid only cases, solid would easily get onto the plate and prevent accurate measurement of surface tension. Therefore, pendant bubble method was applied which needed lots of solution preparation. In order to have more accurate solutions, the same container was used and water was added to the initial solution to change its concentration.

Both methods show constant value for pure water which is around 72 *mN/m*.

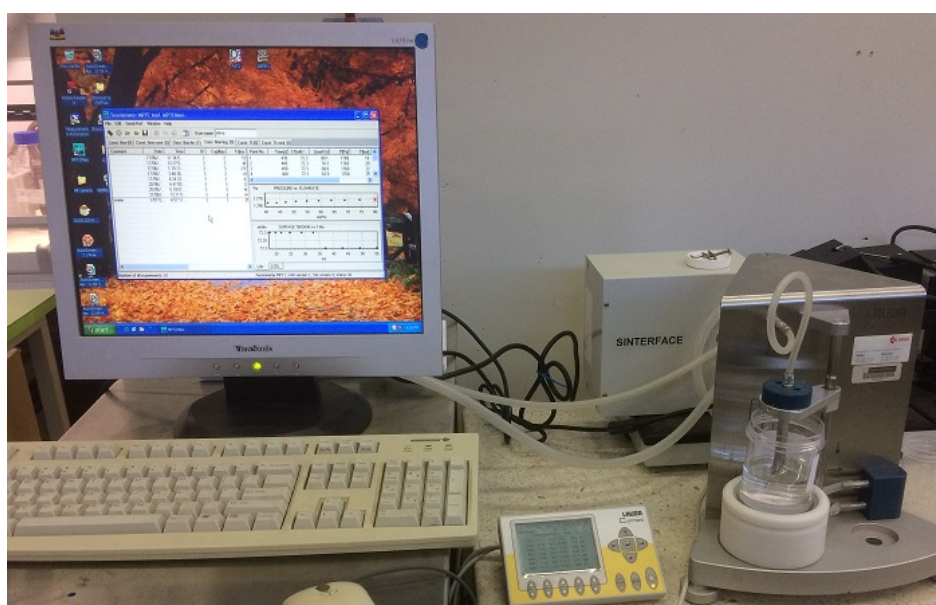


**Figure 3-8. Solid formed on top of unadjusted decanoic acid solution at 1 mM**

### 3.2.2 DYNAMIC SURFACE TENSION

Dynamic surface tension measurement helps to achieve surface tension data of a solution based on a period of time. Time period refers to when the new interface is produced until the measurement is done.

In this thesis dynamic surface tension is measured using maximum bubble pressure method. This method is based on maximum internal pressure of a gas bubble which is formed in a liquid by means of a capillary. When the bubble pressure reaches its maximum amount, dynamic surface tension is derived from Young Laplace equation. Apparatus used in this experiment include MPT2 (Lauda, Germany) device with capillary tube of 100 microns diameter and a desktop computer for transferring data. The setup is pictured in Figure 3-9.



**Figure 3-9. Dynamic surface tension measurement using maximum bubble pressure method**

Prior to the measurement, calibration for pure water was done. When the value of around  $72 \text{ mN/m}$  appeared as water surface tension, measurement of the solution would start.

The experiment was done for different concentrations of acids at room temperature. The capillary was put inside a sample of acid, required setting was done on the screen and as soon as the start button was pushed the machine started to make air bubbles at the tip of the capillary tube. Surface tension data were then transferred to a computer attached to the instrument.

### 3.2.3 DENSITY MEASUREMENT

In order to calculate surface tension data via MATLAB, density of the phases was required. For each concentration, a sample was separated for density measurement. Device used in this regard was a DMA 4500 instrument from Anton Paar GmbH Company. The measurement is based on the oscillating U-tube principle. Calibration of the device was done before each experiment. Figure 3-10 shows the densitometer used in this study.



Figure 3-10. Density measurement using DMA 4500 Densitometer

### 3.2.4 PH MEASUREMENT

During pendant bubble method,  $pH$  was also measured by connecting the  $pH$  meter to the solution and  $pH$  was recorded while initial solution was diluted. Once a good droplet was formed, several images were taken using a remote control set to take photos every 15 seconds. The  $pH$  of the solution was also recorded for every 15 seconds. This procedure continues until all required concentrations were achieved.

## 3.3 DATA ANALYSIS

To analyse the results obtained from pendant drop experiment, a MATLAB GUI code was applied. This MATLAB-based program calculates the interfacial tension from pendant drop images. The code can be set to run single images or a series of images. The code does two things:

- Finds the edges from the image that is uploaded to it;
- Does a massive numerical optimisation to find two numbers that describe the edges that it has found, based on the Young Laplace Equation.

The optimisation routine is constrained, both to reduce the time required and to ensure that some unreasonable values are not sent back. Cropping the image is to assist in edge detection by limiting distractions/noise in the image. <sup>89</sup>

Some pictures of the code environment are shown below:



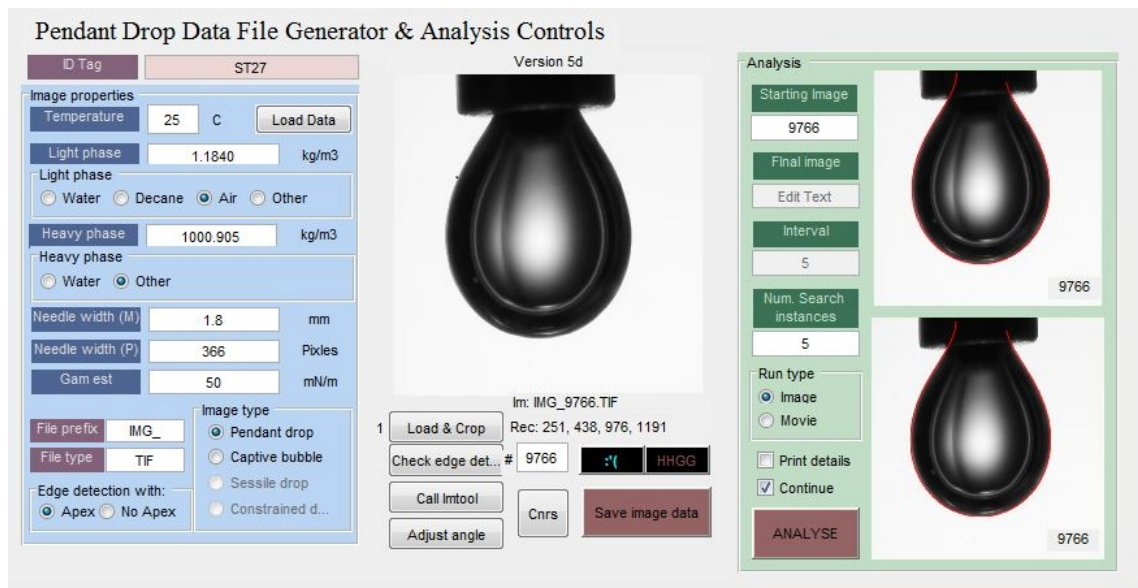
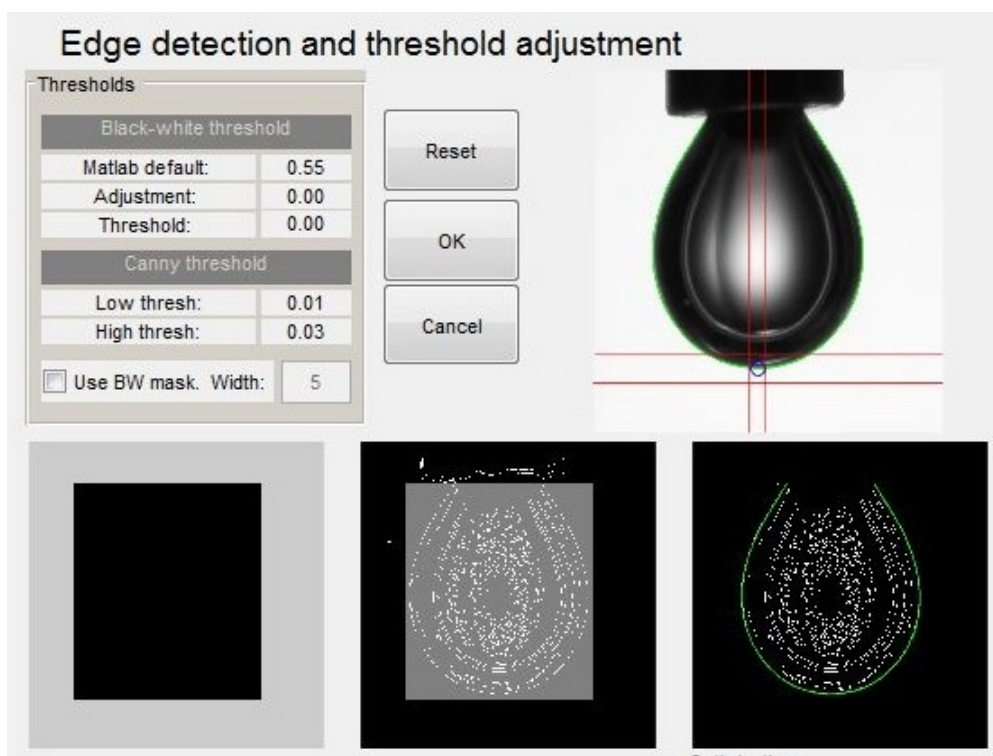
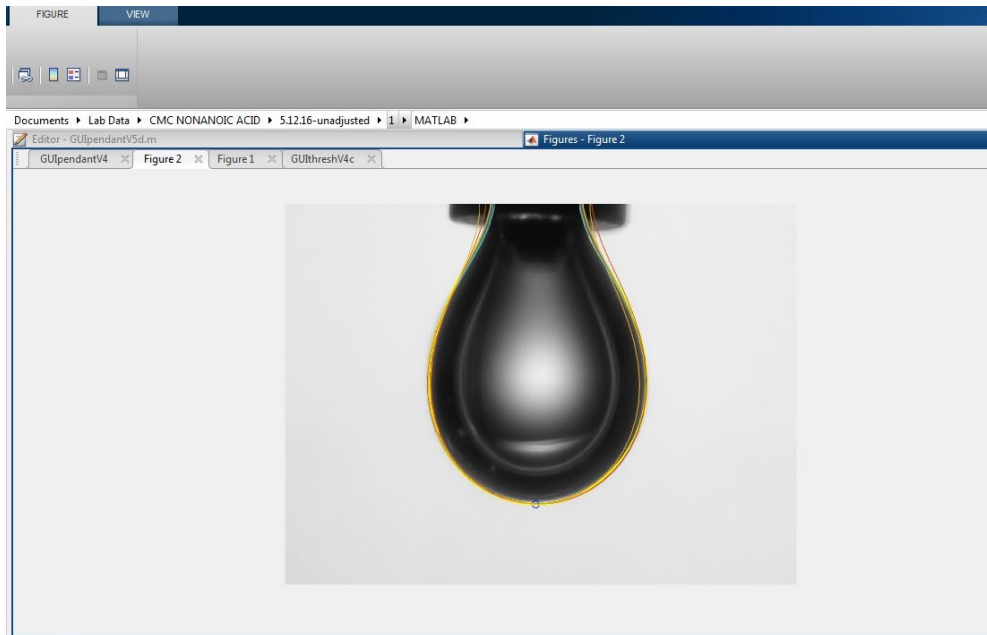


Figure 3-11. Pendant air bubble uploaded and cropped in the MATLAB code





**Figure 3-12. Edge fitting by the MATLAB code**

## 4 ADSORPTION OF DECANOIC ACID AT AIR/WATER INTERFACE

### 4.1 INTRODUCTION

Adsorption of anionic surfactants at the air/water interface plays an important role in industries including soap and detergency. These surfactants contain sodium and potassium salts of straight chain fatty acids and are used widely in foaming and wetting agents, detergents and washing products, household and personal products. However, the nature of these surfactants and their interfacial adsorption remains not well defined. In particular, the quantities and properties of adsorbed surfactants remain unclear. Recent studies have shown that the conventional theory is inadequate to describe the adsorption of ionic surfactants.

It is widely accepted that the surfactant significantly concentrates onto the surface due to its amphiphilic structure. Thermodynamic analysis<sup>90</sup> can be applied to quantify the adsorbed concentration, as illustrated by the famous Gibbs equation:

$$d\gamma = nRT\Gamma d \ln C_b \quad [20]$$

Where  $R$  is the gas constant,  $T$  is the temperature,  $\gamma$  is the surface tension,  $C_b$  is the bulk concentration,  $\Gamma$  is the surface concentration, and  $n$  is the pre-factor. It should be noted that the unit of  $\Gamma$  is *mole/m<sup>2</sup>*, as it is mathematically defined from the Gibbs dividing plane.<sup>91</sup> The pre-factor  $n$  depends on the ionic nature of the surfactant. For instance,  $n$  equals 1 and 2 for non-ionic and ionic surfactants, respectively.<sup>84</sup>

Assuming complete dissociation, equation [20] with  $n=2$  becomes the governing basis for all ionic surfactants. However, recent studies have demonstrated the fundamental obstacles with the application of above equation. In the literature, there was emerging evidence that ionic surfactants can exist in different ionic states within the solution and interface.<sup>92</sup> The co-existence of multiple states is undeniable in the case of Gemini cationic surfactants.<sup>93</sup> For strong electrolytes, the surfactants are effectively ionized in aqueous solution. The existence of non-ionized species happens mostly at interfaces, due to the higher concentrations. For weak

electrolytes such as carboxylic acids, it has been proposed that the surfactant has different ionic states: <sup>8</sup> ionized species dominate the bulk while neutralized species dominate the interface. The adsorption of ionic states is simultaneously controlled by both interfacial adsorption and reaction equilibria.<sup>9</sup> Hence, a proper adsorption model has to include the reaction equilibrium.

The existence of multiple ionic states opens up new opportunities. For instance, the thickness and the ionic nature of the interfacial zone can be properly quantified.<sup>10</sup> The adsorption constants of ionized and neutralized species can be also quantitatively described.

This chapter focuses on the adsorption of a weak electrolyte, decanoic acid. This acid is selected as the starting point of the study and the selection is based on the fact that there were some results of other works on the acid available. Therefore, we could compare some of our findings with the literature. In addition, decanoic acid remains an important and economical surfactant for commercial soaps and detergents. The study combines experimental and theoretical frameworks to verify the adsorption of the acid.

## 4.2 THEORETICAL MODELLING

### 4.2.1 DISSOCIATION CONSTANT

As described in section two, dissociation constant was obtained by measuring *pH* of the solution throughout the experiment and fitting the experimental data to the modelled equation. In case of only decanoic acid existence in water (acid only situation), ionization constant,  $k_a$  is described by equation [7].

In this analysis, the ionization reaction,  $AH + H_2O \leftrightarrow A^- + H_3O^+$ , is incorporated into the adsorption process. The equilibria in the bulk and within the interfacial zone are governed by the reaction constant: <sup>9</sup>

$$k_a = \frac{C_{A^-} C_{H_3O^+}}{C_{AH}} \quad [21]$$

Where  $k_a$  is the reaction constant ( $M$ ), and  $C_i$  ( $i=A^-, H_3O^+$  and  $AH$ ) are the bulk concentrations of their respective species.

Although water is also involved in the reaction, the concentration of water as a solvent is too large ( $\sim 55 M$ ) to be affected by acid ionization. As a result, water is not included in the reaction equilibrium.

At equilibrium state, concentration of hydronium ions and dissolved acid is equal ( $[H_3O^+] = [A^-]$ ). Therefore;

$$k_a = \frac{[H_3O^+][A^-]}{[AH]} = \frac{[A^-]^2}{[AH]} \quad [22]$$

On the other hand, bulk concentration of decanoic acid,  $C_b$  consists of concentration of its dissolved ions and undissolved species.

$$C_b = C_{A^-} + C_{AH} \quad [23]$$

The value of  $k_a$  can be obtained by routine  $pH$  measurements and used to compute the exact concentration of  $A^-$  and  $AH$  in the bulk. From above equations and assumptions,  $pH$  can be achieved from the following formula:

$$pH = -\log([H_3O^+]) = -\log([A^-]) = \log\left(\sqrt{C_b k_a + \frac{k_a^2}{4}} - \frac{k_a}{2}\right) \quad [24]$$

#### 4.2.2 SURFACE TENSION AND ADSORPTION PARAMETERS

The thermodynamic analysis, equation [13] is applied to the system of all species:

$$d\gamma = -RT \sum_i \Gamma_i d \ln C_i \quad [25]$$

Hence, all species (ionized acid, neutralized acid and ions) have to be included into the model. In this model, the ionic-binding concept is applied.<sup>94</sup> The interfacial zone can be divided into two layers:<sup>95</sup>

- The outer layer which contains surfactant tails;
- The inner layer which contains the surfactant heads and other ions.

Both layers are part of the interfacial zone and thus, included in equation [25].

In order to use equation [25] for each species, partial differentiation of  $dy/dC_i$  is required. However, the relationship between  $C_A$  and  $C_{AH}$  is not directly obtainable. The relationship is governed by reaction equilibrium. The reaction equilibrium is then dependent on the concentrations. As the result, the equilibrium at the interface and in the bulk are different. Thus, both equilibria are required. Furthermore, the two species need to be calculated separately before combining into equation [25].

The surface adsorption of each species is governed by an equilibrium between the number of vacant sites on the surface and species concentrations.<sup>94</sup> In this case, the adsorption is based on hydrophobic tails. Hence, the equilibria are given by:

$$K_A = \frac{\Gamma_A}{\Gamma_v C_A} \quad [26]$$

$$K_{AH} = \frac{\Gamma_{AH}}{\Gamma_v C_{AH}} \quad [27]$$

Where  $\Gamma_v$  is the number of vacant sites ( $mole/m^2$ ),  $K_A$  and  $K_{AH}$  are adsorption isotherm equilibrium constants of  $A$ ,  $AH$  ( $M^{-1}$ ). Total available sites on the surface,  $\Gamma_{max}$ , is given by:

$$\Gamma_{max} = \Gamma_v + \Gamma_A + \Gamma_{AH} \quad [28]$$

Combining the above equations we get:

$$\Gamma_v = \frac{\Gamma_{max}}{1 + K_A C_A + K_{AH} C_{AH}} \quad [29]$$

Consequently, the adsorbed concentration of each species is given by:

$$\Gamma_A = \Gamma_{max} \frac{K_A C_A}{1 + K_A C_A + K_{AH} C_{AH}} \quad [30]$$

$$\Gamma_{AH} = \Gamma_{max} \frac{K_{AH} C_{AH}}{1 + K_A C_A + K_{AH} C_{AH}} \quad [31]$$

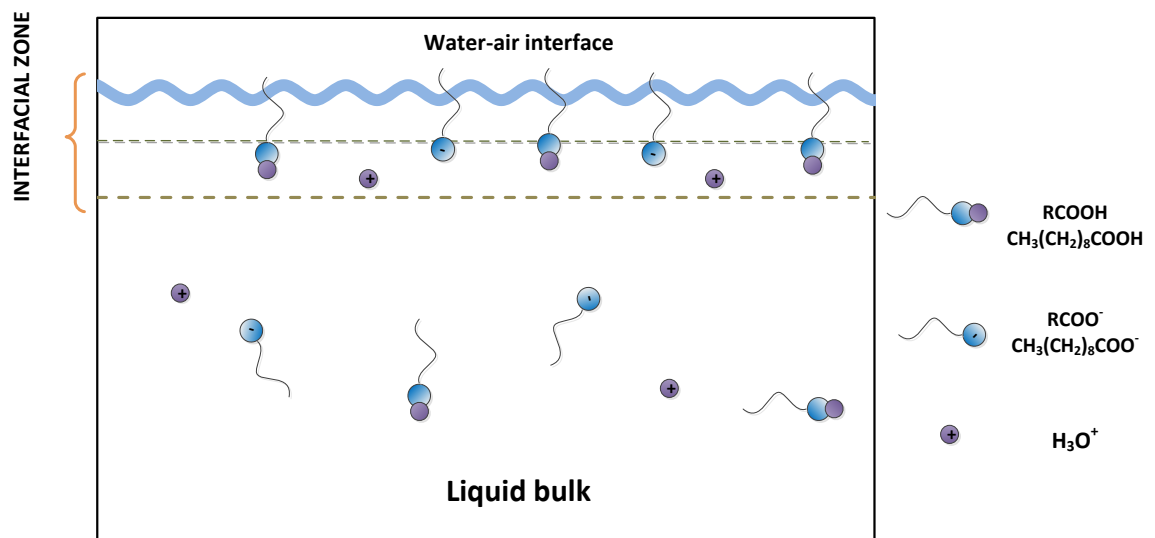
The above two equations follow the Langmuir isotherm for binary mixtures.<sup>85</sup>

The adsorption system has three adsorption parameters:  $K_A$ ,  $K_{AH}$  and  $\Gamma_{max}$ . If only salt-free solution is used, one would get a single set of data and fitting the

theoretical model would be unreliable. Consequently, the study employs another set of conditions: an excessive and constant concentration of  $NaOH$ . The condition can be experimentally controlled. The constant  $Na^+$  concentration can significantly simplify the governing equations. In both cases, equation [25] can be further simplified and used to calculate the adsorption. Since the inclusion of  $Na^+$  and  $OH^-$  does not change the adsorption constants, the model can be applied simultaneously to both conditions to obtain the adsorption parameters.

#### 4.2.2.1 ACID-ONLY SOLUTION

The salt-free solution (unadjusted  $pH$ ) contains three species:  $A^-(RCOO^-)$ ,  $AH$  ( $RCOOH$ ) and  $H_3O^+$ . A schematic of the three species in the interface and bulk is shown in Figure 4-1.



**Figure 4-1. Adsorption of decanoic acid onto air/water interface at ionization equilibrium**

Applying equation [25] to the acid only system results in:

$$d\gamma = -RT(\Gamma_A d \ln C_A + \Gamma_{H_3O} d \ln C_{H_3O} + \Gamma_{AH} d \ln C_{AH}) \quad [32]$$

As neutrality requires  $\Gamma_A = \Gamma_{H_3O}$  and  $C_A = C_{H_3O}$ . Thus, equation [32] will change to:

$$d\gamma = -RT(2\Gamma_A d \ln C_A + \Gamma_{AH} d \ln C_{AH}) \quad [33]$$

In addition, since  $k_a$  is constant, from equation [21] it can be concluded that  $d(\ln C_{AH}) = 2d(\ln C_A)$ . Substitution of these terms into equation [33] results in:

$$d\gamma = -2RT(\Gamma_A + \Gamma_{AH})d \ln C_A \text{ Or } -\frac{1}{2RT} \frac{d\gamma}{d \ln C_A} = \Gamma_A + \Gamma_{AH} \quad [34]$$

Above equation is the governing model to determine adsorption parameters for the condition of only decanoic acid (neutralized and ionized forms) existing in water.

The concentration of ionized acid,  $C_A$  can also be calculated from the total acid concentration ( $C_b = C_A + C_{AH}$ ). From equation [21],  $C_A$  is the root of the following quadratic equation:

$$\frac{C_A^2}{k_a} + C_A = C_b \quad [35]$$

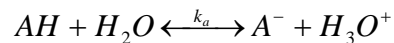
The positive root of the above equation is:

$$C_{H_3O} = C_A = \sqrt{C_b k_a + \frac{k_a^2}{4}} - k_a / 2 \quad [36]$$

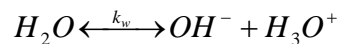
Finally, the total adsorption,  $\Gamma_{total} = \Gamma_A + \Gamma_{AH}$ , can be obtained as a function of  $C_A$  from equations [30], [31], [34] and [36].

#### 4.2.2.2 ACID WITH HIGH AND CONSTANT CONCENTRATION OF NA+

At high NaOH concentration, higher concentration of decanoic acid is achieved. Ionization reaction at this condition is:



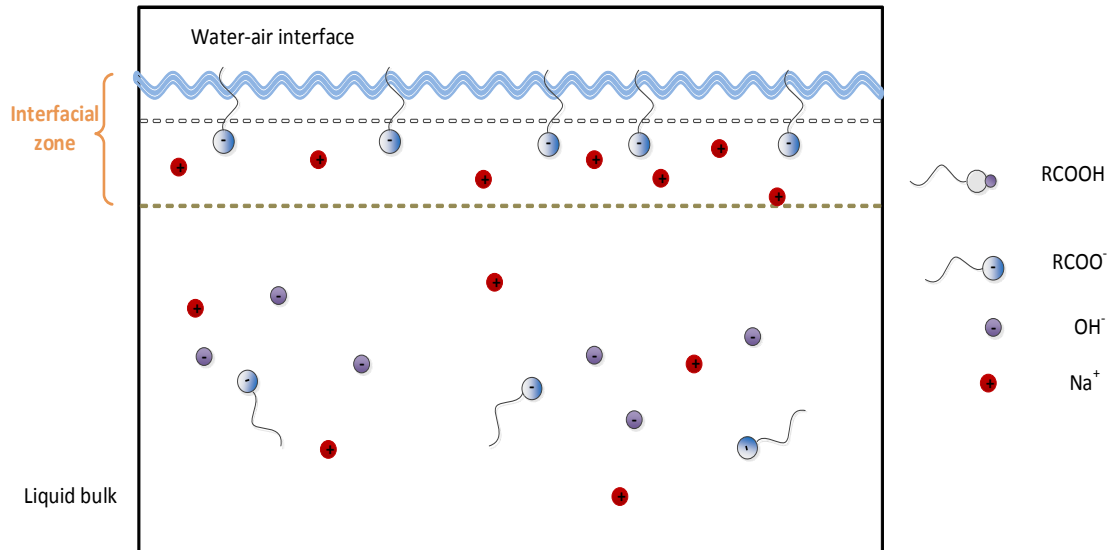
At equilibrium phase, there must be five species in the system including  $A^-$ ,  $OH^-$ ,  $AH$ ,  $Na^+$  and  $H_3O^+$ . As almost all hydronium ions ( $H_3O^+$ ) are presumed to be neutralized by the excessive  $OH^-$ :



Therefore, four species are shown in the bulk and interface (

Figure 4-2). It should be noted that the  $OH^-$  concentration is slightly smaller than the  $Na^+$  concentration due to its neutralization with  $H_3O^+$  ions.





**Figure 4-2. Adsorption of four species in the bulk solution and interfacial zone**

Applying the adsorption model, equation [25] for all four species and considering the bulk concentrations of these species are not constant, would result in a complicated form of equation. So some simplifications are needed. Since  $Na^+$  concentration is not changing during the experiment,  $d \ln (C_{Na^+}) = 0$  and  $Na^+$  is no longer involved in equation [25]. The conditions of constant  $Na^+$  and variable  $C_b$  can be experimentally obtained and consequently were selected for this study.

Therefore equation [25] can be applied in following form:

$$d\gamma = -RT[\Gamma_{AH} d \ln C_{AH} + \Gamma_A d \ln C_A + \Gamma_{OH} d \ln C_{OH}] \quad [37]$$

Also reaction constant can be written as:

$$k_a / k_w = \frac{C_A}{C_{AH} C_{OH}} \quad [38]$$

In above equation,  $k_w$ , ionic product of water is defined as:  $k_w = [H_3O^+] [OH^-]$  which is around  $10^{-14}$  at room temperature. <sup>63</sup> The balance of acid and charges gives:

$$C_{AH} + C_A = C_b \quad [39]$$

$$C_{OH} + C_A = C_{Na} \quad [40]$$

From the equations [38] and [40], the following relationship is achieved:

$$\left(\frac{k_a}{k_w}\right) C_{AH} = C_A / C_{OH} = C_A / (C_{Na} - C_A) \quad [41]$$

By substitution of equation [41] into equation [39], we get:

$$\frac{k_w}{k_a} \frac{C_A}{(C_{Na} - C_A)} + C_A = C_b \quad [42]$$

Logarithmic version of equation [38] is as bellow equations:

$$\ln C_{OH} = \ln C_A - \ln C_{AH} - \ln k_a + \ln k_w \quad [43]$$

And it leads to:

$$d \ln C_{OH} = d \ln C_A - d \ln C_{AH} \quad [44]$$

Therefore equation [37] is simplified as:

$$d\gamma = -RT[(\Gamma_A + \Gamma_{OH})d \ln C_A + (\Gamma_{AH} - \Gamma_{OH})d \ln C_{AH}] \quad [45]$$

Neutrality in the interfacial layer also requires:

$$\Gamma_A + \Gamma_{OH} = \Gamma_{Na} \quad [46]$$

Hence equation [45] reduces to:

$$d\gamma = -RT[(\Gamma_{Na})d \ln C_A + (\Gamma_{AH} + \Gamma_A - \Gamma_{Na})d \ln C_{AH}] \quad [47]$$

Since  $Na^+$  ions are located further inside the bulk, one can assume that the surface concentration of  $Na^+$  is the same as the bulk concentration. Consequently,

$$\Gamma_{Na} = \lambda_s C_{Na} \quad [48]$$

Where  $\lambda_s$  is the thickness of the interfacial layer. At high and constant concentrations of  $Na^+$ , one can assume that  $\lambda_s$  is constant. The assumption is verified later with experimental results.

#### 4.2.2.3 FITTING PROCEDURE

A fitting procedure is applied to both experimental data simultaneously. Since the experimental data only presents  $\gamma$ -versus- $C_b$  relationship, further conversion is required. In case of unadjusted acid, the corresponding  $C_A$  is calculated by equation

[36]. Consequently, the surface tension data are obtained as function of  $C_A$  (i.e.  $\gamma$ -versus- $C_A$ ), and can be fitted by equation [34].

In case of constant  $Na^+$ ,  $C_A$  and  $C_{AH}$  are obtained from  $C_b$  using the bisection method. Consequently, the correlations between  $d\ln C_A$ -versus- $d\ln C_b$  and  $d\ln C_{AH}$ -versus- $d\ln C_b$  are obtained. As shown later on, both  $d\ln(C_A)$ -versus- $d\ln(C_b)$  and  $d\ln(C_{AH})$ -versus- $d\ln(C_b)$  are linear and easy to be applied. The results of bisection method is given in Figure 4-3 and Figure 4-4.

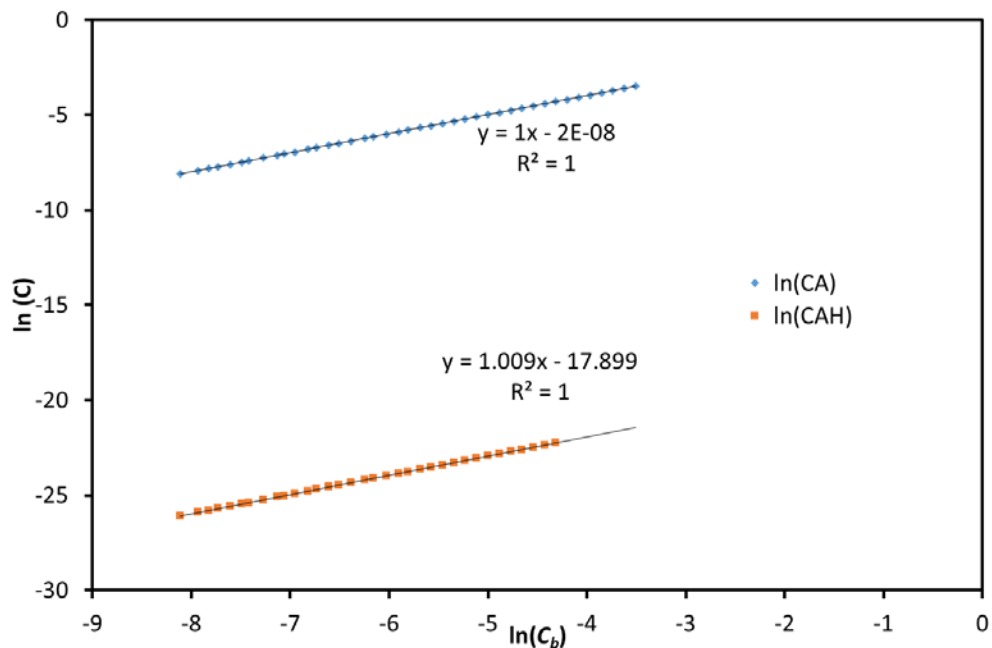


Figure 4-3. Bisection method- Correlations between  $\ln C_A$  and  $\ln C_{AH}$  against  $\ln C_b$

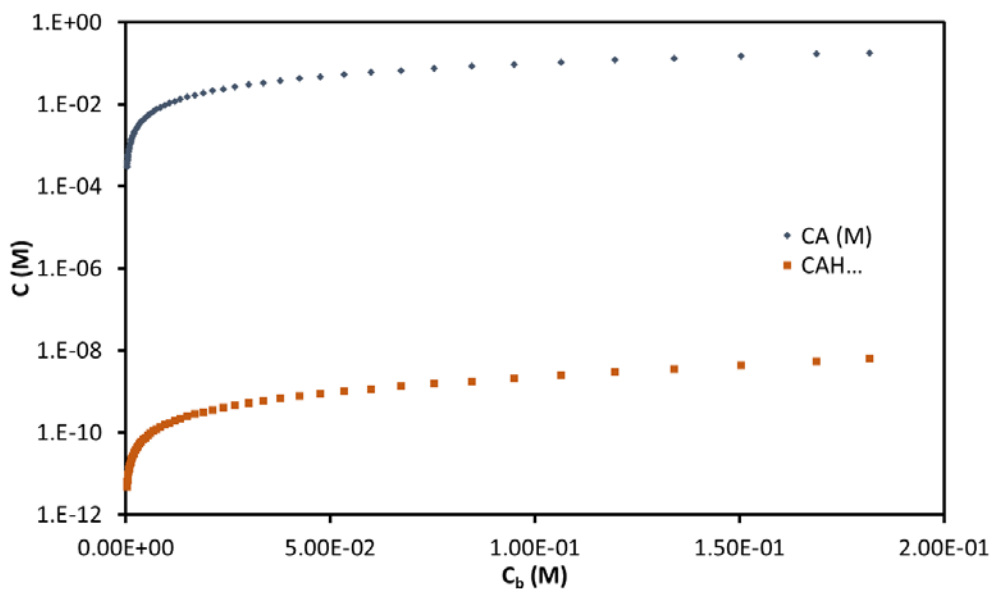


Figure 4-4. Bisection method- Correlations between  $C_A$  and  $C_{AH}$  against  $C_b$

So from the prediction model,  $C_A$  and  $C_{AH}$  can be expressed as functions of  $C_b$ :

$$d(\ln C_A) = \beta_1 d \ln(C_b) \quad [49]$$

$$d(\ln C_{AH}) = \beta_2 d \ln(C_b) \quad [50]$$

Substitution of above equations into equation [47] results in:

$$d\gamma = -RT[(\Gamma_{Na})\beta_1 d \ln C_b + (\Gamma_{AH} + \Gamma_A - \Gamma_{Na})\beta_2 d \ln C_b] \quad [51]$$

Or

$$-\frac{1}{RT} \frac{d\gamma}{d \ln C_b} = \Gamma_{Na}\beta_1 + (\Gamma_{AH} + \Gamma_A - \Gamma_{Na})\beta_2 \quad [52]$$

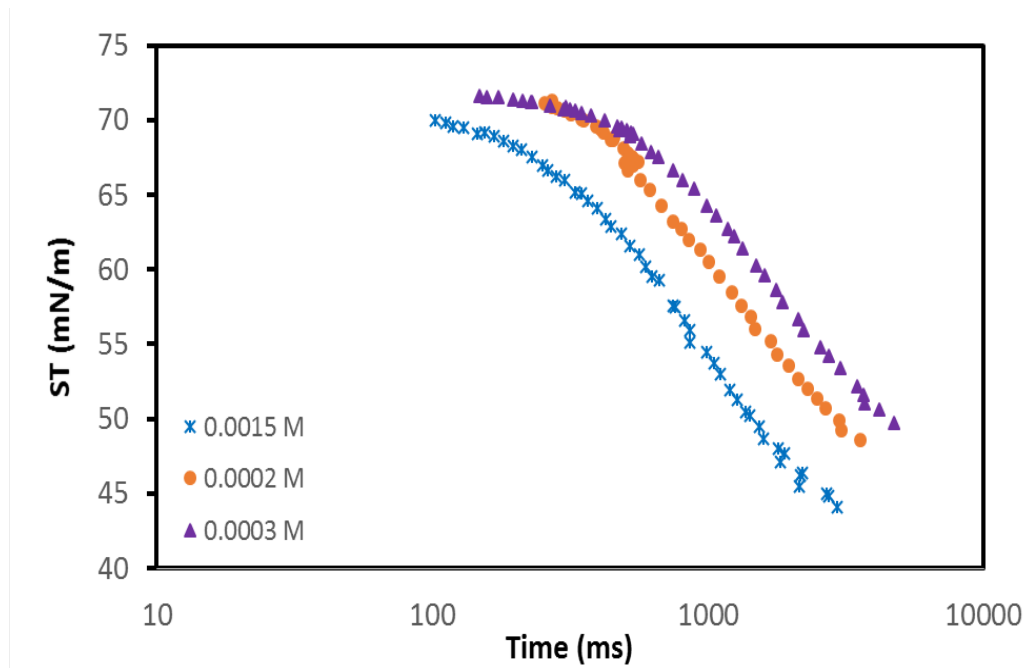
Corresponding adsorption parameters are then obtained at both conditions by fitting the surface tensions: In case of acid only condition by equation [34] and in constant *NaOH* condition by equation [52] to find  $\Gamma_{max}$ ,  $K_A$  and  $K_{AH}$ . The obtained parameters are then used to quantify the adsorption of species.

### 4.3 EXPERIMENTAL RESULTS

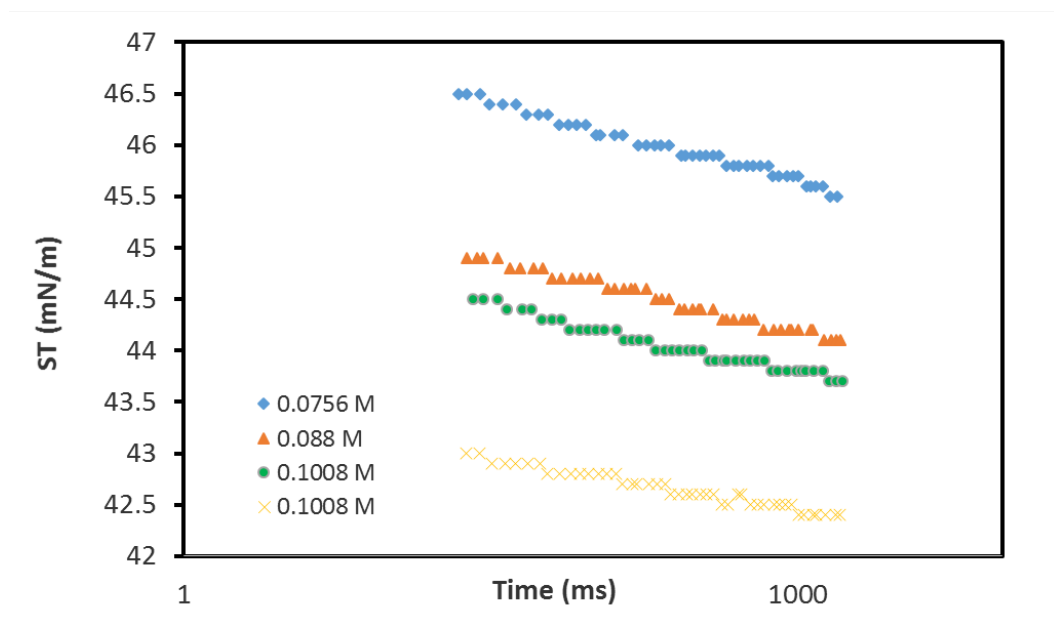
#### 4.3.1 DYNAMIC SURFACE TENSION

Different concentrations of decanoic acid were used in this experiment. One part was prepared at higher concentrations with addition of sodium hydroxide. The other part was made at lower concentrations without addition of sodium hydroxide. The obtained data from the device was then plotted in graphs. The corresponding diagrams are shown in Figure 4-5 and

Figure 4-6.



**Figure 4-5. Dynamic surface tension data for decanoic acid at low concentrations without NaOH**



**Figure 4-6. Dynamic surface tension data for decanoic acid at high concentrations with NaOH**

However, the results showed that dynamic surface tension data for decanoic acid as an anionic surfactant are really fast and could not be used in the thesis. Further work is required to establish this.

### 4.3.2 DISSOCIATION CONSTANT

In case of unadjusted  $pH$  or acid only condition, dissociation constant was obtained by fitting experimental data of  $pH$  measurement to the model described in equation [24]. The solubility cannot be confirmed visually (i.e. by observing the solid formation on the surface) for the unadjusted solution. However, the surface tension in Figure 4-11 indicated that the surface is not saturated for  $C_b \leq 0.4 \text{ mM}$ . Hence, the  $pH$  data up to  $0.4 \text{ mM}$  were used to quantify the ionization constant. The  $pH$  data as function of acid concentration are shown in Figure 4-7. It should be noted that the  $pH$  at low concentrations is dominated by the self-ionization of water.

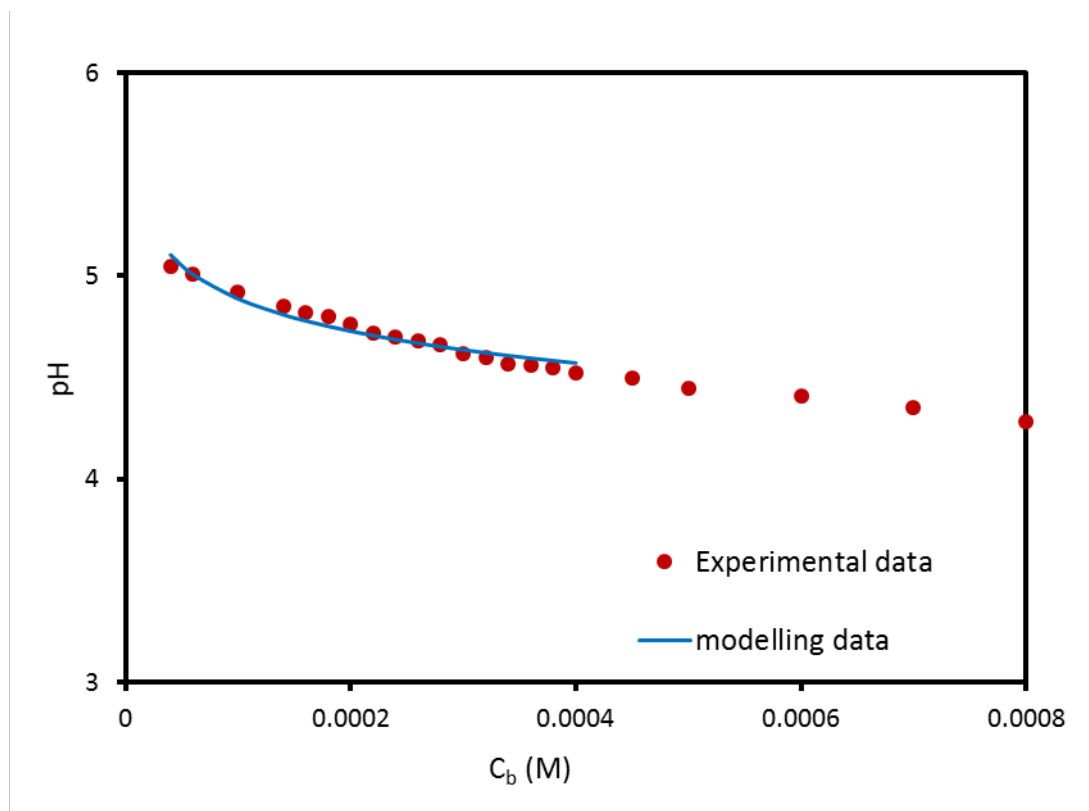


Figure 4-7. Decanoic acid  $pH$  data in relation to its concentration in bulk solution

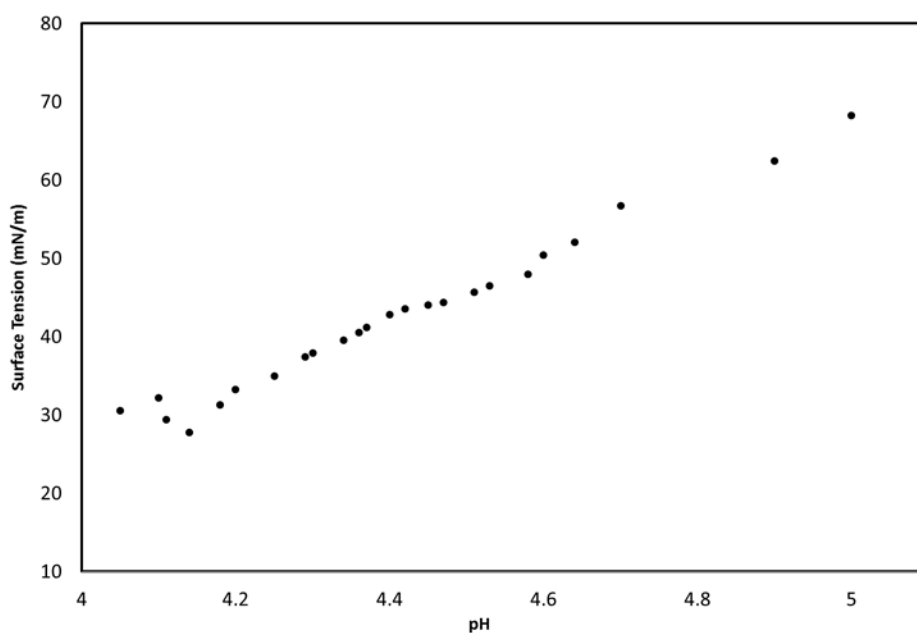
### 4.3.3 SURFACE ACTIVITY

In order to understand surface activity<sup>96,97</sup> of a species in an interface, investigation is usually done on surface tension changes with respect to change in a solution property such as  $pH$  or concentration.<sup>57</sup>

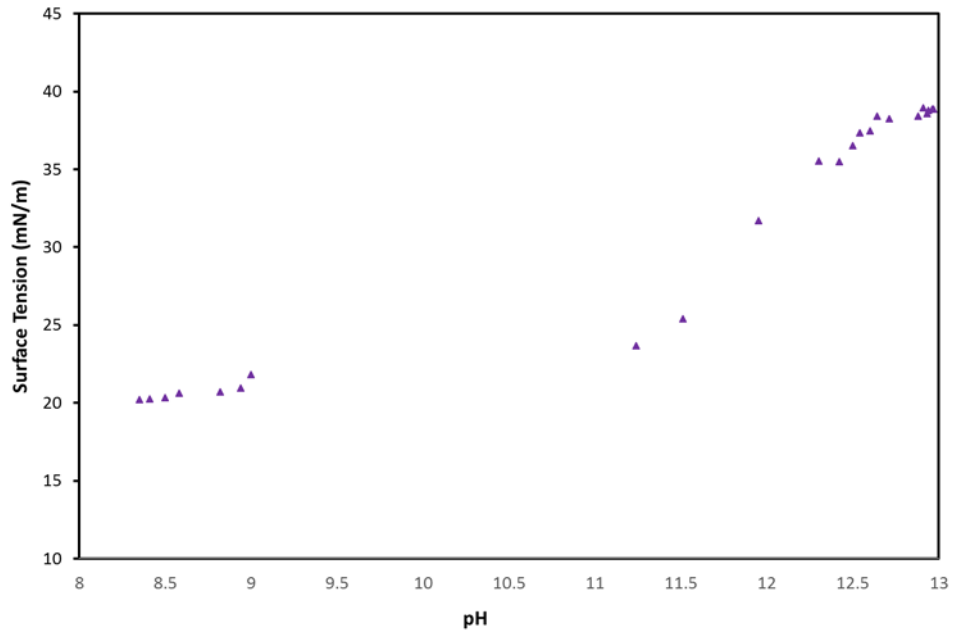
Figure 4-8, Figure 4-9 and Figure 4-10 show surface tension changes at different  $pH$  ranges. These graphs indicate that surface tension increases by increasing  $pH$ . As a result, surface activity decreases with raising surface tension. For first experiment,  $pH$  from 4 to 5, decanoic acid concentration ranged from 0.04  $mM$  to 0.001  $M$ , acid solution was prepared without addition of any  $NaOH$  into water. The amount of  $pH$  changes as a result of diluting the initial solution by adding controlled volume of water.

In second experiment,  $pH$  from 8 to 13, decanoic acid concentration was 0.09  $M$  which was prepared by addition of 0.4 wt. %  $NaOH$  into the solution and  $pH$  changed as a result of adding 0.05 ml  $HCl$  32% into the system.

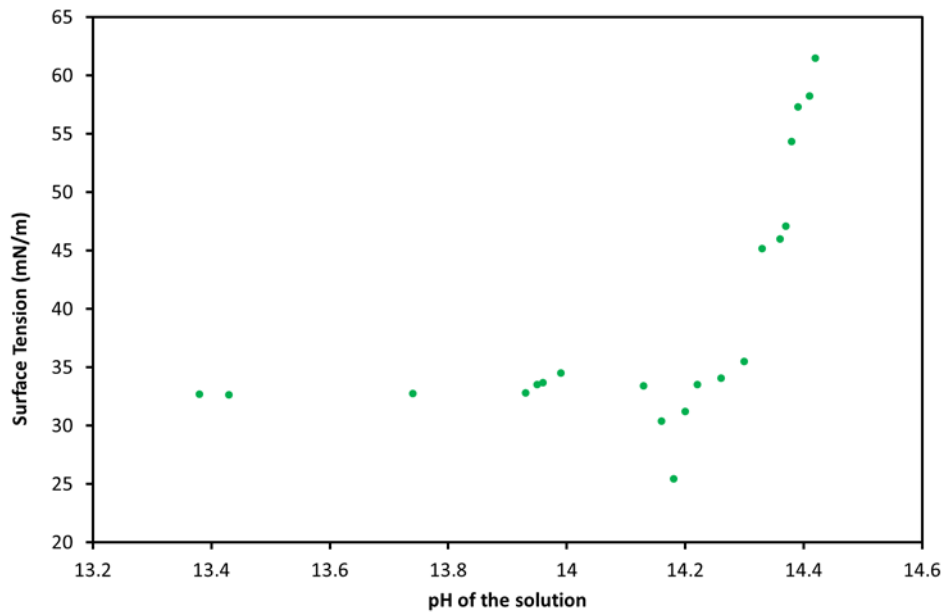
In the last graph,  $pH$  13 to 14, decanoic acid initial concentration was 0.2  $M$  (3.4 wt. %) and was prepared by adding 0.9 wt. %  $NaOH$  to the solution. Dilution was done by adding a solution of 1 wt. %  $NaOH$  into water and final concentration was 0.001  $M$  (0.017 wt. %).



**Figure 4-8. Decanoic acid surface tension data changes in accordance with  $pH$  4 to 5**



**Figure 4-9. Decanoic acid surface tension data changes in accordance with pH 8 to 13**



**Figure 4-10. Decanoic acid surface tension data changes in accordance with pH 13 to 14**

The results, as shown above, indicate that surface tension rises by increasing  $pH$  which proves that surface activity drops by raising  $pH$ .

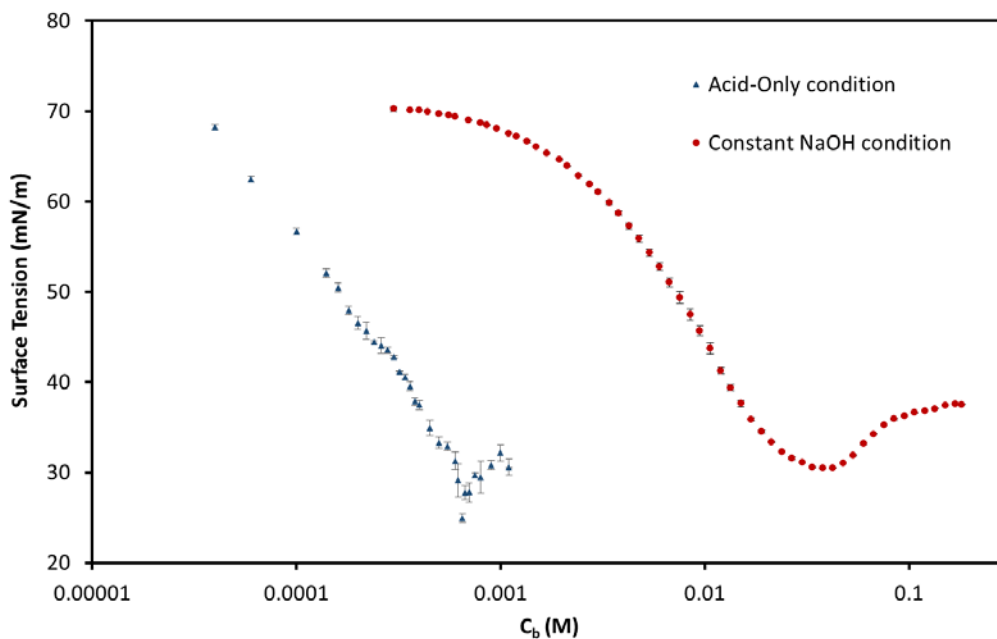


#### 4.3.4 SURFACE TENSION

Surface tension data were obtained from two sets of experiments explained before. One includes only decanoic acid in water without addition of sodium hydroxide. In this case, acid concentration was lower since higher concentration of decanoic acid was not achieved without adding sodium hydroxide to the solution. Pendant bubble method was applied here for concentrations between 0.04 *mM* and 1.1 *mM*.

The other case includes sodium hydroxide in the system which leads to complete ionization of decanoic acid. Surface tension measurement was performed applying Wilhelmy plate method. Decanoic acid concentrations ranged from 0 to 0.2 *M*.

The results of surface tension data in relation to bulk concentration of acid at both experimental conditions are shown in Figure 4-11.



**Figure 4-11. Surface tension as a function of bulk concentration**

For constant concentrations of  $Na^+$  (0.22 *M*), the solubility was greater than 0.4 *M*. In this instance, the acid is fully ionized and soluble. The *pH* of *NaOH* solution was 14.45 and was used as a starting point. The region around *CMC* ( $\sim 0.04$  *M*) demonstrated a typical dip for anionic surfactant.

For the unadjusted *pH*, the surface tension was measured up to 1 *mM*, which is two orders of magnitude lower than the other case. It should be noted that the lowest

surface tension, around 0.7 mM, might not correspond to the critical micelle concentration. Instead, the region may indicate surface aggregate or limited solubility.

#### 4.4 MODELING RESULTS

The modelling consists of the following steps:

1. The ionization constant,  $k_a$ , is obtained by fitting  $pH$  data;
2. Surface tensions at both conditions are fitted to find the corresponding adsorption;
  - a. In acid-only condition (unadjusted  $pH$ ):  $\Gamma_A + \Gamma_{AH}$  by equation [34];
  - b. In the case of constant  $Na^+$  concentration (adjusted  $pH$ ):  $\Gamma_{AH} + \Gamma_A - \Gamma_{Na}$  by equation [52].
3. The adsorption was then fitted to equation [30] and [31] simultaneously to find  $\Gamma_{max}$ ,  $\Gamma_{Na}$ ,  $K_A$  and  $K_{AH}$ .

##### 4.4.1 DISSOCIATION CONSTANT

Equation [24] was applied for decanoic acid solution in case of unadjusted  $pH$  solution or acid-only condition. The ionization constant,  $k_a$  and the corresponding  $pK_a$  are given in Table 4-1. It should be noted that the reported  $pK_a$  in the literature are not consistent, and varied from 4.9<sup>74</sup> to 6.8<sup>69</sup> or even 7.2<sup>66</sup> one reason for discordancy is that the high-chain acid can form micelles, such formation will increase the apparent  $pK_a$ . For instance, it can increase to 10 for  $C_{17}COOH$ , due to micelles formation. Also different methodologies and experimental conditions can affect the results.

**Table 4-1. Dissociation constant modelling results**

Ionization constant, $k_a$	1.92E-06
$pK_a$	5.72

#### 4.4.2 SURFACE TENSION AND ADSORPTION PARAMETERS

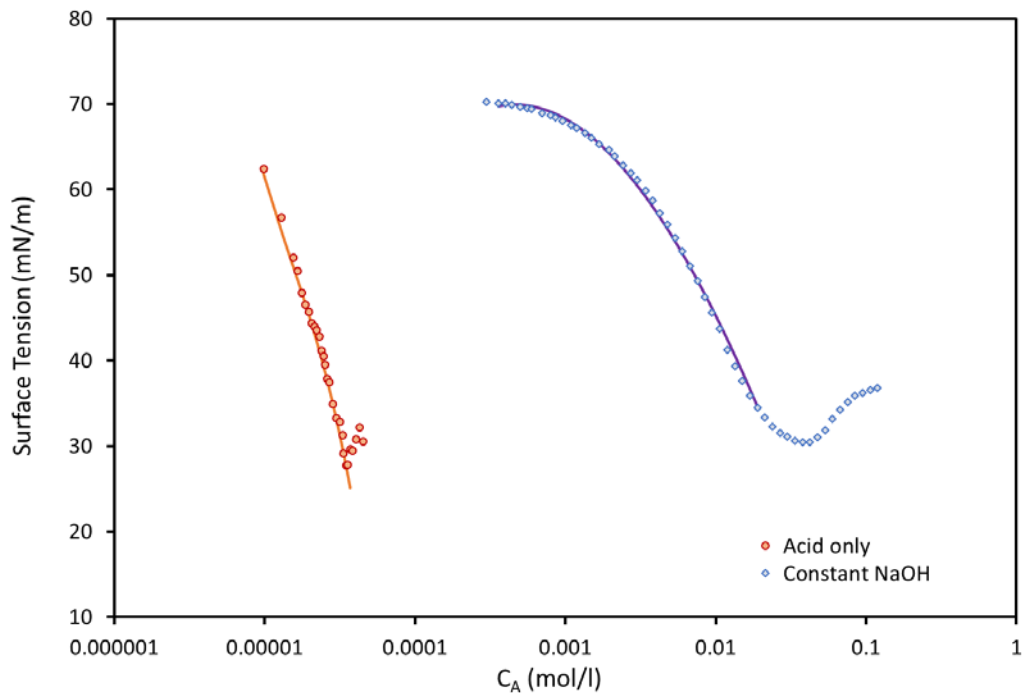
From the neutron reflectometry analysis of anionic surfactants,<sup>98</sup> the adsorption should remain unsaturated to  $\sim 80\%$  of *CMC*. Since the theoretical model in this study was only applicable to unsaturated adsorption, the lower ranges (0.01 M and 0.06 mM respectively) were selected for modelling. The surface tension was fitted with the one-parameter equation:<sup>99</sup>

$$\gamma(C_A) = \gamma_0 e^{-\chi C_A} \quad [53]$$

Where  $\chi$  is a new adsorption constant which has the same unit as K. The best-fitted values of  $\chi$  are presented in Table 4-2 for unadjusted and adjusted *pH* cases. The fittings for both conditions are presented in Figure 4-12.

**Table 4-2. Adsorption constant modelling results (decanoic acid)**

Experimental conditions	$\chi$
Acid only condition	$2.96 \times 10^4 \text{ M}^{-1}$
Constant NaOH condition	$47.82 \text{ M}^{-1}$



**Figure 4-12. Modelling surface tension as a function of  $C_A$**

To define surface concentrations at both conditions, the slope of the surface tension data were obtained by differentiating equation [53].

$$\frac{d\gamma(C_A)}{d(\ln C_A)} = \chi\gamma_0 \exp(\chi C_A + \ln C_A) \quad [54]$$

To reach above equation, following mathematical procedure was applied:

$$\frac{d(\gamma_0 e^{-\chi C_A})}{d(\ln C_A)} \ln C_A = f_A, e^{f_A} = C_A \frac{d(\gamma_0 \exp(-\chi e^{f_A}))}{df_A}$$

$$\frac{\gamma_0 d(\exp(-\chi e^{f_A}))}{df_A} \underline{u = \chi e^{f_A}, \frac{de^u}{du} = e^u} = \frac{\gamma_0 d(e^u)}{du} \frac{du}{df_A}$$

$$\frac{\gamma_0 d(\exp(-\chi e^{f_A}))}{df_A} = \gamma_0 \exp(\chi e^{f_A}) \chi e^{f_A} = \gamma_0 \chi e^{\chi C_A} e^{\ln C_A} = \gamma_0 \chi e^{\chi C_A + \ln C_A}$$

In case of acid only, substituting equations [30] and [31] into [34] gives:

$$-\frac{1}{2RT} \frac{d\gamma}{d \ln C_A} = \frac{\Gamma_{\max} (K_A C_A + K_{AH} C_{AH})}{1 + K_A C_A + K_{AH} C_{AH}} \quad [55]$$

Equalizing equation [54] and [55] gives adsorption parameters.

In case of constant *NaOH* condition, by substituting equations [30] and [31] into equation [52] we get:

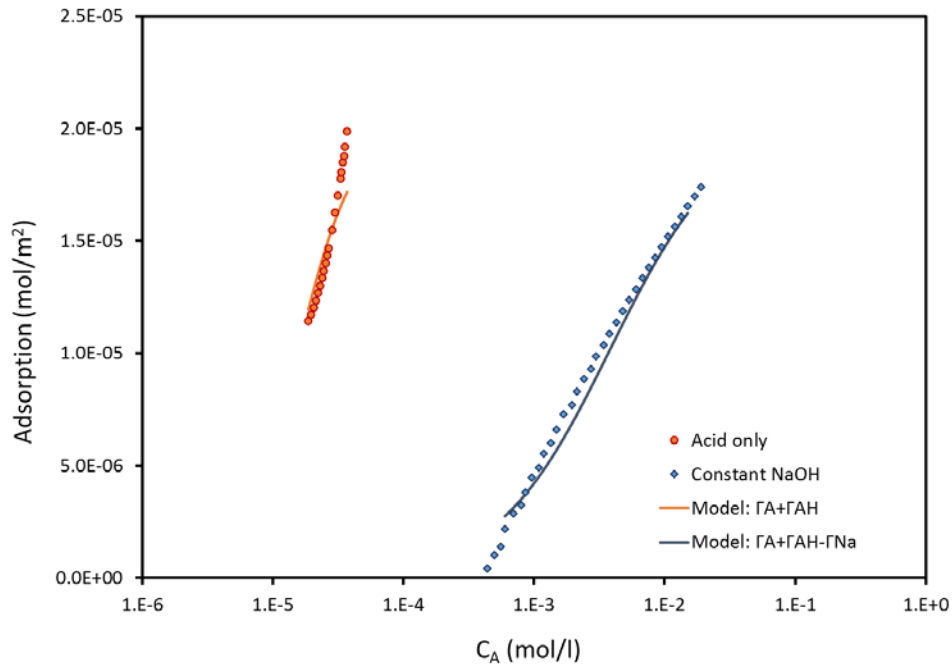
$$-\frac{1}{RT} \frac{d\gamma}{d \ln C_b} = \Gamma_{Na} \beta_1 + \left( \Gamma_{\max} \left\{ \frac{K_A C_A + K_{AH} C_{AH}}{1 + K_A C_A + K_{AH} C_{AH}} \right\} - \Gamma_{Na} \right) \beta_2 \quad [56]$$

By equalizing equation [54] and [56] the adsorption constants were then found.

The data for both conditions are shown in Figure 4-13. It can be seen that the model describes both cases successfully, excepting the high acid concentration at constant  $C_{Na+}$ . The differences may arise from the assumption of constant  $\Gamma_{Na}$ . At high adsorbed concentrations, it is expected that  $\Gamma_{Na}$  may increase slightly with increasing  $\Gamma_A$ . The fitting parameters are  $\Gamma_{max}$ ,  $\Gamma_{Na}$ ,  $K_A$  and  $K_{AH}$ . The best-fitted results are given in Table 4-3.

**Table 4-3. Adsorption parameters for decanoic acid**

$\Gamma_{\max}$ (mol/m <sup>2</sup> )	$\Gamma_{\text{Na}}$ (mol/m <sup>2</sup> )	$K_{\text{A}}$ (M <sup>-1</sup> )	$K_{\text{AH}}$ (M <sup>-1</sup> )
$2.02 \times 10^{-5}$	$1.1 \times 10^{-7}$	261.13	7925

**Figure 4-13. Adsorption at unadjusted pH and constant Na<sup>+</sup> conditions**

## 4.5 SUMMARY

A new binary model was proposed for the adsorption of a carboxylic acid at the air/water interface. The model consists of the adsorption of surfactant tails and ionic binding around the surfactant heads. The model was successfully applied at two physical conditions simultaneously. The adsorption constants for both neutralized and ionized acids were successfully quantified. It was found that the adsorption constant for the neutralized species is much higher than that of the ionized species. The inner ionic layer was physically consistent with an ionic diffuse layer in case of the salt-free solution. At high and constant concentration of  $\text{Na}^+$ , the ionic layer is approximately equal to the diameter of hydrated  $\text{Na}^+$ , which is

consistent with double layer at high ionic concentrations. The model lays important groundwork for modelling surfactant adsorption with chemical reactions.

## 5 ADSORPTION OF NONANOIC ACID AT AIR/WATER INTERFACE

### 5.1 INTRODUCTION

The adsorption and surface activities of surfactants are determined by surface tension measurement here. In general, the adsorption is governed by a balance between hydrophobic and hydrophilic parts of the surfactants. As mentioned previously, the hydrophobic part of a surfactant is the hydrocarbon tail. Hence, shorter hydrocarbon will reduce hydrophobicity of the surfactant. The influence of hydrocarbon length on surfactant has been evidenced in the literature.<sup>42</sup> One of the most notable effects is the increase of the *CMC*. Hence, it is expected that changing hydrocarbon tail length has significant effects on ionization of carboxylic acids at the air/water interface.

Longer acid,  $C_{11}H_{22}O_2$  was also available to test but it was a bit challenging to run the same sets of experiments on undecanoic acid like decanoic acid. The acid had very low solubility in water which made it difficult and unreliable to perform pendant drop experiment. It was also impossible to run Wilhelmy method as undecanoic acid solution would turn into solid as soon as it was cooled down.

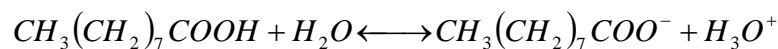
Therefore, a shorter carbon length, nonanoic acid,  $C_9H_{18}O_2$  was studied, while  $C_{11}H_{22}O_2$  was also available but the increased length dramatically reduces solubility and makes surface tension measurement difficult. This chapter dedicates to the adsorption of nonanoic acid.

Previously a new theoretical framework was introduced to successfully model adsorption of decanoic acid,  $C_{10}H_{20}O_2$ , at air/water interface. The applicability of this framework to adsorption of nonanoic acid in air/water interface is studied in this chapter. The same theoretical model from chapter 4 is applied. The obtained adsorption parameters were critically compared against values of decanoic acid.

## 5.2 THEORETICAL MODELLING

### 5.2.1 DISSOCIATION CONSTANT

Dissociation constant was assessed using the same method that was detailed for decanoic acid in chapter 4 using *pH* measurement. The *pH* of nonanoic acid solution was recorded throughout the experiment and experimental data were fitted to the modelling equation. It should be noted that acid solution was prepared without addition of sodium hydroxide. Ionization equation is described as:



Considering  $CH_3(CH_2)_7COO^-$  as “A<sup>-</sup>” and  $CH_3(CH_2)_7COOH$  as “AH”, ionization constant,  $k_a$  and *pH* are defined by equations [22] and [24]:

### 5.2.2 SURFACE TENSION AND ADSORPTION PARAMETERS

As described in previous chapter for decanoic acid, the equilibria are given by equation [26] and [27] and the adsorbed concentration of each species is given by equation [30] and [31].

#### 5.2.2.1 ACID-ONLY SOLUTION

The salt-free solution (acid-only condition) contains three species: A<sup>-</sup>(RCOO<sup>-</sup>), AH (RCOOH) and H<sub>3</sub>O<sup>+</sup>. It is previously explained that the governing model to determine adsorption parameters for the condition of only nonanoic acid existing in water is equation [34]. The concentration of ionized acid, C<sub>A</sub> can also be calculated from equation [35]. And finally, concentration of hydronium ions can be calculated from equation [36]. And total adsorption can be obtained as a function of C<sub>A</sub>.

#### 5.2.2.2 ACID WITH HIGH AND CONSTANT CONCENTRATION OF NA<sup>+</sup>

At equilibrium, four species are presented in the bulk and interface and applicable adsorption model is obtained by equation [47].



### 5.2.2.3 FITTING PROCEDURE

The procedure here is the same as applied procedure for decanoic acid. The results of correlations between  $d\ln(C_A)$ -versus- $d\ln(C_b)$  and  $d\ln(C_{AH})$ -versus- $d\ln(C_b)$  as well as  $C_A$  and  $C_{AH}$  against  $C_b$  are shown in Figure 5-1 and Figure 5-2.

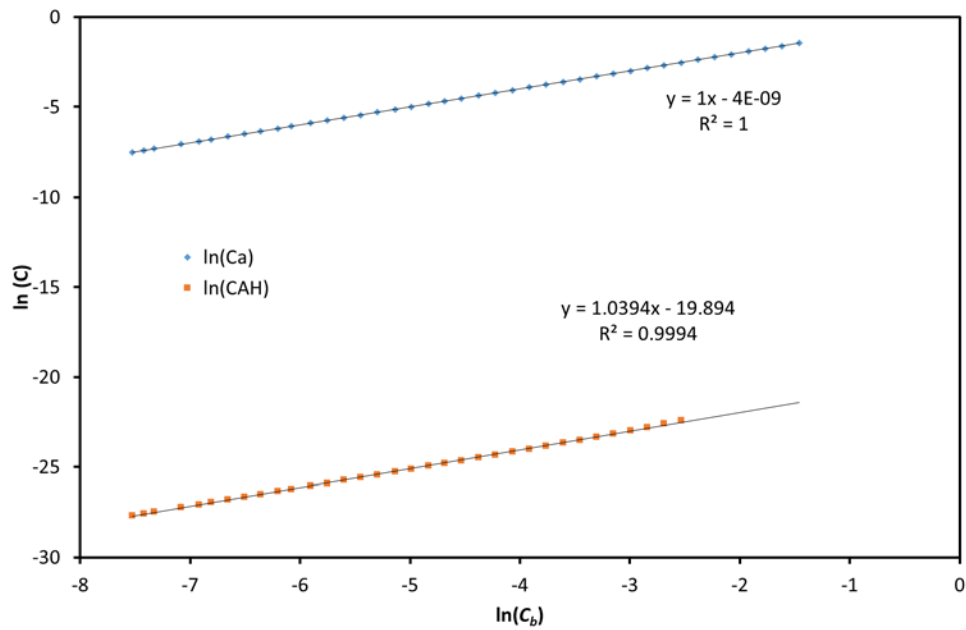


Figure 5-1. Bisection method- Correlations between  $\ln C_A$  and  $\ln C_{AH}$  against  $\ln C_b$

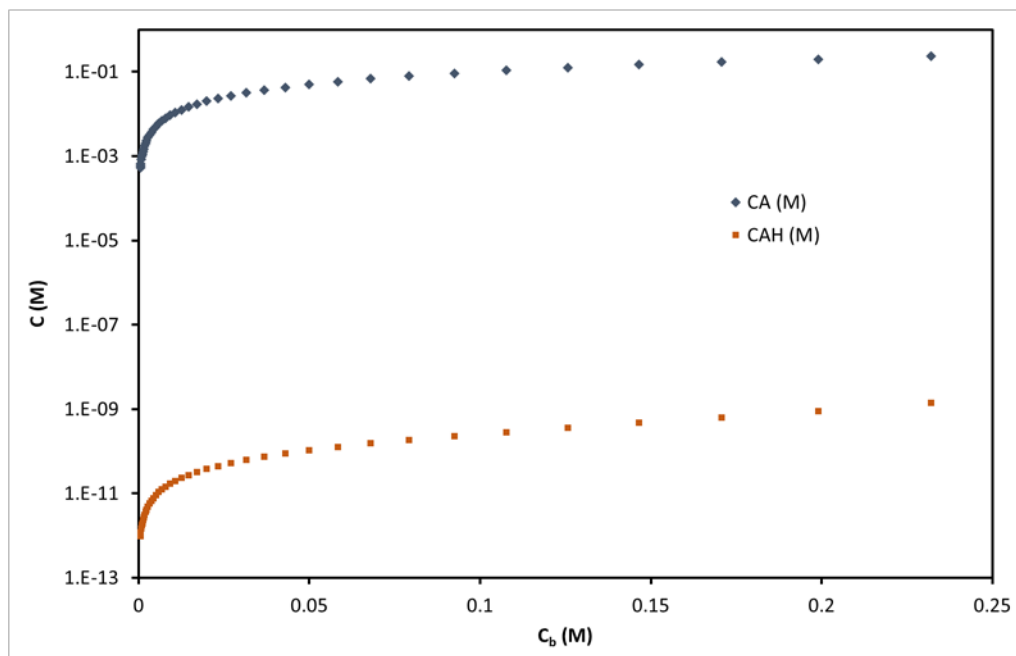


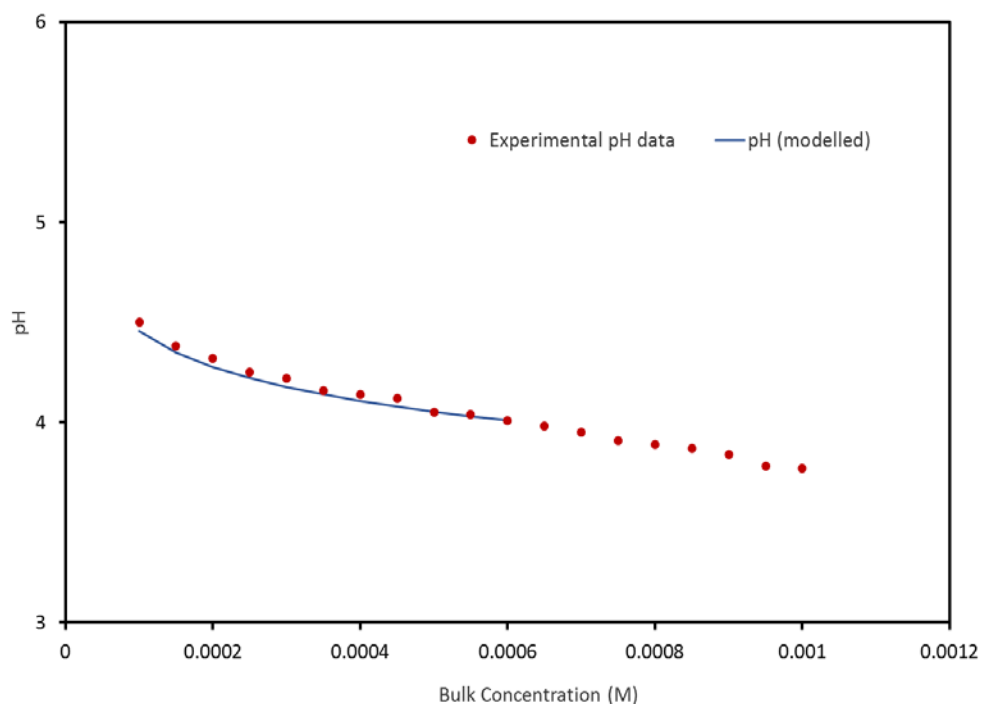
Figure 5-2. Bisection method- Correlations between  $C_A$  and  $C_{AH}$  against  $C_b$

## 5.3 EXPERIMENTAL RESULTS

### 5.3.1 DISSOCIATION CONSTANT

Dissociation constant for nonanoic acid solution,  $k_a$  was obtained by *routine pH* measurements and used to compute the exact concentration of *A and AH* in the bulk. From above equations and assumptions, *pH* can be achieved from equation [24]. The values of *pH* as function of acid concentrations are shown in Figure 5-3. It should be noted that the *pH* at low concentrations is dominated by the self-ionization of water.

A possible explanation for the results in Figure 5-3 is that the surface is saturated for concentrations higher than 0.6 *mM*. Therefore, *pH* data up to 0.6 *mM* was applied to calculate ionization constant.



**Figure 5-3. Nonanoic acid pH data in relation to its concentration in bulk solution**

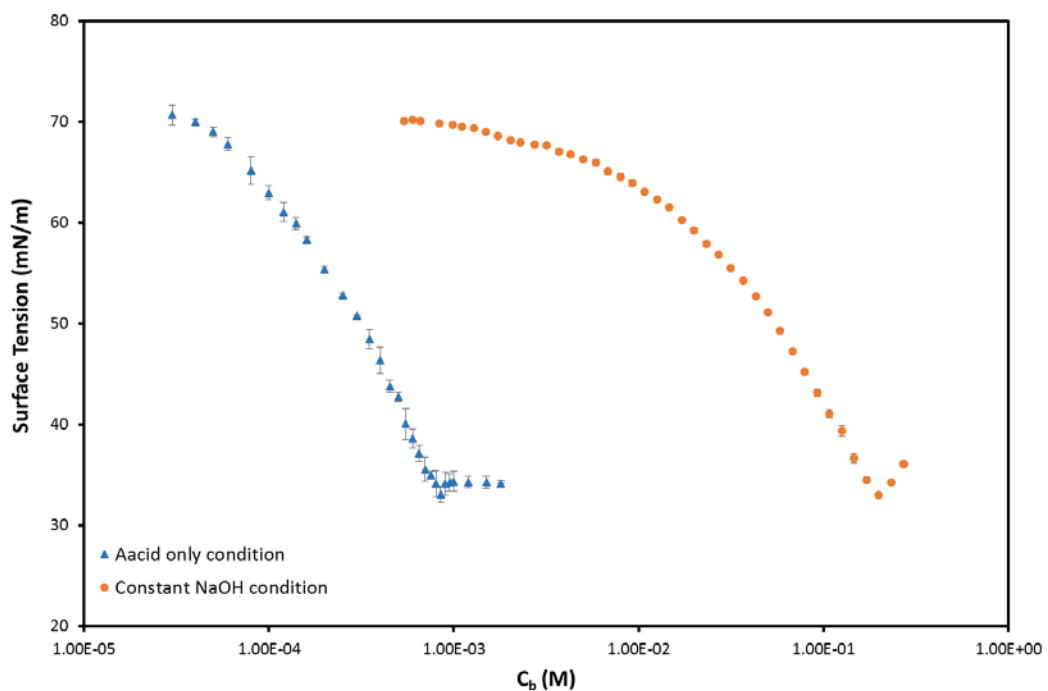
### 5.3.2 SURFACE TENSION

As described before, surface tension data were obtained from two sets of experiments: nonanoic acid in water without addition of sodium hydroxide and constant *NaOH* condition. Pendant bubble method was used for concentrations

between 0.03 *mM* and 1.8 *mM* and Wilhelmy plate method was used for 0 to 0.27 *M*. The results for surface tension data in relation to bulk concentration of acid are shown in Figure 5-4.

For constant concentrations of  $Na^+$  (0.33 *M*), the solubility was greater than 0.4 *M*. In this instance, the acid is fully ionized and soluble. The *pH* of *NaOH* solution was 14.45 and was used as a starting point. The region around *CMC* ( $\sim 0.2$  *M*) demonstrated a typical dip for anionic surfactant.

For the unadjusted *pH*, the surface tension was measured up to 1.8 *mM*, which is two orders of magnitude lower than the other case. It should be noted that the lowest surface tension, around 0.8 *mM*, might not correspond to the critical micelle concentration. Instead, the region may indicate surface aggregate or limited solubility.



**Figure 5-4. Surface tension as a function of bulk concentration**

## 5.4 MODELLING RESULTS

As described before, the modelling consists of fitting *pH* data to obtain the ionization constant,  $k_a$  and fitting surface tensions at both conditions to find the

corresponding adsorption. Finally, adsorption was fitted to equations [30] and [31] simultaneously to find  $\Gamma_{max}$ ,  $\Gamma_{Na}$ ,  $K_A$  and  $K_{AH}$ .

#### 5.4.1 DISSOCIATION CONSTANT

In case of acid only condition, experimental  $pH$  data were fitted to equation [24]. Results are shown in Table 5-1:

**Table 5-1. Dissociation constant**

Ionization constant, $k_a$	$1.70 \times 10^{-5} \text{ M}$
$pK_a$	4.77

The value is consistent with the literature value for nonanoic acid.<sup>72, 67</sup>

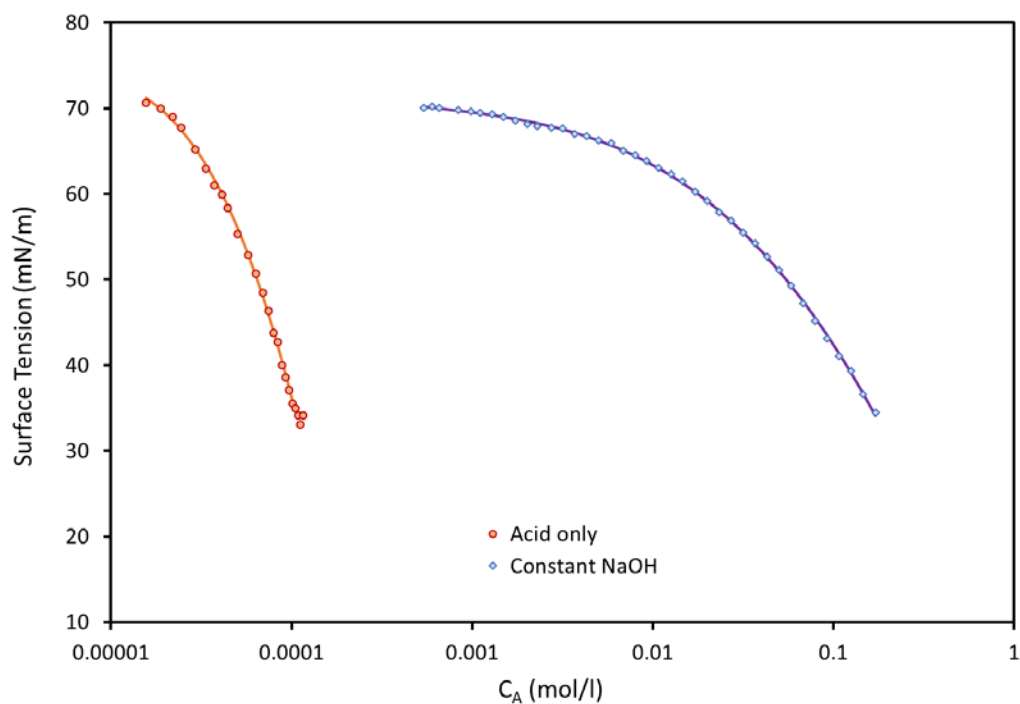
#### 5.4.2 SURFACE TENSION AND ADSORPTION PARAMETERS

Since micelles or aggregates interfere with surfactant adsorption, the theoretical model in this study was only applicable to unsaturated adsorption and the lower ranges, 0.03 M and 0.1 mM respectively were selected for modelling at constant  $Na^+$  concentration and acid-only conditions. The best-fitted values of  $\chi$  are presented in Table 5-2:

**Table 5-2. Adsorption constant**

Experimental conditions	$\chi$
Acid only condition	$8.05 \times 10^3 \text{ M}^{-1}$
Constant $NaOH$ condition	$8.38 \text{ M}^{-1}$

The fittings for both conditions are presented in Figure 5-5.



**Figure 5-5. Modelling surface tension as a function of  $C_A$**

To define surface concentrations at both conditions ( $\Gamma_A + \Gamma_{AH}$  for unadjusted  $pH$  and  $\Gamma_{AH} + \Gamma_A - \Gamma_{Na}$  for constant  $Na^+$  concentration), equations [54], [55] and [56] were applied. The fitting parameters are  $\Gamma_{max}$ ,  $\Gamma_{Na}$ ,  $K_A$  and  $K_{AH}$ . The best-fitted results are given in Table 5-3:

**Table 5-3. Adsorption parameters for nonanoic acid**

$\Gamma_{max}$ (mol/m <sup>2</sup> )	$\Gamma_{Na}$ (mol/m <sup>2</sup> )	$K_A$ (M <sup>-1</sup> )	$K_{AH}$ (M <sup>-1</sup> )
$1.97 \times 10^{-5}$	$1.65 \times 10^{-7}$	30.33	8274

The adsorption data for both conditions are presented in Figure 5-6.

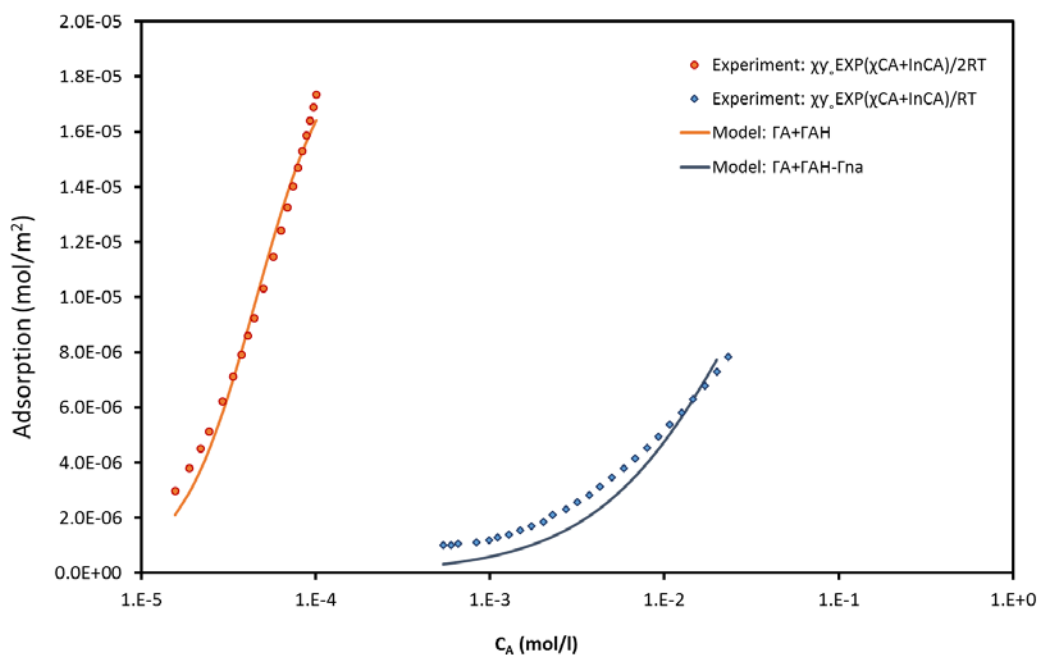


Figure 5-6. Adsorption of nonanoic acid at acid-only and constant  $\text{Na}^+$  conditions

## 5.5 COMPARISON BETWEEN $\text{C}_9$ AND $\text{C}_{10}$ ACIDS

In this section results of experimental and theoretical work done in chapter 4 and 5, applying decanoic acid and nonanoic acid, are compared with each other. The most significant results are shown in Table 5-4.

Table 5-4. Results of decanoic acid and nonanoic acid measurements

Physical Properties	Decanoic acid	Nonanoic acid
Chemical Formula	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	$\text{CH}_3(\text{CH}_2)_7\text{COOH}$
Molar Mass	172.26	158.24
CMC @ acid only cond.	0.7 mM	0.85 mM
Surface tension at above mentioned CMC	27.8 mN/m	33.05 mN/m
CMC @ constant $\text{Na}^+$ cond.	37.8 mM	199 mM
Surface tension at above mentioned CMC	30.4 mN/m	32.9 mN/m
Dissociation constant, $\text{pK}_a$	5.72	4.77

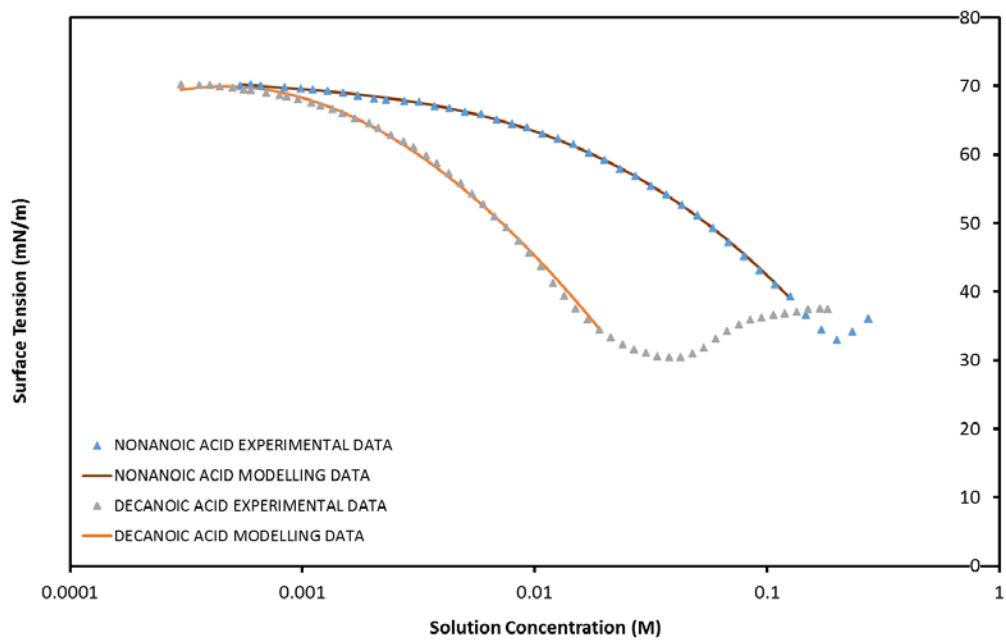
Adsorption Parameters	Decanoic acid	Nonanoic acid
Adsorption constant, $\chi$ @ acid only cond.	$2.96 \times 10^4 \text{ M}^{-1}$	$8.05 \times 10^5 \text{ M}^{-1}$
Adsorption constant, $\chi$ @ constant $\text{Na}^+$ cond.	$47.82 \text{ M}^{-1}$	$8.38 \text{ M}^{-1}$
Total adsorption concentration, $\Gamma_{\text{max}}$	$2.02 \times 10^{-5} \text{ mol/m}^2$	$1.97 \times 10^{-5} \text{ mol/m}^2$
Adsorption isotherm constant of A, $K_A$	$261.13 \text{ M}^{-1}$	$30.33 \text{ M}^{-1}$
Adsorption isotherm constant of AH, $K_{\text{AH}}$	$7.92 \times 10^3 \text{ M}^{-1}$	$8.27 \times 10^3 \text{ M}^{-1}$
Adsorption concentration of Na, $\Gamma_{\text{Na}}$	$1.10 \times 10^{-7} \text{ mol/m}^2$	$1.65 \times 10^{-7} \text{ mol/m}^2$

From the data of Table 5-4, we can make these conclusions:

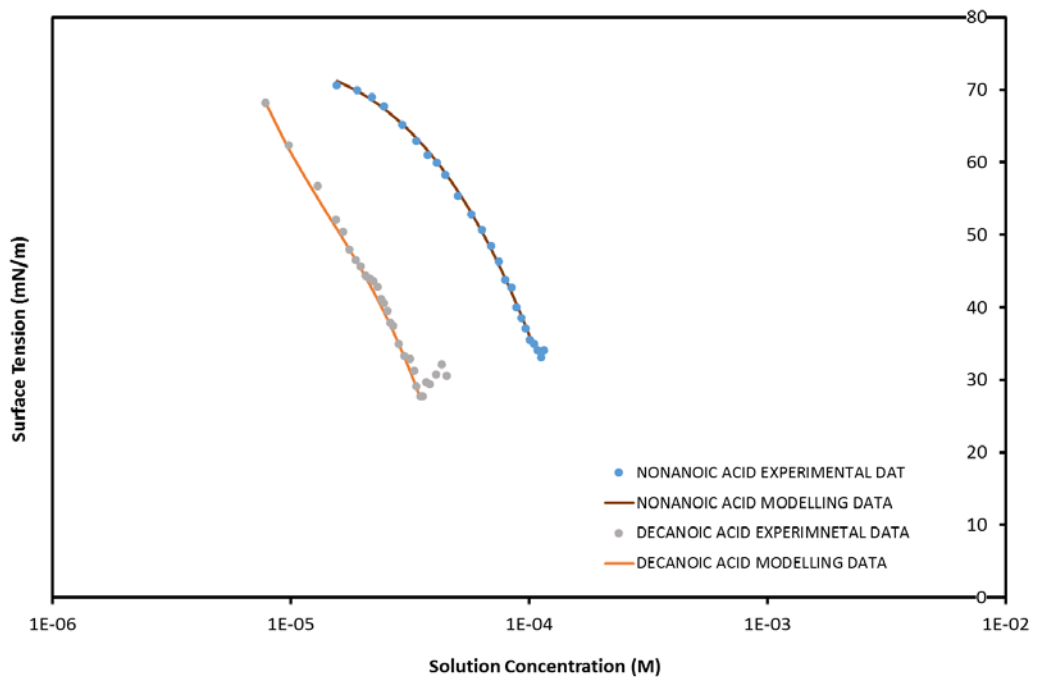
### 5.5.1 PHYSICAL PROPERTIES

Physical properties such as *CMC*,  $pK_a$  and surface tension are almost consistent with the literature.

- Critical Micelle Concentration data for nonanoic acid are higher than decanoic acid in both experimental conditions which is corresponding to the literature. As mentioned in the literature review, shorter carboxylic acid reaches *CMC* value at higher concentration; Interestingly, *CMC* data were observed to decrease by raising carboxylic chain in both experimental conditions as shown in Figure 5-7 and Figure 5-8;



**Figure 5-7. Experimental and modelling surface tension data for Decanoic acid and Nonanoic acid at constant  $\text{Na}^+$  condition**



**Figure 5-8. Experimental and modelling surface tension data for decanoic acid and nonanoic acid at Acid only condition**

- It is obvious in above graphs that surface tension data of decanoic acid are lower than nonanoic acid. Comparing these data for both acids shows values



of surface tension decreases with hydrocarbon length rise. They also suggest that intermolecular interactions decreases as acid carbon number increases.

- As can be seen from the above table and graphs,  $pK_a$  increases by increasing chain length of the fatty acid since intermolecular interactions become less. Data from several sources have identified the increased  $pK_a$  is associated with hydrocarbon chain length.

## 5.5.2 ADSORPTION PARAMETERS

The most interesting finding of this research was adsorption parameters at the interface. The obtained values can be used to reveal the nature of the adsorption.

### 5.5.2.1 Neutralized versus ionized species

First, the physical meaning of  $K_A$  and  $K_{AH}$  need to be explained. Equations [26] and [27] can be rewritten as:

$$\Gamma_A = K_A C_A \Gamma_v \quad [57]$$

$$\Gamma_{AH} = K_{AH} C_{AH} \Gamma_v \quad [58]$$

In the above equations, it can be seen that a higher  $K_A$  would mean higher adsorption at the same bulk concentration. Consequently, the values of  $K_A$  and  $K_{AH}$  indicated the adsorption potential of a molecule onto the interface. The relationship between  $K$  values in Table 5-4 can be used to quantify the adsorption ability of the species.

It can be seen that  $K_{AH} \gg K_A$  for both  $C_{10}$  and  $C_9$ . This indicates that  $AH$  adsorption is stronger than  $A$ . The underlying reason is the hydrophilicity of  $-COO^-$  is stronger than  $COOH$ , due to electrostatic binding with water  $H$ -bonds.

### 5.5.2.2 Ionized states of $C_{10}$ versus $C_9$

The value of  $K_A$  decreases almost 8 times from  $C_{10}$  to  $C_9$ , ( $261 M^{-1}$  to  $30 M^{-1}$ ). This means  $C_{10}$  has higher adsorption capacity, which is consistent with increasing hydrophobicity. This can be further confirmed by molecular simulation.

### 5.5.2.3 Neutralized states of $C_{10}$ versus $C_9$

Values of  $K_{AH}$  for decanoic acid and nonanoic acid (Table 5-4) are almost the same for two acids. In cases, the whole molecules are hydrophobic (the head  $COOH$  is no longer charged). Certainly,  $C_9H_{21}$  has higher hydrophobicity than  $C_8H_{17}$ . However, the increased hydrophobicity is marginal for the molecules at the whole.

### 5.5.2.4 Total adsorption concentration

From above findings, it can be concluded that carboxylic length only has a significant influence on ionized state.<sup>42</sup> Considering adsorption potential is the net effect of the both hydrophobicity and hydrophilicity, this can be graphically demonstrated in Figure 5-9 and Figure 5-10. Here, the molecules are qualitatively divided by hydrophobic and hydrophilic parts. For ionized species, the hydrophilic part is very large, hence a marginal increment in hydrophobicity (from 9 to 10 carbons) has a significant effect on the net hydrophobicity/hydrophilicity. For neutralized species, the hydrophilicity is less important, the whole molecule is dominated by the hydrophobicity. Therefore, a marginal increment in hydrophobicity (from 9 to 10 carbons) has little impact on the net effect. One can symbolically indicate the hydrophobicity/ hydrophilicity as red/green region in the Figure 5-9 and Figure 5-10. The adsorption potential is then net effect, that hydrophobicity subtracting hydrophilicity.

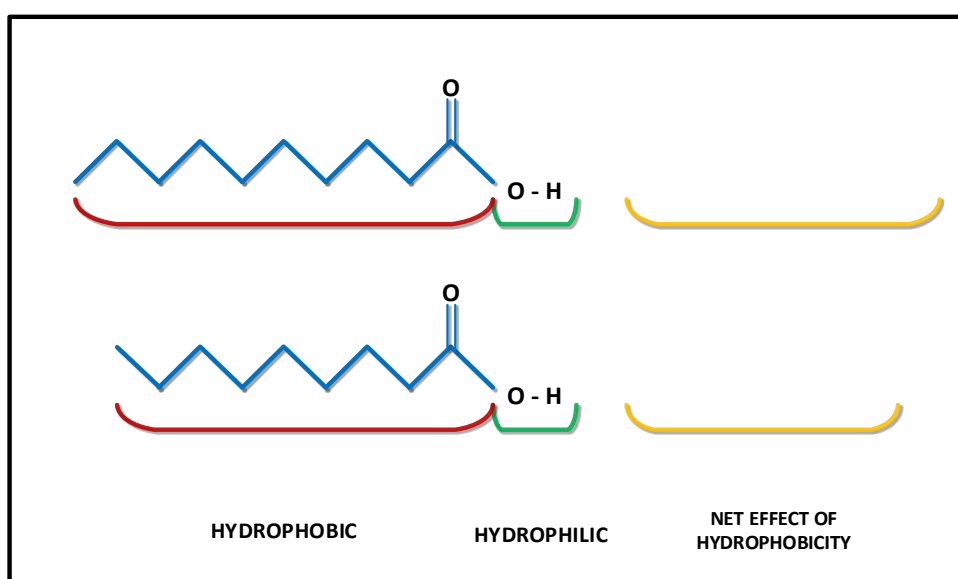


Figure 5-9. Effects of chain length on hydrophobicity of neutralized acids

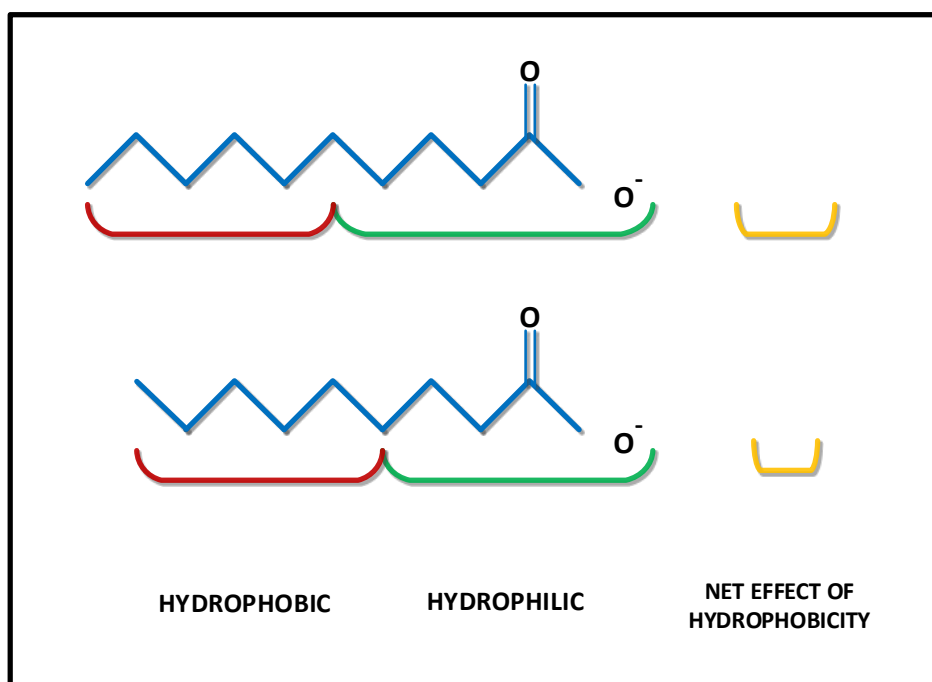


Figure 5-10. Effects of chain length on hydrophobicity of ionized acids

## 5.6 SUMMARY

The proposed model for decanoic acid was successfully applied to nonanoic acid. The model was further investigated by fitting to experimental results. Interesting findings were observed by comparing adsorption and physical properties of two acids. Physical parameters such as *CMC* and  $pK_a$  match those observed in earlier studies. By decreasing acid chain length:

- Critical Micelle Concentration data increased;
- Acid dissociation constant decreased;

On the other hand, adsorption parameters obtained in this study show significant results on the effects of chain length on behaviour of fatty acids at air/water interface. By changing condition from longer surfactant to shorter one:

- Total adsorption concentration did not change much;
- Adsorption constant for neutralized acid did not change much;
- Adsorption constant for ionized species decreased by 8 times;

- Adsorption model was better fitting for shorter acid;

The above results can be explained systematically from hydrophobic and hydrophilic nature of the species.

## 6 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 SUMMARY

Surface active agents are not stable in any bulk solutions because of their dual affinity to polar and nonpolar species. These molecules tend to accumulate in interfaces to orient their hydrophobic nonpolar groups into nonpolar medium and their hydrophilic polar group into water based solutions. Therefore they affect interfacial properties even with a small concentration in the bulk. Study of adsorption and tension behaviour of ionic surfactants at the air–water interface plays a significant role in various industrial processes.<sup>51, 84</sup>

Adsorption models help to predict the detailed behaviour of these molecules at interfaces. However, most models applied to describe ionic surfactants adsorption at interfaces have been derived from adsorption isotherms which are originally used for non-ionic surfactants. Such equations cannot account for ionic surfactants with ionization reaction. Theoretical models that account for ionization, fall into the category of models based on adsorption isotherm of Gibbs which the surface excess of each ion equals to the sum of all excesses in the monolayer and electrical double layer.<sup>86, 100</sup>

In this study, new methodology was applied to measure surface tension of two carboxylic acids as anionic surfactants at two proposed conditions. Decanoic acid was first investigated at air/water interface. Then shorter nonanoic acid was studied to further confirm achieved data. Surface tension measurement was carried out using pendant bubble and Wilhelmy plate methods for acid-only condition and constant  $Na^+$  states respectively. Using the same method for both conditions was not possible as acid solubility depression was an obstacle to get accurate results. Therefore, Wilhelmy plate was used for high concentration solutions with constant concentration of sodium hydroxide. Surface tension values were then calculated using a MATLAB code by analysing bubble shapes. Finally, surface tension data were applied to quantify adsorption characteristics of both acids. The  $pH$  data were also recorded to obtain dissociation constant.

In this work, a new model was introduced to predict adsorption behaviour of ionic surfactants. Proposed model was applied to both acids. Experimental data were then applied to the theoretical model introduced in this work. Interestingly, the framework created to model adsorption behaviour of decanoic acid was successfully applied to nonanoic acid. The results from this investigation show that the theoretical framework was well applicable to the experimental data. However, shorter acid showed better fittings. From analysing adsorption parameters, neutralized acid showed more surface activity than ionized acid.

Overall, interfacial and adsorption parameters of both acids are compared. Comparing the results of these two surfactants, introduced new findings on the effect of hydrocarbon chain length on physical and adsorption parameters of surfactants at air/water interface.

The  $CMC$ ,  $pK_a$  and other physical parameters support previous research in this area. Higher  $CMC$  and lower  $pK_a$  were observed for acid with shorter chain length.

The most surprising aspect of the study is in the adsorption data. Raising chain length had significant effect on ionized acid as  $K_A$  for decanoic acid was seen to be eight times higher than nonanoic acid. However,  $K_{AH}$  did not change much. Which indicates carbon number only affects ionized state.

## 6.2 RECOMMENDATIONS

The present study was designed to introduce new methodology and theoretical framework to determine adsorption behaviour of fatty acids at air/water interface. However, most interesting results were achieved by comparing the data of two different carboxylic acids and yet, several questions remained unanswered at present.

This work can be collaborated with a surface potential study to give more insights into the effects of chain length on interfacial behaviour of surfactants at air/water interface.

Shorter acids are suggested to be tested in future research studies on this subject to further investigate the impacts of chain length on adsorption parameters. On the other hand, longer acids are difficult to dissolve in water and this is an important issue for future research. Thus, further investigations on shorter carboxylic acids such as octanoic acid can be helpful to confirm the findings of this work.

As displayed in Table 5-4, considering one acid data, neutralized acid is packed more than ionized acid. Also comparing both acids results, it can be seen that ionized acid is packed more in the interface in case of longer chain length. To further investigate these effects, molecular simulation is suggested to be done on carboxylic acids of different hydrocarbon length to confirm the findings.

As discussed before, some dynamic measurements were done on decanoic acid. However, these results were not very encouraging. More dynamic experiment on different fatty acids are required in future work to establish dynamic effects.

Finally, as seen in adsorption graphs for constant  $Na^+$  condition, fitting is not desirable. To be able to achieve better fitting results, more complicated model is required. Extended framework should consider  $\Gamma_{Na}$  as a variable term which leads to no simplification and therefore more challenging future work.

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## 7 POSSIBLE INDUSTRIAL APPLICATIONS OF THE WORK

As reported in the history, the first surfactant produced and used by human was soap which was made by Sumerians 2500 B.C and was used for washing their woollen clothing. It is also evidenced that Sumerians used their soap for medicinal application. On the other hand, the Gauls and Germans have applied soap for beauty and cosmetics purposes from 23 to 70 AD.<sup>101</sup>

Surfactants are now widely used in different industries. For instance, surfactants types which are main materials for detergents, personal care and household products, consist the majority of the usage of surfactants produced. As explained in chapter 2 of this study, surfactants section, these chemicals tend to accumulate at the interfaces. Therefore, they alter interfacial characteristics. Some of these influences include emulsification, cleaning, wetting, lubricity, and control of foam and static electricity.<sup>102</sup>

Areas of surfactants applications can be divided into consumer products category and industrial application. Industrial applications cover a wide range of utilizations such as pharmaceuticals, foods, agriculture, textiles and fibres, pest control, paint, plastic industry, chemical industry, metal processing, mining and floatation and adhesives. In industrial manufacturing and production, surfactants are required for cleaning processes of the surfaces such as degreasing and defatting. Since surfactants are more chemically stable than alkalis, oxidising agents and acids, they are more favoured to be used in cleaning purposes.<sup>101</sup>

To fulfil the market demand for surfactants, study of their adsorption behaviour can help improve the synthesis method and production optimization.



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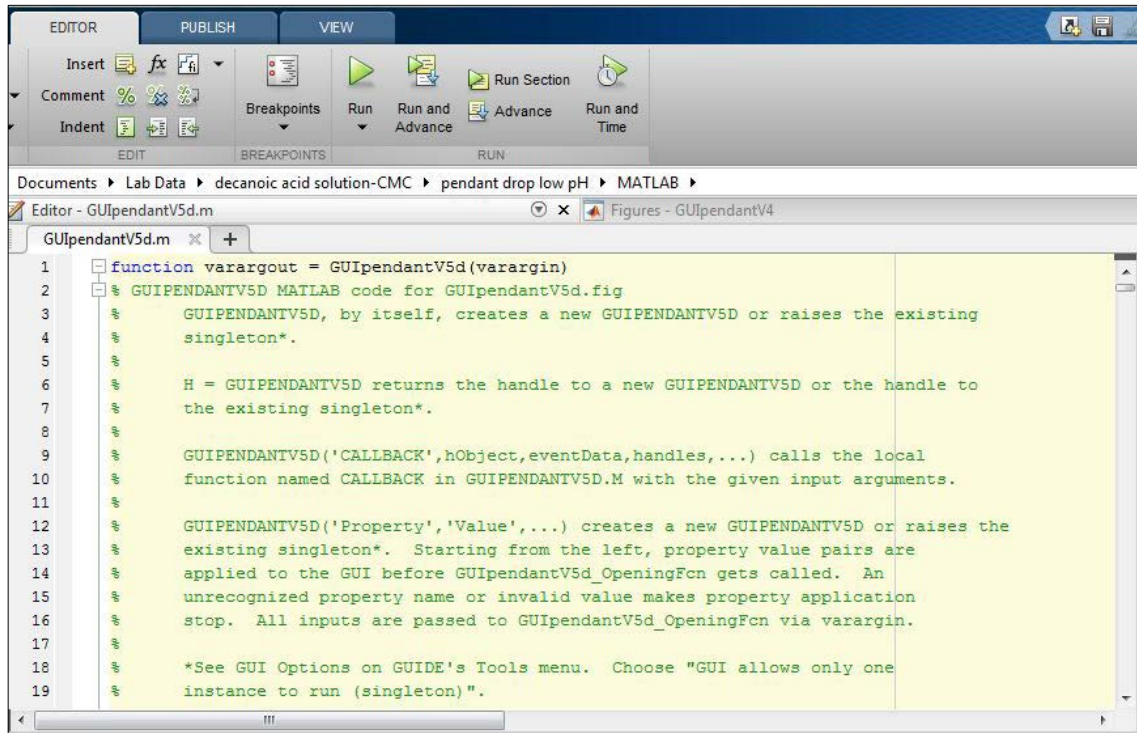
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## 9 APPENDIX

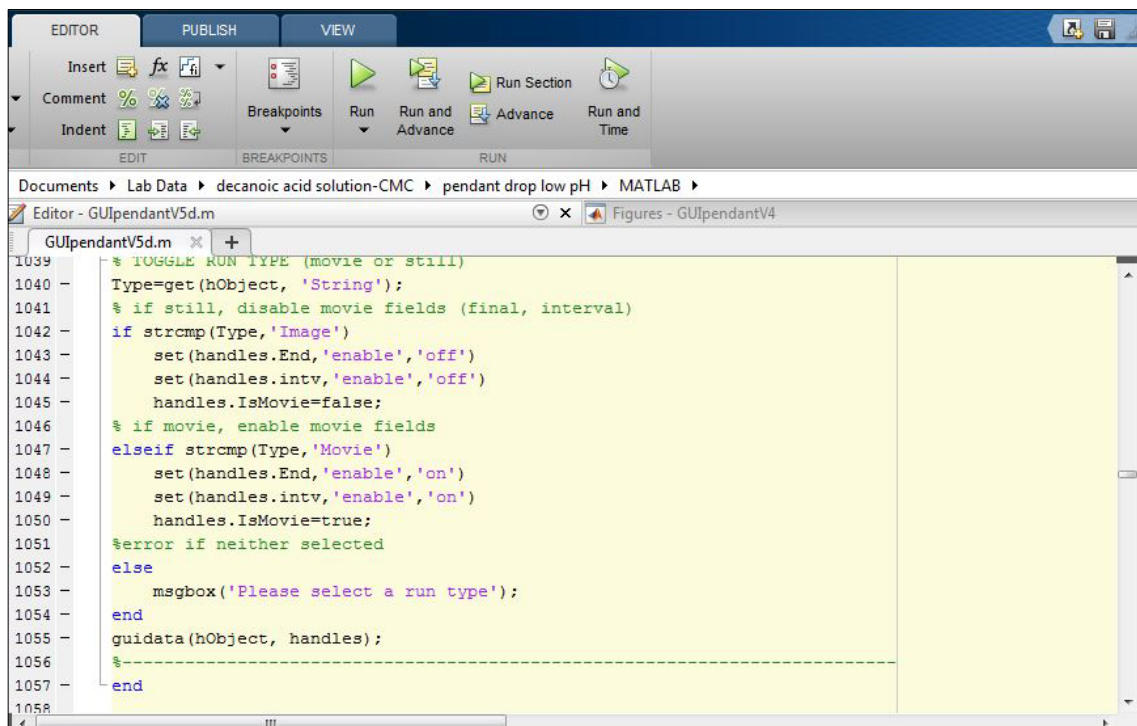
MATLAB Code:



```

1 function varargout = GUIpendantV5d(varargin)
2 % GUIPENDANTV5D MATLAB code for GUIpendantV5d.fig
3 % GUIPENDANTV5D, by itself, creates a new GUIPENDANTV5D or raises the existing
4 % singleton*.
5 %
6 % H = GUIPENDANTV5D returns the handle to a new GUIPENDANTV5D or the handle to
7 % the existing singleton*.
8 %
9 % GUIPENDANTV5D('CALLBACK',hObject,eventData,handles,...) calls the local
10 % function named CALLBACK in GUIPENDANTV5D.M with the given input arguments.
11 %
12 % GUIPENDANTV5D('Property','Value',...) creates a new GUIPENDANTV5D or raises the
13 % existing singleton*. Starting from the left, property value pairs are
14 % applied to the GUI before GUIpendantV5d_OpeningFcn gets called. An
15 % unrecognized property name or invalid value makes property application
16 % stop. All inputs are passed to GUIpendantV5d_OpeningFcn via varargin.
17 %
18 % *See GUI Options on GUIDE's Tools menu. Choose "GUI allows only one
19 % instance to run (singleton)".

```



```

1039 % TOGGLE RUN TYPE (movie or still)
1040 Type=get(hObject, 'String');
1041 % if still, disable movie fields (final, interval)
1042 if strcmp(Type, 'Image')
1043     set(handles.End, 'enable', 'off')
1044     set(handles.intv, 'enable', 'off')
1045     handles.IsMovie=false;
1046 % if movie, enable movie fields
1047 elseif strcmp(Type, 'Movie')
1048     set(handles.End, 'enable', 'on')
1049     set(handles.intv, 'enable', 'on')
1050     handles.IsMovie=true;
1051 %error if neither selected
1052 else
1053     msgbox('Please select a run type');
1054 end
1055 guidata(hObject, handles);
1056 %-----
1057 end
1058

```

```

EDITOR      PUBLISH  VIEW
Insert      fx      A
Comment     %      %
Indent     [ ]     [ ]
Breakpoints Run Run and Advance Run and Time
EDIT        BREAKPOINTS  RUN

Documents  Lab Data  ▶ decanoic acid solution-CMC  ▶ pendant drop low pH  ▶ MATLAB  ▶
Editor - GUIpendantV5d.m
GUIpendantV5d.m  x
  1064  % IUGHLK RUN TYPE (movie or still)
  1065  -----
  1066  end
  1067
  1068  %% DropAnalysisNA
  1069  % This function calculates the interfacial tension using the ADSA-P method.
  1070  % The program uses Canny Edge Detection to determine the profile of the
  1071  % droplet. Numerical integration of the Young Laplace equations provides the
  1072  % theoretical curves showing the meridian profile.
  1073  %
  1074  % According to Boucher et al. (1980), the Young-Laplace equations for the
  1075  % pendant drop configuration:
  1076  %     $$ LaTeX Equations here $$
  1077  %
  1078  % Multivariate optimisation (a, x0, r0) determine the best fit parameters
  1079  % for the curve, from which the interfacial tension is calculated.
  1080  %
  1081  % Fitting is conducted N_ times, using 50 random points per run
  1082  % (uniform distribution). The final answer is the statistical average and
  1083  % 95% confidence intervals generated during the run.
  1084  %
  1085  % This code is called from the Pendant Drop GUI "analysis" callback.
  1086  %
  1087  % MODIFIED FOR PENDANT DROP WITH NO APEX
  1088  %
  1089  %% Function
  1090  function [GamBest, GamAve, Emin, GamSD, ci95, ResultsF, XBest, YBest, abbrev]=DropAnalysisNA(folder,Grey, PhysProps, Tag, ImCase,PrintYN
  1091
  
```

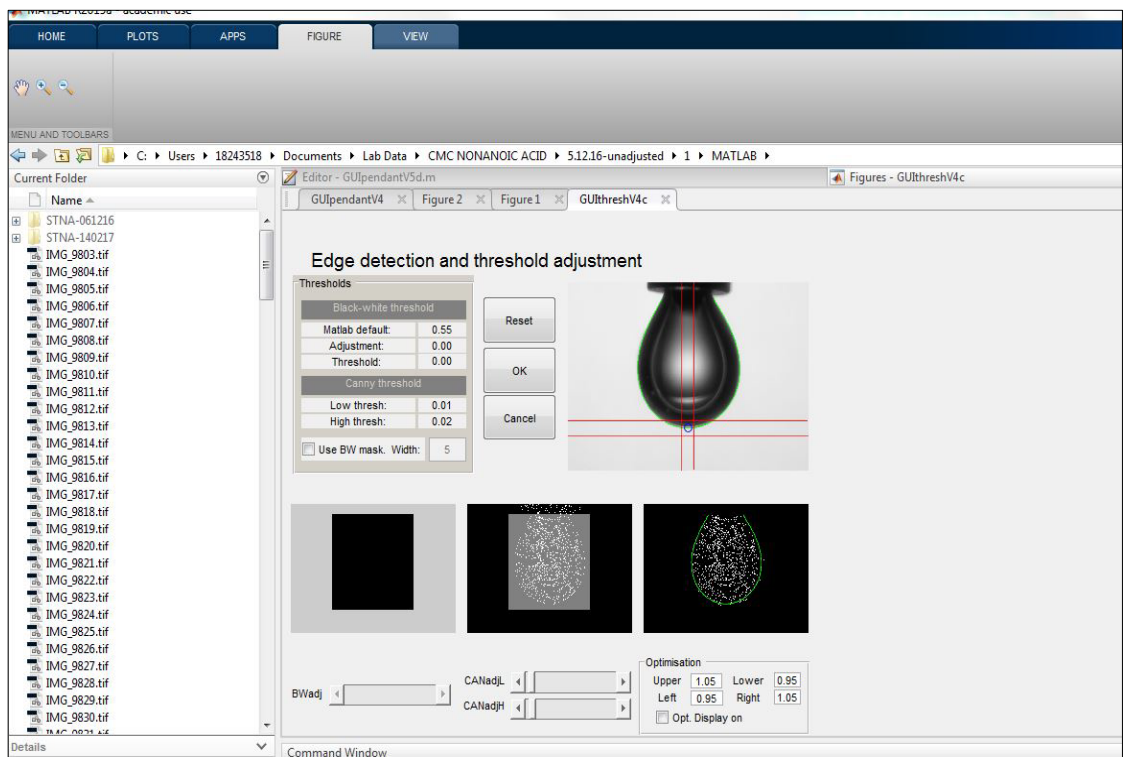
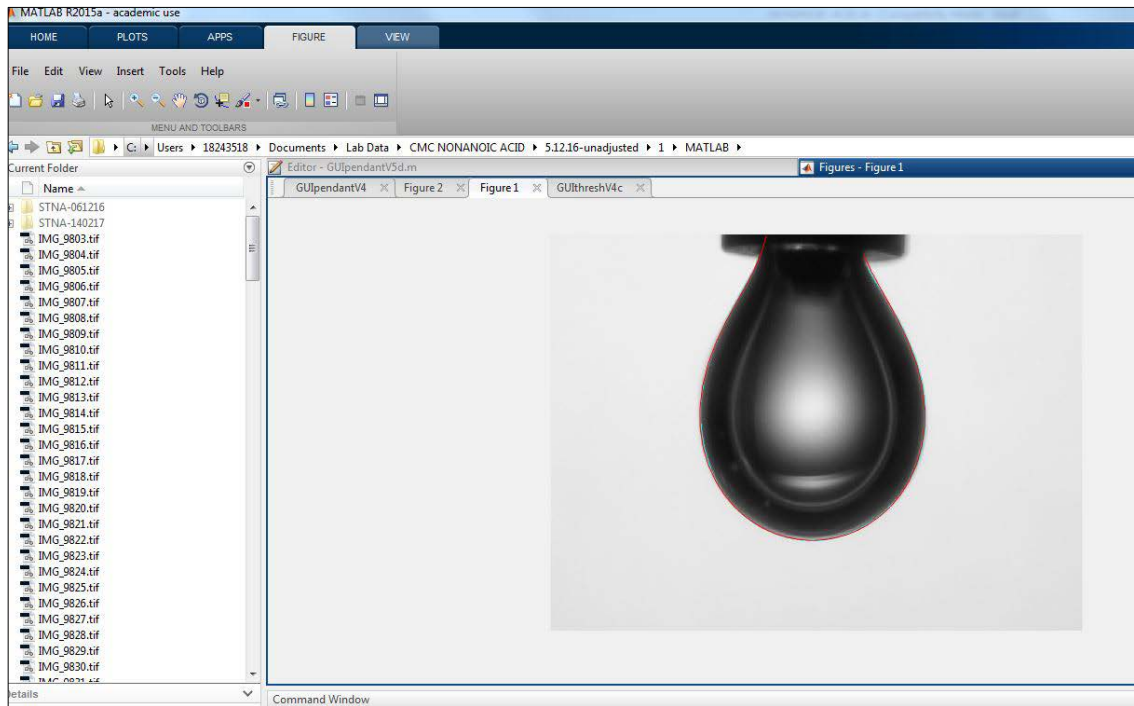
MATLAB Figures:

The screenshot shows the MATLAB GUI for 'Edge detection and threshold adjustment'. The main window displays a pendant drop image with a red vertical line and a blue horizontal line. Below the image are three preview windows showing the original image, the edge detection result, and the thresholded result. The 'Thresholds' section includes controls for 'Black-white threshold' (Matlab default: 0.55, Adjustment: 0.00, Threshold: 0.00) and 'Canny threshold' (Low thresh: 0.01, High thresh: 0.02). There are also 'Reset', 'OK', and 'Cancel' buttons. The 'Optimisation' section shows 'Upper: 1.05, Lower: 0.95, Left: 0.95, Right: 1.05' and an 'Opt. Display on' checkbox. The 'Command Window' at the bottom shows the following text:

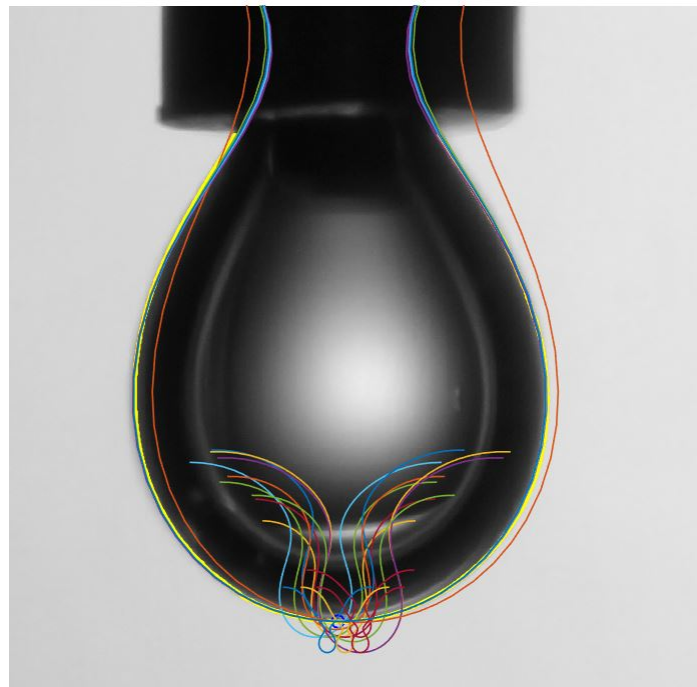
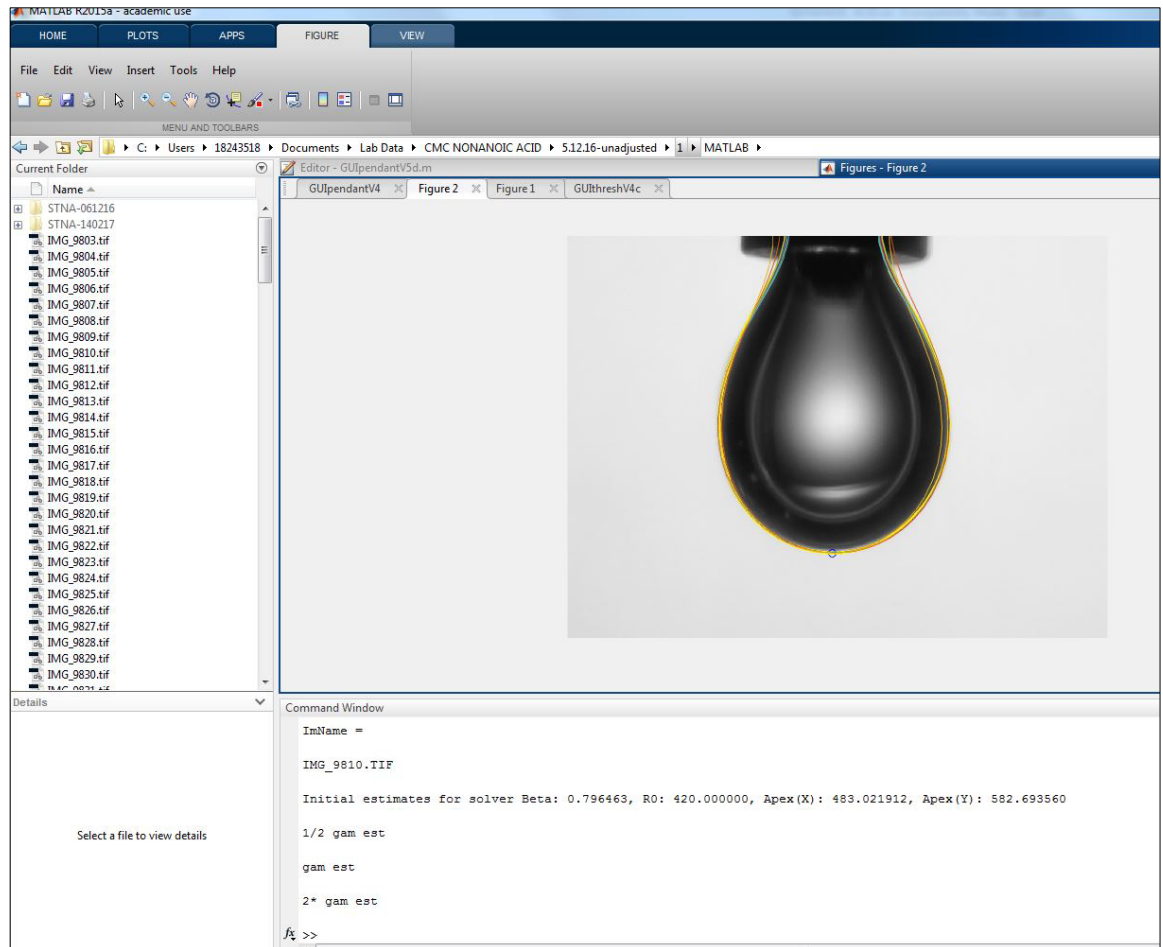
```

Command Window
BW adj: 1.00; Canny Low: 0.01, Canny High: 0.03BW adj: 0.00; Canny Low: 0.01, Canny High: 0.03
OpDisp =
OFF
Threshold data saved. Returning to main GUI.
Please identify the general region of interest, suitable for all frames
Pendant drop.
Please select the fitting area - Whole bubble with Apex(click and drag box):\n
Apex (left) not found - probably only one side has been found.

Using minimum point.
BW adj: 1.00; Canny Low: 0.01, Canny High: 0.02BW adj: 0.00; Canny Low: 0.01, Canny High: 0.02>>
  
```







5/15/2017

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