Faculty of Graduate Studies

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Polymer/Surfactant Mixture Activity at the Cyclohexane/Water Interface and the Removal of Surfactant by Graphene Oxide Nanoparticles

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Committee Decision

We, the undersigned, approve the Master's Thesis of *Sohaib Fayeez AbuGaith.*

Thesis Title: **Polymer/Surfactant Mixture Activity at the Cyclohexane/Water Interface and the Removal of Surfactant by Graphene Oxide Nanoparticles**

This thesis successfully defended on 15/May/2024 and approved by:

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Dedication

*My happiness can't be expressed, thanks for Allah for my achievement, I would like to dedicate my thesis to my parents who have been my source of inspiration, guide and give me the strength when I thought to give up, Thanks to my **father and mother** to their endless love and support they have given me and are still doing.*

*I would like to dedicate this work to my supervisor **Dr. Sami Makharza**, and Co-Supervisor **Dr. Ahmed Ayyad**.*

Acknowledgment

*I would like to extend my gratitude and recognition to my supervisor **Sami Makharza** and Co-Supervisor **Dr. Ahmed Ayyad** for all of their support and advice throughout this research.*

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List of Abbreviations

BAC Benzyldimethylhexadecylammonium Chloride

SDBS Sodium dodecyl benzene Sulfonate

SDS sodium dodecyl sulfate

NaPSS Sodium polystyrene sulfonate

PAACl Polyallylamine hydrochloride

PVA Polyvinyl Alcohol

CMC Critical micelles concentration

IFT Interfacial tension

ST Surface tension

GO Graphene Oxide

CNTs Carbon Nano-tubes

SWCNTs Single walled carbon Nano-tubes

MWCNTs Multi walled carbon Nano-tubes

C_e Concentration at equilibrium (mM)

C_i Initial concentration (mM)

%R Percentage of removal

%T Percentage of transmission

IC dye Indigo Carmine dye

FT-IR Fourier-transform infrared spectroscopy

UV-vis Ultra violet-visible spectroscopy

Abstract:

This thesis investigates measurements of interfacial tension of polymer/surfactant mixtures at oil-water interface and removal of (BAC, cationic surfactant) from water using graphene oxide nanoparticles.

In this thesis, we have studied the adsorption of Sodium polystyrene sulfonate, (NaPSS, anionic polyelectrolyte)/Benzyldimethylhexadecylammonium Chloride (BAC, cationic surfactant), Polyallylamine hydrochloride (PAACl, cationic polyelectrolyte)/sodium dodecyl benzene sulfonate (SDBS, anionic surfactant) and Polyvinyl alcohol (PVA, neutral water soluble polymer)/sodium dodecyl benzene sulfonate (SDBS) at the Cyclohexane-water interface. Individual polyelectrolytes NaPSS and PAACl are interfacial inactive. Polyvinyl Alcohol shows interfacial activity comparable to surface active agents due to its H-bonding forming capacity. For the system SDBS/PAACl, a hump in the interfacial tension was observed with maxima in the interfacial tension. This is explained by changes of the amount of different polyelectrolyte/surfactant complex structures at the interface and their competition with complexes in the bulk. No hump nor maxima in the interfacial tension was observed for the system BAC/NaPSS but surprisingly an increase in the interfacial tension was observed. This increase is due to insufficient BAC molecules to neutralize the charges at the repeating units of NaPSS. To the best of our knowledge the finding here for the oppositely charge polymer/surfactant systems studied at the cyclohexane interface are reported for the first time.

Graphene oxide nanoparticles were prepared and used to remove cationic surfactant BAC, graphene oxide gives high efficiency in the removal of cationic surfactant from water, where the unremoved amount of BAC surfactant after adsorption process was determined by

spectrophotometric study after complexation with oppositely charged synthetic dye (Indigo carmine).

Chapter One:

Introduction

The introduction of this thesis has been divided into two parts. The first one is an introduction to surface and colloidal science, the second part is an introduction to nanoscience.

1.1 Introduction to Surface and Colloidal Science

Surface science is a major division of physical chemistry that studies the characteristics, properties and behavior of molecules at or near the surface or interface.

1.1.1 Surface tension

It is defined as the work to increase the area of a surface isothermally and reversibly by unit amount area. Surface tension is a significant factor in many natural phenomena, such as capillary action, droplet shape, and the formation of capillary waves on liquid surfaces [1].

1.1.2 Interfacial Tension

Interfacial tension is an occurrence that, at the molecular scale an interface can form between liquids, solids, gases and combination of these states. interfacial tension is equally correctly described as a measure of how much energy is required to make a unit area of interface between two immiscible liquids, thus taking units of Joules per square meter – equivalent to the more commonly used Newton's per meter[2].

Attraction forces hold the molecules of a liquid together. The total force of attraction on any molecule present in the liquid's bulk averages zero, In the direction towards the bulk, the net force on a surface molecule is not zero, to increase surface area, the force must be

counteracted; the energy consumed by this process is known as surface energy[1]. Liquid-liquid interface and balance of forces on molecules of liquids are shown in *Figure 1.1*
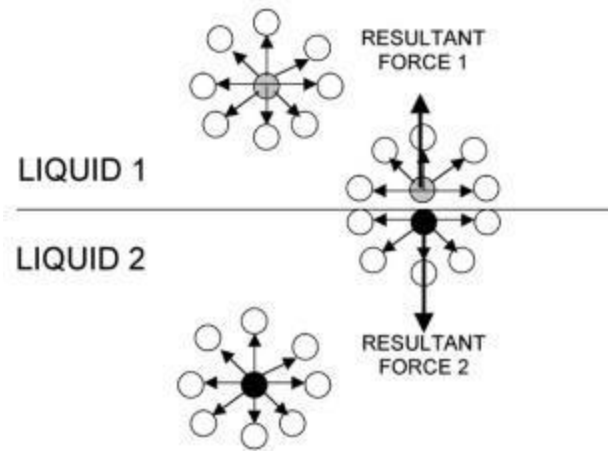
Figure 1.1: Liquide-liquid interface and balance of forces on molecules of liquids.

1.1.3 Surfactants

Surfactants (surface-active agents) are a group of chemicals that have a polar, water-soluble head group and a nonpolar hydrocarbon tail group that is insoluble in water[3], [4]. Therefore, surfactants are a combination of hydrophobic and hydrophilic properties in a molecule. When dissolved in water at low concentrations, surfactant molecules occur in the form of monomers as shown in *Figure 1.2 (A),* at higher concentrations The surfactant molecules stick together in micelles. As shown in *Figure 1.2 (B)* reducing free energy from the system. Threshold concentration at which this occurs is known as critical micelle concentration (CMC) [5].
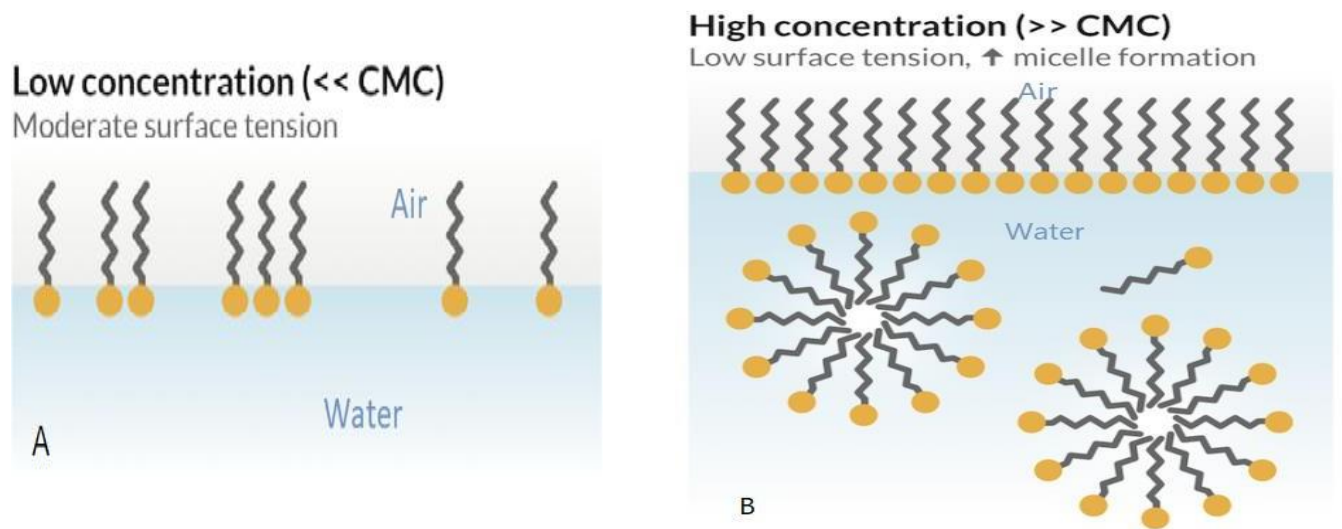
Figure 1.2: Schematic diagram of surfactant molecules in aqueous solvent at: (A) low
concentration of surfactant, (B) high concentration of surfactant formation of micelle

1.1.3.1 Types of Surfactants

Surfactants are usually classified as anionic, cationic, amphoteric, and nonionic, depending
on their head group charge [6]. The class of surfactant molecules describes its
physicochemical properties and applications.

1.1.3.1.1 Anionic Surfactants:

Surfactants that are oldest and most commonly used are anionic. High cleansing power and
good wetting properties of this group make the anionic surfactant the most used in detergents
or common soaps with general formula ($RCOO^-Na^+$), alkyl benzene sulphonates ($R_6H_4 SO_3^-Na^+$) and alkyl sulphates ($RSO_4^- Na^+$), The hydrophilic component is either carboxyl,
sulphate, sulphonate, or phosphate which is usually neutralized by an alkali metal cation.

4

Petrochemical products can be removed from polluted soil using anionic surfactants. In a study, anionic surfactants performed the best in removing diesel oil adsorbed on different soils[7].

1.1.3.1.2 Cationic Surfactants

These molecules have a hydrophobic hydrocarbon chain that is linked to a positively charged head-group, other alkyl groups, such as methyl or benzyl groups, serve as substitutes, most common type of theses surfactant is quaternary ammonium compounds [$RN(CH_3)_3^+ X^-$]. Due to their antibacterial activity against both Gram-negative and Gram-positive bacteria, long chain quaternary ammonium compounds are also utilized as disinfectants[8].

1.1.3.1.3 Nonionic surfactants

The superficial activity of non-ionic surfactants results from an equilibrium between the hydrophilic and hydrophobic structures contained in the surfactant molecule. The hydrophobic portion of non-ionic surfactants is usually a fatty acid , long-chain alkyl phenol derivative or linear alcohol, while The hydrophilic part is typically a chain of ethylene oxide that is of various lengths, nonionic surfactant is widely used wetting agents, emulsifiers and foam stabilization agents, they are also have been successfully used in various biotechnological processes to facilitate solubilization and increase drug carrier stability[9] . Most pesticide formulations incorporate nonionic surfactants[10].

1.1.3.1.4 Amphoteric Surfactants

The pH is a factor in the behavior of amphoteric surfactants, the charge of their molecules can be changed from net cationic to anionic from low to high pH , with zwitterion behavior at intermediate pH [11]. Sulfobetaines $(RN^+(CH_3)_2CH_2CH_2SO_3^-)$ or Botanies$(RN^+(CH_3)_2CH_2COO^-)$ are examples of synthetic surfactants while the long chain of amino acids $(RNH_2^+CH_2COOH^-)$ are examples of neutral zwitterion substances, their initial use was as a substitute for traditional fatty alkanolamides as foam boosters in dishwashing due to their favorable weight/effect ratio that offsets their high production cost**[4,** 12]**.**

1.1.4 Polyelectrolytes(PEs)

Polyelectrolyte is a macromolecular material with repeating units that dissociates into a highly charged polymeric molecule when placed in a polar solvent to produce a polymeric chain with negative (polyanions) of positive (polycations) charge [13] ,so polycations and polyanions at an almost neutral pH are known as polyelectrolytes[14]. the electrical neutrality in the solution is maintained by counter ions that have oppositely charged charges, which compensate for the positive or negative charges on the monomer units. Polyelectrolytes can be classified into different types, including origin, composition, molecular architecture, and electrochemistry, based on origin, they can be divided as synthetic and inorganic i.e. polyacrylic and polymethacrylic acids and their salts, neutral(biological) polyelectrolytes just like DNA.

Polyelectrolytes can be used in a wide variety of applications because of their unique properties, which is derived from the ion group along their polymer chain. i.e. water treatment [15] , drug delivery [16] , food processing [17], and can be used in sensors[18].

1.1.4.1 Complexes of Polyelectrolyte(PECs)

PEs are able to form complexes that contain one or more oppositely charged ions. The attraction between oppositely charged species can result in the formation of polyelectrolyte complexes, PE complexation is primarily observed between species that have opposite charges (i.e., PE–PE, PE–drug, PE–nucleic-acid, and PE–surfactant) [19] .

The first type is polyelectrolyte surfactant complex (like cationic polyelectrolyte attracted with anionic surfactant and vice versa)

The second type formed when two oppositely charged polyelectrolyte (anionic polyelectrolyte with cationic polyelectrolyte).

1.1.4.1.1 Oppositely Charged Polyelectrolyte Complexes(PECs):

The formation of polyelectrolyte complexes can be triggered by the attraction between oppositely charged groups when polyelectrolytes are mixed in water, these polymeric interactions between chains resulted in the formation of nonpermanent networks without the use of chemical cross-linkers[20].

The stability and formation of polyelectrolyte complexes depends on many factors such as the degree of polymerization of each PEs, the concentration of PEs, charge distribution on each PEs chain, as well as the temperature and the PH of reaction medium [21], [22]

1.1.4.1.2 Structural Model of PECs

Depending on the degree of polymerization , charge ratio and structural priorities of both polyelectrolyte , the model structural of polyelectrolyte can be classified into two types ; nonstoichiometric water soluble or stoichiometric water insoluble PECs[23].
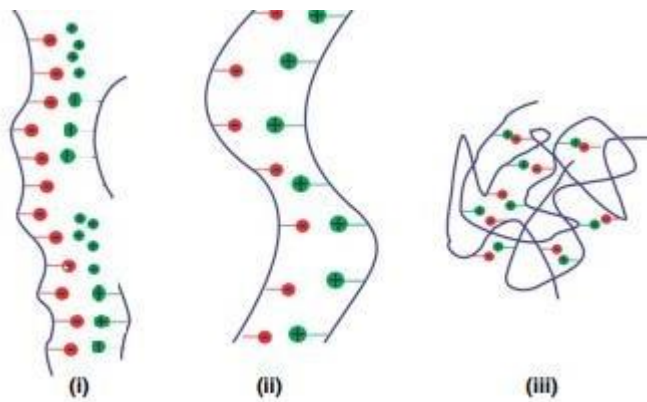
Figure 1.3: (i): Nonstoichiometric complex with ratio of functional group of >1 or <1 , (ii): Stoichiometric complexes with equal ratio of oppositely charged functional group.(iii)Stoichiometric complex with less ordered chain.

1.1.4.1.3 Non-Stoichiometric Water Soluble PECs

This type of PECs usually formed when large molar mass of ionic groups in PEs mixed with another low molar mass of oppositely charged groups of PEs in nonstoichiometric ratio.

1.1.4.1.4 Stoichiometric Water Insoluble PECs

Usually most synthetic PEs behave like stoichiometric PECs, these types of PECs formed when (1:1) ratio of strong ionic group of PEs are mixed , as well as these type of complex based on characteristics of ionic groups in PEs, molecular weights , and external condition of the reaction [24].

1.1.4.2 Polyelectrolyte surfactant complexes(PESCs)

The interaction between polyelectrolyte and surfactant is quite strong because of both electrostatic interaction between charged parts of complex, and hydrophobic interaction between alkyl chains of polyelectrolyte and surfactant[25]as shown in *Figure1*.4
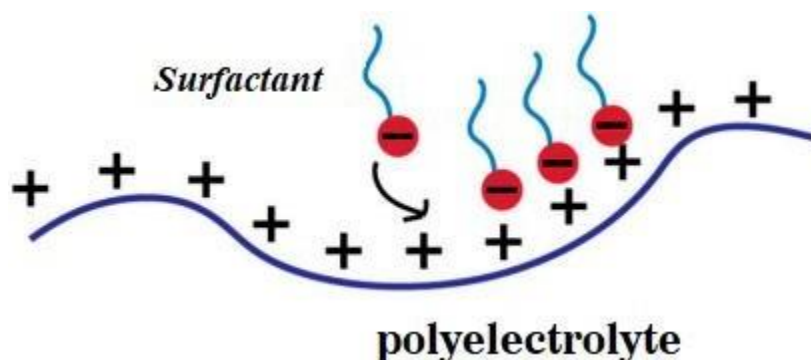
Figure 1.**4:** Electrostatic interaction between polyelectrolyte and surfactant below CMC of surfactant[26]**.**

This unique molecular structure of PESCs will define the unusual mechanical, electrical and biological properties, which could be useful in medical, cosmetic, coating, and other technological application[27]**.**

1.1.5 Measurements of Surface and Interfacial Tension:

The measurements of surface and interfacial tension of a liquid can be done by several techniques, in this part three main techniques will be discussed briefly:

1.1.5.1 Du Noüy Ring Method

As shown in *figure 1.5*, this technique is based on the interaction of platinum-iridium ring with the surface of the liquid. In this method the ring is immersed below the surface of the liquid by mechanical movement of the stage where counter glass was placed, after submerging the ring, the stage is lowered slowly until the ring reached the surface of liquid, the maximum force which needed to separate the platinum-iridium ring from the liquid is proportional to surface or interfacial tension as shown in *equation (1-1)*[28].

$$\gamma = \frac{F}{L \cos \emptyset} \qquad\qquad (1\text{-}1)$$

Where; γ is the surface tension, $\emptyset$ the contact angel between platinum ring and the surface and L is the wetted length .

Some disadvantages of this method is the ring itself and its designed, it's difficult to keep the ring absolute parallel with the surface of the liquid, because its quit simple. One of these limitation of this method which experienced in this research is the inability to measure interfacial tension of solution at extremely low value near 5 Mn /m.
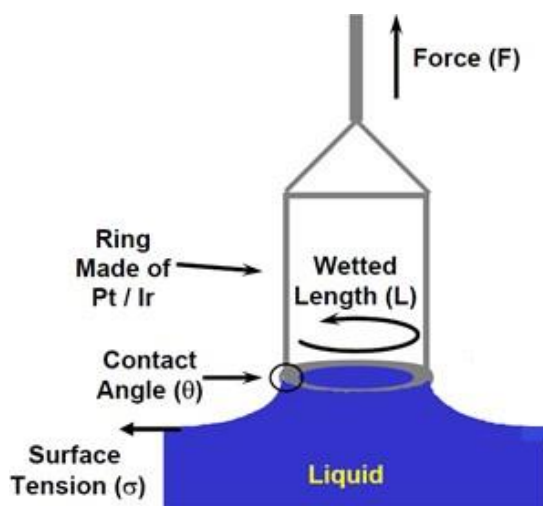
Figure 1.5: A sketch for Du Noüy ring method for measuring the surface or interfacial tension of liquid/air and liquid/liquid interface.

1.1.5.2 Wilhelmy Plate Method

The plate is flat piece of platinum or glass. The plate is simply touched to the relaxed equilibrium surface and the stage where the liquid counter placed gradually raised without need to stretched or perturbed the surface.

The meniscus is formed only on the perimeter of the plate, which causes downward pull of the plate. This method is quite similar to the ring method, but the plate is not in motion thus the inter surface in equilibrium state as shown in sketch on *Figure 6* [29], [30]
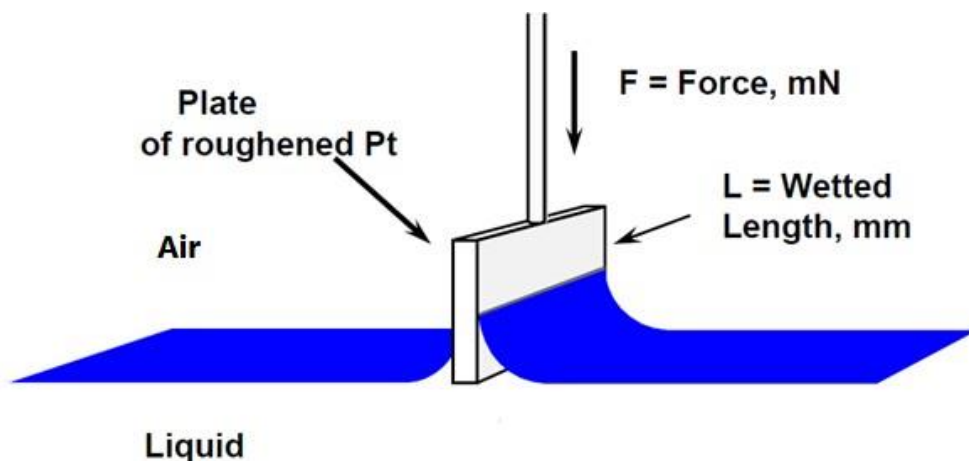
Figure 1.6: A schematic sketch for Wilhelmy plate method for measuring surface or interfacial tension.

1.1.5.3 Capillary rise method:

The capillary phenomenon is largely responsible for many natural processes and human activities, i.e., It is the capillarity that brings water to the upper layer of soils, capillary action also cause liquid to rise upward through the capillaries in the stems of the plants, this method was described in the following *Figure 1.7*:
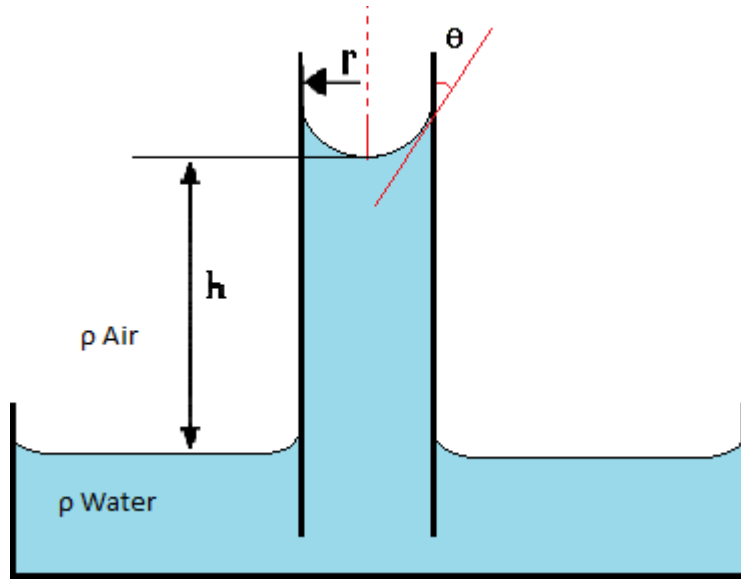
Figure 1.7: capillary tube immersed in water and the liquid goes up inside the tube.

In experimental part of this method, the capillary tube is cleaned and then established in the liquid or solution, In the case of aqueous solution or water, the cohesive forces between the molecules of liquid is less than the adhesive forces between the tube walls and liquid molecules[31], [32], so the liquid goes up in the capillary tube, surface tension of the liquid is related to the highest reached by the liquid according to *equation (1-2):*

$$\gamma = \frac{\rho g h r}{2 cos\emptyset} \qquad \qquad \textbf{(1- 2)}$$

Where γ is the surface tension, ρ is the density of the phase, **h** is the highest of the liquid from surface to the bottom of the meniscus inside the tube, and $\emptyset$ is the contact angle between meniscus and capillary tube.

1.2 Introduction to Nanoscience and Nanotechnology:

Nanoscience and nanotechnology are considered to be the most important research science in the 20th century. Therefore, nanoscience can be defined as science, technology, and engineering preforming at nanoscale usually (from 1 to 100nm) and sometimes it can also deal with objects higher than 100nm. *Figure (8)* shows a comparison between nanomaterials and other larger materials. Thus, wide range of novel application such as physics, chemistry, biology, engineering, and medicine can be created by this unique phenomenon.[33], [34]. Nanotechnology has a distinct feature that is greatly increased in the ratio of surface area to volume presented in numerous nanoscale materials leading to new development in surface-based science, Therefore, nanoscale materials can change the physico-chemical properties of bulk materials, such as color, strength, and thermal resistance and so on, due to their small size and well-organized structure [35].

So the nanoscale materials can be defined as a set of substances which have at least one dimension with length less than about 100 nm, numerous industries are currently employing nanoscale materials. For instance, carbon black particles make rubber tires resistant to wear [36], nanofibers are also wide range of application such as water filtration and drug delivery system [37].
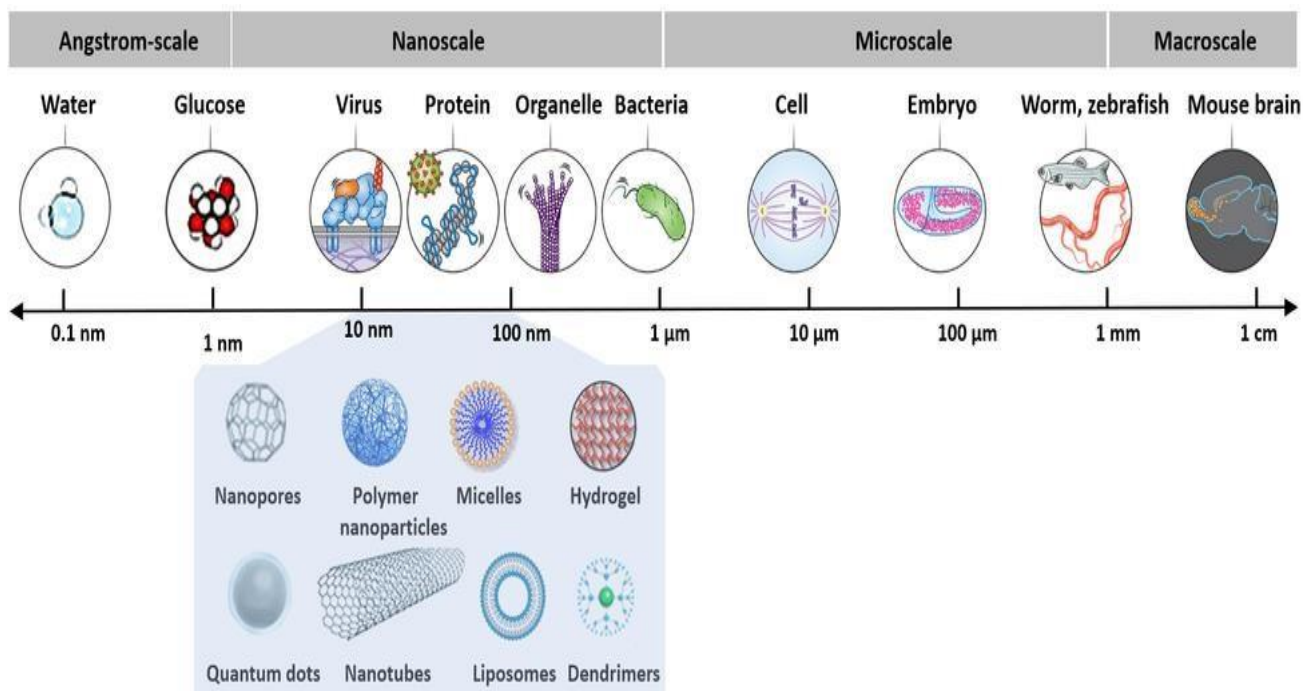
Figure1.8: Size comparison between nanoscale particles with other larger size materials [38]**.**

1.2.1 Carbon Based Nanomaterials

Carbon is the 6th element in the periodic table. It is identified by the letter "C". The element is distributed widely in the universe it is found in abundance in the sun, stars, atmosphere and most plats, free carbon can be found naturally in three allotropic forms: amorphous, graphite, and diamond. Graphite is a material that is considered one of the softest, while diamond is considered one of the hardest, Carbon atoms are arranged in a honeycomb lattice by graphite to form graphene layers, which were spaced 3.34 Å between sheets [39]**.**

Carbon is the main component of these nanomaterials, cavity spheres, ellipsoids and tubes are the most common forms of this category of nanomaterials, Carbon nanomaterials that are shaped like spherical and ellipsoidal are called fullerenes, while cylindrical shapes are called

carbon nanotubes, the reason why carbon based materials are often chosen is because of their superior physical properties and relatively low weight, carbon based nanomaterials can be found in many fields such as energy conservation[40], [41].

1.2.1.1 Graphene

Graphene is a sheet that is only one atom thick and is made of sp^2-hybrided carbon. Graphene's 2D honeycomb lattice structure is unique and allows for its thinness and strength to be unparalleled in the universe [42], this unique lattice structure endows it with many excellent physical and chemical properties as shown in *Figure 9*.
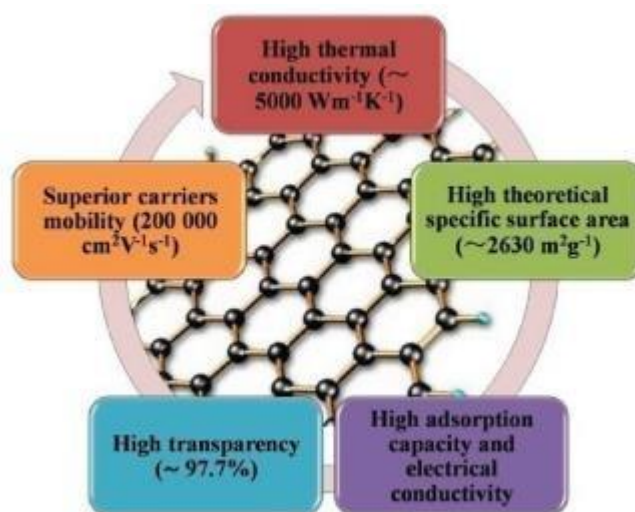
Figure 1.9 : Some superior properties of graphene [43].

These apparent advantages of pure graphene includes, high thermal conductivity (5000 W m^{-1} K^{-1}) [44], a very large theoretical specific surface area (2630 m^2 g^{-1})[45], and high adsorption capacity for many inorganic and organic molecules[46], [47].

Chemical functions or nanomaterials can be effectively anchored with the help of graphene. And therefore, graphene-based nanomaterials have high attentions as novel material in environmental applications. One of the most popular graphene-based material is graphene oxide (GO).

GO is an oxidized form of graphene with high density of oxygen functional groups (hydroxyl, carboxyl, carbonyl, and epoxy) on chemical lattice [48] as shown in *Figure 1.10*.
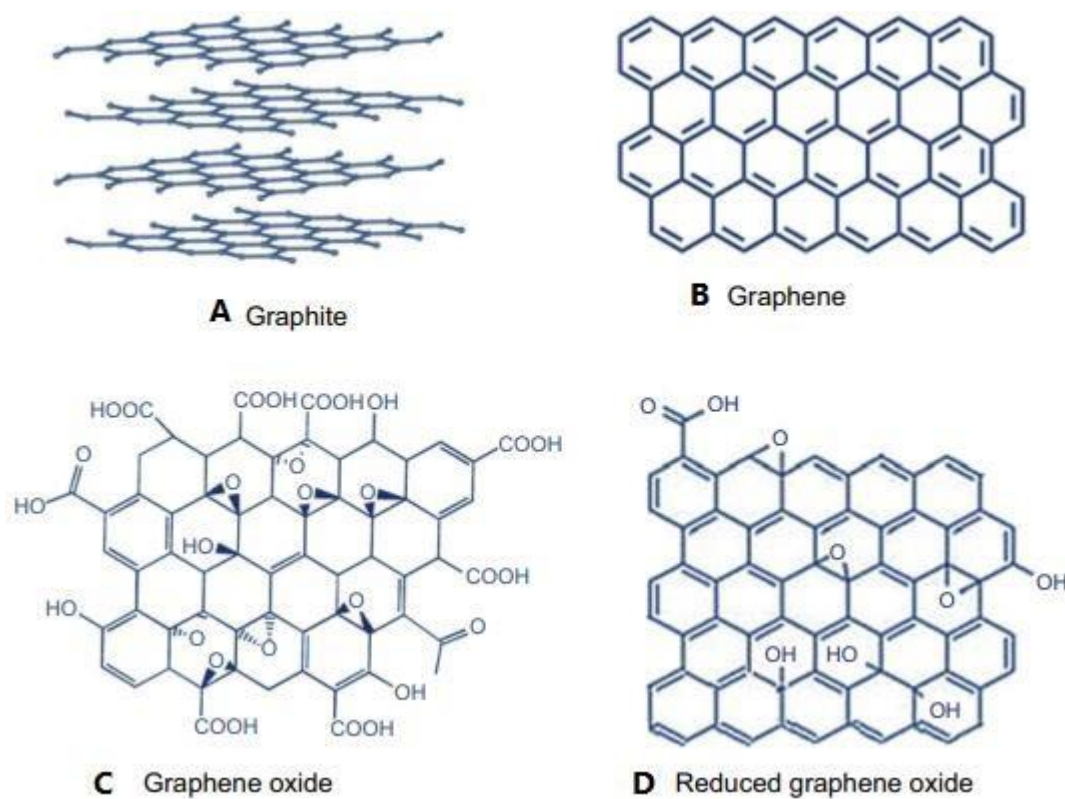
Figure 1.10: Structure of different carbon-based nanomaterials: A) Graphite B) Graphene

C) Graphene oxide D) Reduced graphene oxide [49].

1.2.1.2 Carbon Nanotube (CNTs)

Carbon nanotubes(CNTs) are cylindrical macromolecular tubes made of graphite sheets that are rollable and have a length of 1 to 100 μm and a diameter of 1 to 25 nm. The walls of these tubes are made up from hexagonal lattice of carbon atoms [50]. Due to their many potential applications, carbon nanotubes have gained attention from the scientific community as part of a new class of carbon-based nanomaterials. Two kinds of carbon nanotubes, single-walled carbon nanotubes (SWCNTs) and multiple-walled carbon nanotubes (MWCNTs) are classified.

A single-walled nanotube is formed when graphene sheet is rolled up, this graphene sheet is made up of benzene type hexagonal rings of carbon atoms [51]. The size of MWCNTs is larger and they are made of multiple single-walled tubes that are stacked inside each other. The term MWCNT refers to nanostructures that have an outer diameter less than 15 nm. Structures above that size are labeled as carbon nanofibers, which are not single molecules but strands of layered-graphite sheets[52]. Because carbon nanotubes have large length-to-diameter ratio of around 10^4 times, they can be considered almost one-dimensional structures [53].

The novel properties of these CNTs make them potentially useful in many applications somewhat similar to and sometimes superior to the properties of many materials, such as thermal conductivity that is comparable to that of diamonds, it has a tensile strength that is 100 times stronger than steel[54]. In addition, they have high electrical conductivity; as high as copper, and it is one of the novel electrical properties of CNTs [55].

1.2.1.3 Fullerenes:

Fullerenes consist of hollow carbon cage molecules that have sp^2 hybridization. The first discovery was made by Kroto et al. in 1985 [56]. The arrangement of carbon atoms in fullerenes is either ellipsoid, cylindrical, or spherical. For example Buckminsterfullerene is a closed spherical cage structural with hexagonal and pentagonal carbon rings with short code C_{60}. The formula C_n is commonly used to describe fullerenes, with n representing the number of carbon atoms present in the cage being an even number, many possible fullerenes structural derivative are found (*e.g.* C_{20}, C_{32}, C_{36}, C_{50}, and C_{60}) as shown in *Figure 1.11*:
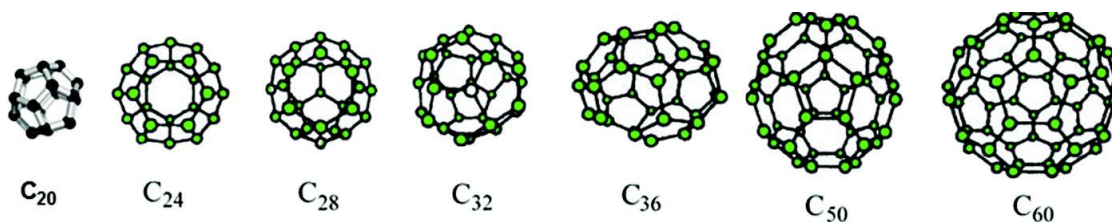
Figure 1.11: Different structural types of fullerenes [57].

Since the discovery of C60, the attention of researchers has become strictly devoted to study its unique properties. Investigation into the properties of fullerenes has led to potential use in medicine, including as light-activated antimicrobial agents, heat resistance, superconductivity, and biocompatibility [58], photovoltaic devices [59], biomedical devices [60]. The use of fullerenes can be constrained because of issues arises when mixing them with water-based solutions. Developing methods for the synthesis of water-soluble fullerene

derivatives on an industrial scale is attracting particular interest due to these potential issue. The water-soluble classes of fullerene derivatives that are most promising include carboxylated fullerene [58].

1.2.2 Adsorption

The process of adsorption involves a molecule or ion, called adsorbate, sticking at the interface of two phases (e.g. liquid-liquid, gas-liquid, gas-solid and liquid solid interface) [61].

As shown in *Figure 1.12* the substance which adsorbed another substance is called adsorbent and the adsorbate term refers to the substances that are retained on an adsorbent.
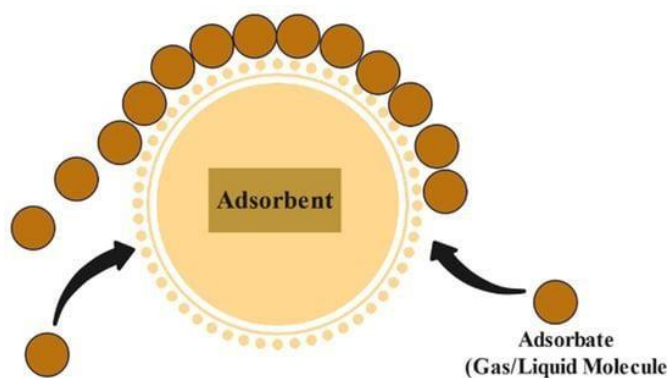
Figure 1.12: Adsorption process between adsorbate and adsorbent.

Two major types of adsorption are found depending on the force which attach adsorbate with the adsorbent, which are chemical adsorption and physical adsorption.

1.2.2.1 Chemical adsorption

Chemical adsorption also called chemisorption, the attraction between adsorbate and adsorbent result of generation of new chemical bond like (ionic or covalent) by chemical reaction. This attraction is usually very strong and irreversible. Chemisorption is more selective that occurs between certain adsorbate and adsorbent. Chemisorption is typically a single-layer process that only occurs when the adsorbent has direct contact with the surface [62].

1.2.2.2 Physical adsorption

Physisorption or physical adsorption, is a result of relatively weak attraction between adsorbate and adsorbent which is physical attraction resulting from Van der Waal's forces. Physical adsorption may take place and the particles diffuse along the surface of adsorbent not on specific location, being this kind of adsorption is weak, it is easily to reversed. Physical adsorption can occur at all surface if the temperature and pressure are favorable. If conditions are right, physical adsorption can result in molecules being adsorbed and creating multiple layers [63,62].

1.3 Research objectives

The main objectives of this thesis are:

I.   Study the activity of cationic, anionic and neutral polyelectrolyte at water-cyclohexane interfaces.

II. Study the activity of cationic polyelectrolyte with oppositely charged surfactant at water cyclohexane interfaces.

III.   Study the activity of anionic polyelectrolyte with oppositely charged surfactant at water cyclohexane interfaces.

IV.   Preparation and characterization of graphene oxide nanoparticles and study its efficiency in removal of cationic surfactant from aqueous solutions.

Chapter 2

Materials and Experimental

Techniques

2.1 Materials:

2.1.1 Surfactants

1. Sodium dodecylbenzenesulfonate (SDBS) is an anionic surfactant that has molecular formula (C18H29NaO3S). It is a white-to yellow powder, with molar mass of 348.48 g. mole $^{-1}$, as shown in *Figure 2.1.a.* It was obtained from Sigma Aldrich

2. . Benzyl dimethyl hexadecyl ammonium chloride(BAC). Is an inorganic cationic surfactant, white powder, with molar mass of 396.09 g. mole $^{-1}$ It is supplied from Sigma Aldrich. The structural formula of BAC is shown in *Figure 2.1.b.*
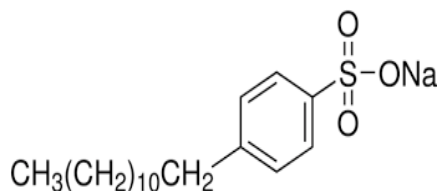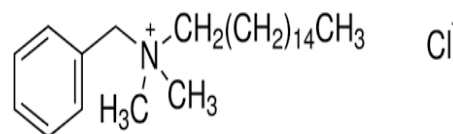
| Figure 2.1A | Figure 2.1 B |

Figure 2.1: *A)* the structural formula of Sodium dodecylbenzenesulfonate (SDBS).

B) structural formula of Benzyldimethylhexadecylammonium chloride (BAC).

2.1.2 Polyelectrolytes:

1. *Poly* (allylamine hydrochloride*) PAACl*, is white crystal cationic polyelectrolyte with average molecular weight of ~17,500 g. mole $^{-1.}$ It is supplied from Sigma Aldrich; the structural formula of PAACl is shown in *Figure 2.2.a*

2. *Poly (sodium 4-styrenesulfonate) NaPSS*, has formula $(C_8H_7NaO_3S)$ $_n$. This anionic polyelectrolyte has molar mass average ~ 70,000 g. mole $^{-1}$, manufactured in Sigma Aldrich, the repeating unit of this polyelectrolyte shown in Figure2.2. b

3. *Poly(vinylalkohol) PVA*. Is a water soluble neutral polyelectrolyte, with average molecular weight of ~31,000 g. mole$^{-1,}$ obtained from Sigma Aldrich. The molecularstructure of this polyelectrolyte is shown in *Figure 2.2.c*
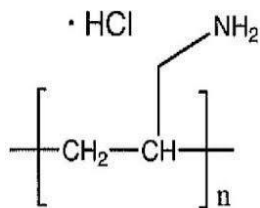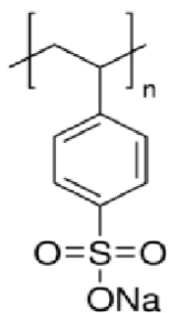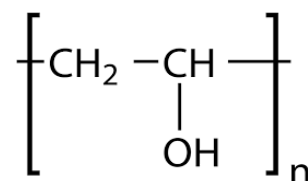
Fig 2.2.a   **Fig 2.2.b**   **Fig 2.2.c**

Figure 2.2: Structural formula of **a)** Poly (allylamine hydrochloride), **b)** Poly (sodium 4-styrenesulfonate) and **c)** Poly(vinylalkohol).

2.1.3 Solvents

Cyclohexane used was high purity (99.7%) and was obtained from *Honeywell Riedel-de Haën™*

2.1.4 Chemical used at Graphene Oxide Nanoparticles Preparation:

Graphite powder, sodium chloride (99.9%) from *Sigma Aldrich*, sulfuric acid (95%), potassium permanganate with purity of (99%), hydrogen peroxide (32%), hydrochloric acid (32%).

2.1.5 Dyes:

Indigo carmine(IC) inorganic anionic dye, from *Riedel-de Haën* (*Germany*), with molar mass of 466.36 g. mole^{-1}, and has molecular structure as shown in Figure 2.3.
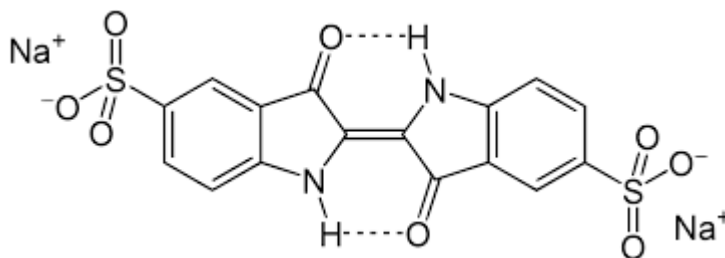
Figure 2.3: Molecular structure of indigo carmine dye.

2.2 Equipment and Tools

2.2.1 Tensiometer

Surface or interfacial tension was measured using an advanced K100 – MK3 tensiometer from (Krüss, Germany) using the plate method as shown in *Figure 2.4*, this tensiometer is fully automatic and computerized, with high resolution (± 0.01 mN/m), It is fitted with a force sensor that is highly accurate and does not need to be recalibrated.

Figure 2.4: Force tensiometer K100 – MK3 device from (Krüss, Germany).

2.2.2 Spectrophotometer:

The concentration of surfactant-dye complex was measured using UVD-3200 from (LABOMED, INC. USA), as shown in *Figure 2.5* it is a high performance UV-Vis double beam automatic scanning spectrophotometer, with wavelength range from 190 to 1100 nm.
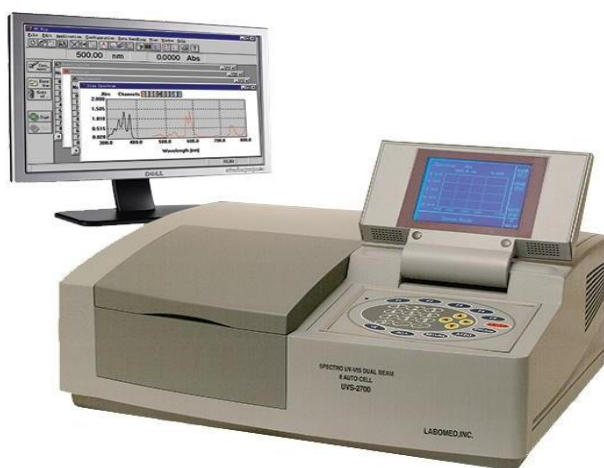
Figure 2.5: shows the UVD-3200 spectrophotometer.

2.2.3 Infrared Analysis

Graphene oxide and surfactant-dye complex were characterized using FT-IR spectrum two purchased from (Perkin-Elmer, USA) with wavelength range of (4000–400 cm-1). The device is shown in *Figure2.6*:

Figure 2.6: FT-IR spectrum two apparatus with range of (4000–400 cm-1).

2.3 Methods

2.3.1 Surface and Interfacial tension

Preparation of solutions and measurement procedure will be discussed in this section. In the beginning, all glassware such as (beakers, volumetric flasks, pipets) were cleaned by filling them with distilled water and then submerged in a hot water bath for 90 min and rinsed with fresh distilled water.

Water that was used to prepare solutions and clean tools was expressed as distilled water and before each preparation process, the surface tension of this water was measured to make sure the water is completely clean and free of any impurities. To insure the tensiometer works well, and before each measurement the beaker which used for measure prepared solution was cleaned several times by distilled water and then by the solution itself, to confirm there is no

remainder of the previous measured solution. The accepted value of surface tension of distilled water was between 71-72mN/m.

The interfacial tension was measured according to apparatus direction as following

I. Detection of oil phase (cyclohexane) surface by using at least 43.6 mL of cyclohexane.

II. Remove the beaker which contains the oil phase, at least 15.6 mL from the aqueous phase was placed in another clean beaker.

III. The plate was immersed in the aqueous phase, and then the oil phase was poured over the aqueous phase. This situation was kept before the measurement process began for 20 min. This is done to reach maximum surface stability and equilibrium.

The platinum plate was cleaned before each measurement by using propane flame, which the plate was heated to redness of surface to remove impurities according to the manufacturers instruction. A systematic methodology of this procedure is shown in *Scheme1*.

```
┌─────────────────────────────────────────────────────┐
│        Cleaning of two beakers and the plate          │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│   Detection of lighter phase (cyclohexane) in the first│
│                      beaker                            │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│   Remove the first beaker and put on the second beaker │
│     that contains aqueous phase (water) on the stage   │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│   The cyclohexane was poured over aqueous phase, and   │
│       stay for 20 min before measurements.             │
└─────────────────────────────────────────────────────┘
```
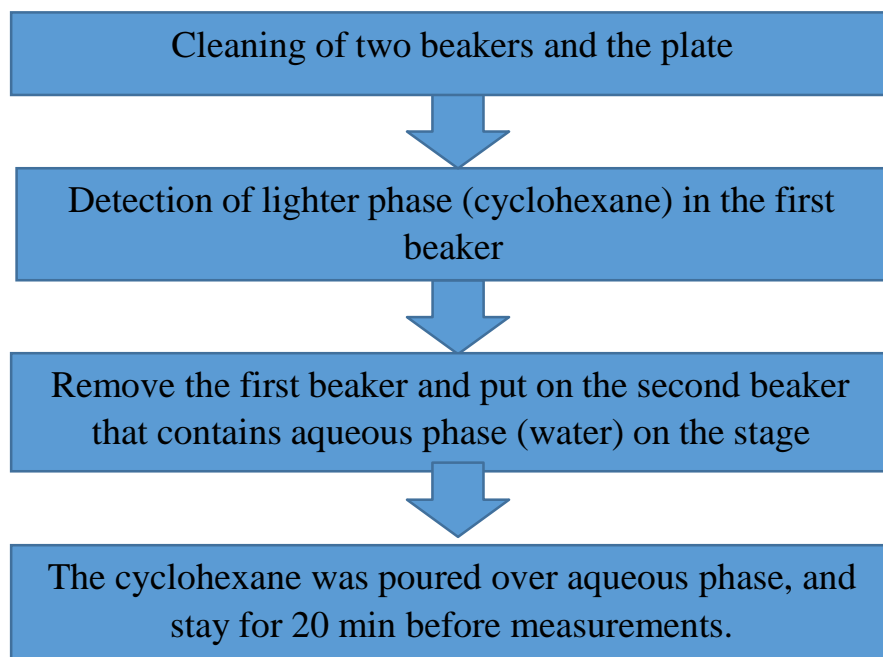
Scheme 1: Systematic methodology of interfacial tension measurements.

Preparation of different concentrations of polyelectrolyte or surfactants was carried out by successive dilution. 100 mL from the first stock solution was used to prepare a series of diluted concentrations by divide it to two parts, one of them was used for the measurement, and the other was diluted with 50 mL of distilled water. This procedure was carried out to reach the lowest concentration needed.

In the case of polyelectrolyte-surfactant mixture, the polyelectrolyte and surfactant was prepared individually. 1L of one concentration of polyelectrolyte was prepared and on the other hand a series of different concentration from surfactant was also prepared. Each 50mL from all surfactant concentrations was mixed with another 50mL of polyelectrolyte. Note that when the surfactant and polyelectrolyte were mixed, the concentration of surfactant

and polyelectrolyte was changed, all of these concentration are tabulated in tables in appendix A in the last chapter.

2.3.2 Removal of Surfactant from water using Graphene Oxide Nanoparticles:

Graphene oxide was prepared by using hummer's method [64] as shown in following scheme2:
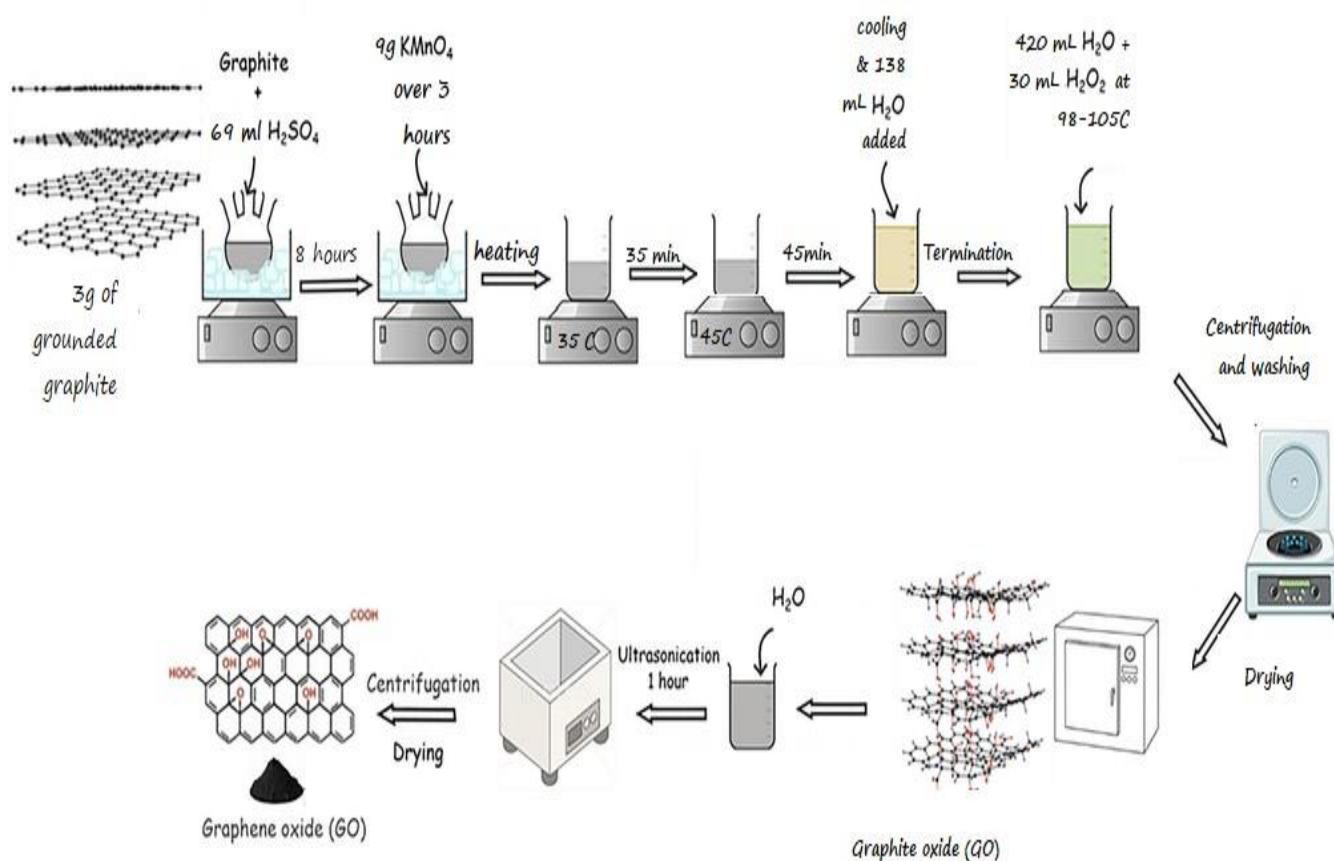
Scheme2 : graphene oxide preparation by hummers method.

A 0.0571 gm from preprepared graphene oxide Nanoparticles with size of 450 ± 35nm[65] was used to remove surfactant from aqueous solution. 2mM and 4mM solutions of BAC was prepared and graphene oxide was added to these solutions. After 24 hours the graphene oxide with adsorbent was filtrated. The remaining surfactant in the filtrated solution was determined by uv-spectrascope based on complexation the surfactant with oppositely charged dye. A systematic methodology of this procedure is shown in scheme2.

2.3.3 Complexation of Surfactant with Dye

The remaining cationic surfactant (BAC) can't be measured directly using uv-visble spectroscopy. but by complexation the cationic surfactant with oppositely charged dye (indigo carmine). The complex formed can be measured. A calibration curve for this complex was created as follows:

I.   Four samples of surfactant were prepared (0.1, 0.2, 0.3 and 0.4mM), respectively.

II.   The dye with 1mM concentration was added to each sample individually.

III.   The addition of dye over each surfactant sample was done at the same time to the absorbance measurement of the complex which forms.

VI.   The addition of dye was continued until it reaches the maximum absorbance which means all of surfactant was attached to the dye where complex is formed.

Preparation of samples	• preparation of 2 sampels from surfactant. • put 0.0571 g from GO to each sample. • filtrate after 24 hours.
complexation with dye	• remaining surfactant was complexed with dye .
Establishment of surfactan-dye calipration carve	• with the range from 1mM to 0.4mM, the remains surfactant was determined.
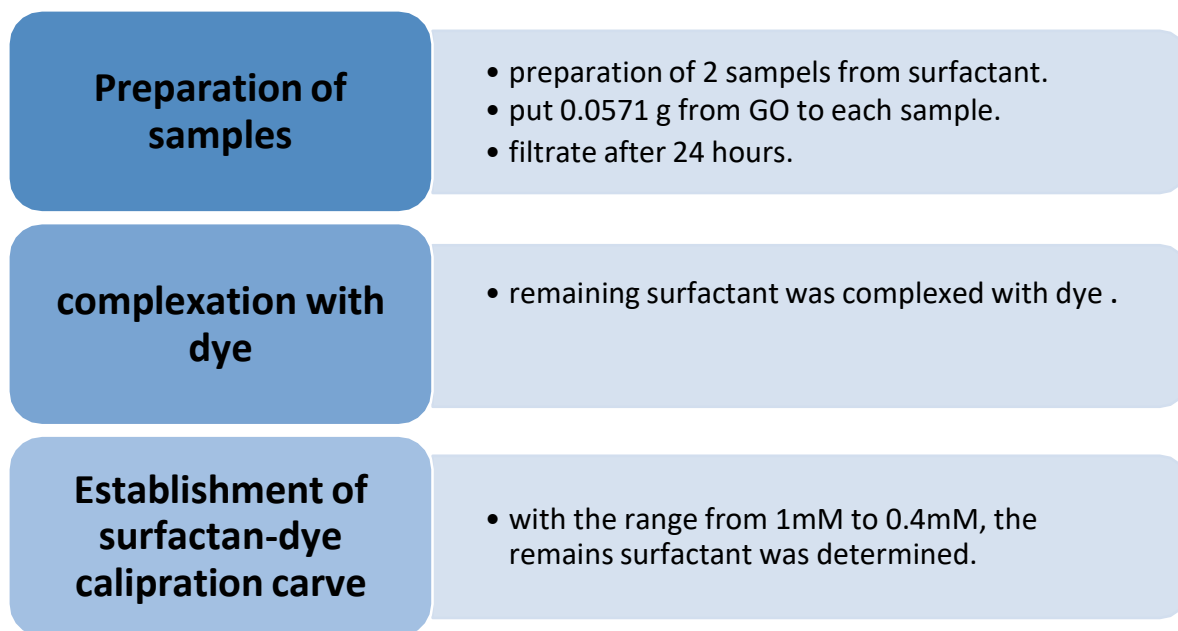
Scheme 3: Systematic methodology of surfactant removal by graphene oxide.

2.3.4 Surface Tension of BAC as Function of IC Volume Addition

Three different concentration from BAC surfactant were prepared (0.0625mM, 0,1mM, and 0.3 mM) by successive dilution. For each concentration, the dye was added using micro pipet. The surface tension was measured for each 0.1 mL addition from dye.

Chapter 3

Results and discussion

In this part of this thesis, the results were divided into two subjects, the first one is a full-fledged study of polymer-surfactant complexes activity at cyclohexane water interfaces, the second part is preliminary results of surfactant removal from water phase by using graphene oxide nanoparticles.

Part1: Polymer/surfactant mixtures activity at cyclohexane/water interface:

3.1.1 Surface/ Interfacial tension of SDBS:

The surface and interfacial tension was measured by using force tensiometer K100 – MK3 device from (Krüss, Germany) at 293 K, the measurement was carried out by using plate method, The bare cyclohexane-water interfacial tension was measured to be 49.6 mN/m which is in good agreement with the value of 48.92 mN/m reported by Viviana et al[66]. as *figure 3.1* shows the aqueous solution of SDBS-air and the aqueous solution of SDBS-cyclohexane interfacial tension at 293 K.
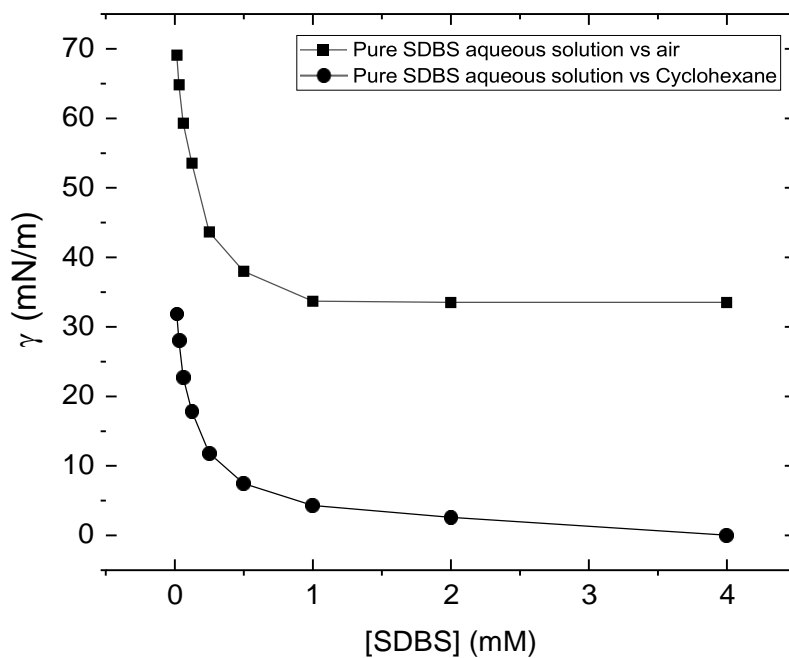
Figure 3.1: Aqueous solution of SDBS-air (solid squares) and aqueous solution-cyclohexane of SDBS (solid circles) interfacial tension at 293 K. The lines are drawn to guide the eye.

As is well known, the surface and the interfacial tension decreases with increasing the anionic surfactant SDBS concentration. The critical micelle concentration of SDBS was determined to be 0.61 mM. The reported values for the CMC of SDBS are at 303 K or higher and no comparison can be made here. Data analysis shown in Table-A1

3.1.2 Surface/ Interfacial tension of BAC:

Aqueous solution of BAC-air (solid squares) surface tension and aqueous BAC solution-cyclohexane (solid circles) interfacial tension at 293 K are shown in *figure 3.2* The CMC

for cationic surfactant BAC was determined to be 0.54 mM.
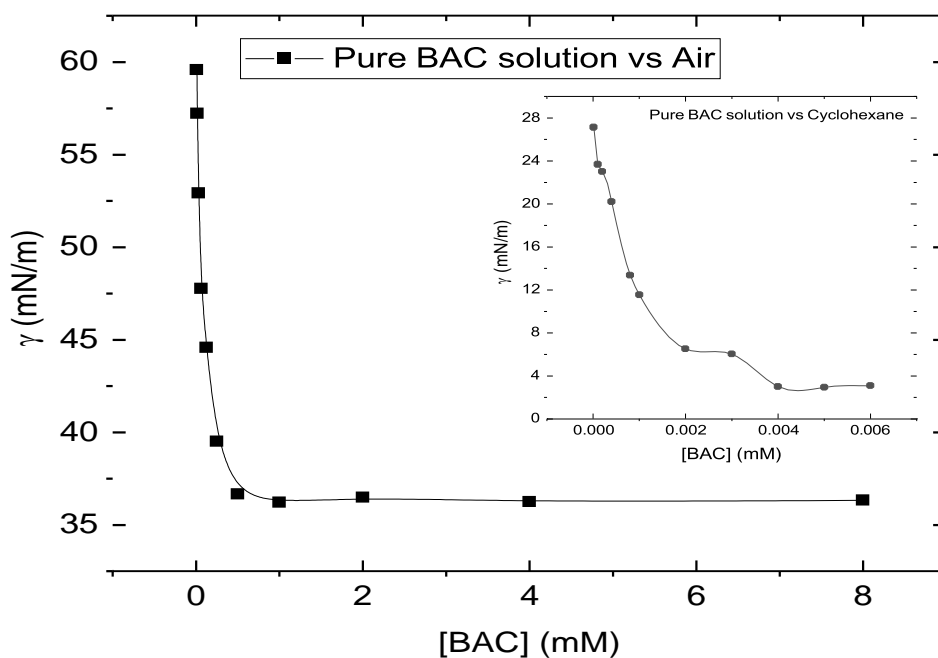
Figure 3.2 Aqueous solution of BAC-air (solid squares) and (inset) aqueous BAC solution-cyclohexane (solid circles) interfacial tension at 293 K. The lines are drawn to guide the eye.

The value of CMC determined by us is in reasonable agreement with that of George *et al*[67]. In the inset figure, note that the concentration of BAC is very low, which implies that the cationic surfactant shows interfacial activity at very low concentration. This is good for practical applications since a tiny amount is needed to obtain surface activity. Another hint is that the saturation of the cyclohexane-water interfacial tension occurs two times at two different concentrations. Note that these experiments were repeated more than one time and the same behavior was found.

3.1.3 Interfacial Tension of PAACl and NaPSS:

Figure 3.3 shows the cyclohexane-water interfacial tension with added either NaPSS (solid squares) or added PAACl (solid circles). The outcome of these measurements is that there is very weak activity of the individual polyelectrolytes at the interface studied.
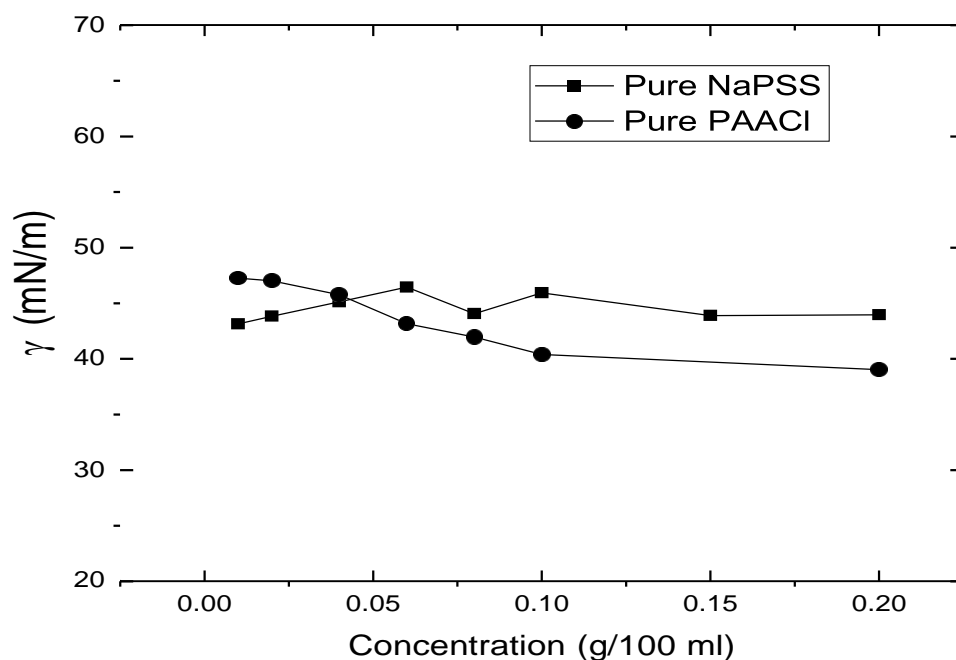
Figure 3.3: Cyclohexane-water interfacial tension with added either NaPSS (solid squares) or PAACl (circles). The solid lines are drawn to guide the eye.

3.1.4 Surface / Interfacial Tension of PVA:

Figure 3.4 shows the surface tension of PVA at the air-water interface (solid squares) and at the cyclohexane-water interface (solid circles(. As is clear form figure 4, this water soluble polymer displays surface activity similar to that of surface active agents. At the air-water interface, measurements of the surface tension of this neutral polymer are well known and

reported [68]. However, at the cyclohexane-water interface measurements are lacking. The surface activity of this water soluble polymer (solute) stems from the hydroxyl group (-OH) on its repeating unit. This functional group is capable of forming hydrogen bonding with water molecules (the solvent). Both water and PVA make mutual interaction and migration to the surface. Now because of their different structures,
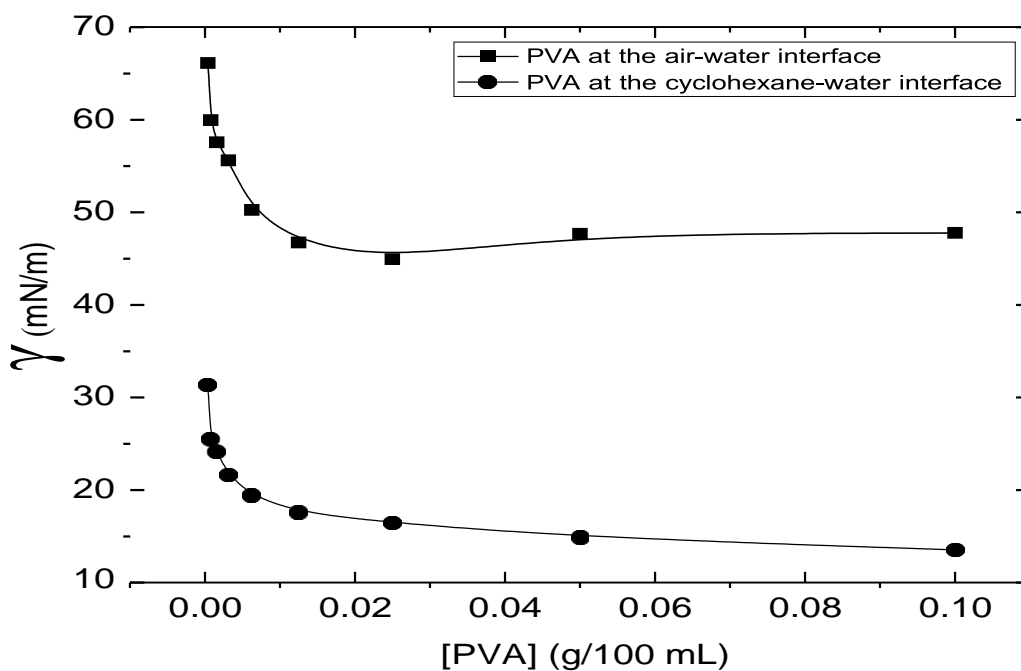
Figure 3.4: Surface tension PVA aqueous solution at the air-water (solid squares) and at the cyclohexane interface (solid circles). The lines are drawn to guide the eye.

PVA exerts different field of attractive forces. In this situation there will be a state of high free energy in the bulk and the PVA will migrate to the surface where there is a lower state of free energy comparing to the bulk. This is the main cause of its surface activity.

3.1.5 Interfacial Tension PVA as a Function of [SDBS]:

Figure 3.5 shows the interfacial tension of 0.02 g PVA in solution as a function of SDBS concentration (solid circles) and 0.2 g PVA in solution (solid triangles) at the cyclohexane-water interface plotted together with the interfacial tension of pure SDBS solution at the same interface (solid squares) for comparison. The solid lines are drawn to guide the eye. Clearly the presence of the anionic surfactant SDBS lower the interfacial tension of solution at low SDBS concentration from 35 mN/m to about 12 mN/m for 0.02 g PVA to 9 mN/m for 0.2 g PVA. However, at higher SDBS concentration (above the CMC of SDBS) there is almost no further decrease in the interfacial tension. Note that PVA is neutral polymer and does not make strong interaction with SDBS (Weak interaction).
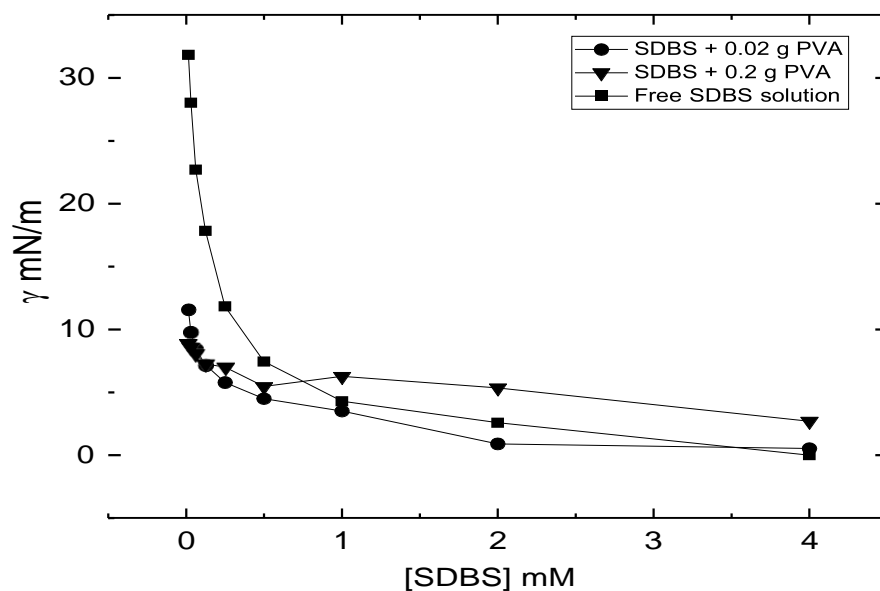
Figure 3.5: Interfacial tension of 0.02 g PVA in solution a function of SDBS concentration at the cyclohexane-water interface (solid circle) and 0.2 g PVA in solution (solid triangles) plotted together with the interfacial tension of free SDBS solution for comparison.

3.1.6 Interfacial Tension of PAACl as a Function of SDBS:

The interracial tension of different PAACl amounts in solution of 0.001 g/100ml (solid circles), 0.003 g / 100 ml (solid triangles) and 0.005 g/100 ml (solid stars) as a function of SDBS concentration at the cyclohexane-water interface, plotted together with free SDBS solution (solid squares) is shown in Figure 5.6, The solid lines are drawn to guide the eye.
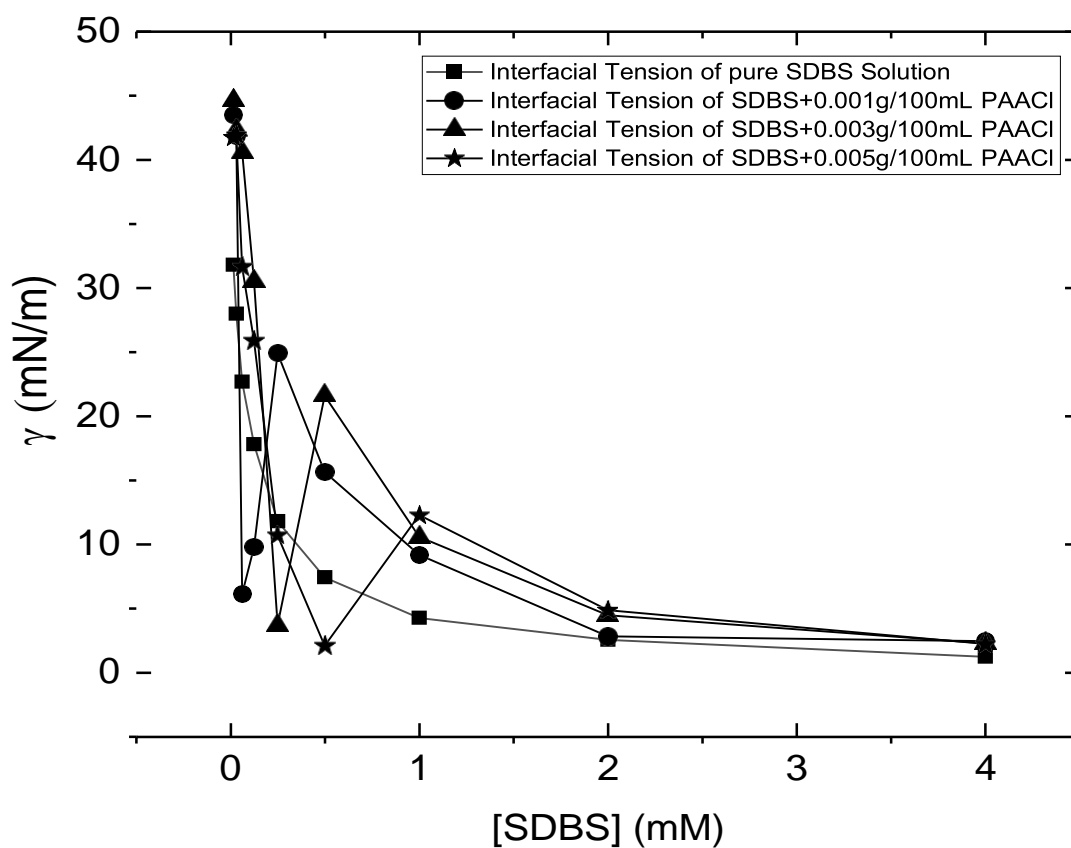
Figure3.6: Interfacial tension of different PAACl amounts in solution of 0.001 g/100ml (solid circles), 0.003 g / 100 ml (solid triangles) and 0.005 g/100 ml (solid stars) as a function of SDBS concentration plotted together with free SDBS solution (solid squares). The solid lines are drawn to guide the eye.

In figure 3.6, the interfacial tension of SDBS/PAACl system displays a hump as a function of SDBS concentration. The maximum of the hump shifts to higher SDBS concentration as the amount of PAACl increases in solution. Staples *et al* [69]studied the system sodium dodecyl sulfate (SDS)/poly(dimethyldiallyammonium chloride) at the water-air interface and observed a hump in the surface tension plot against SDS concentration.

Their system is anionic surfactant/cationic polyelectrolyte meaning it is an oppositely charges surfactant/polymer system. Unfortunately, there are no studies at the oil/water interface of this complex system to compare with. It seems that a hump in the surface tension behavior in these systems is not a rare phenomenon. To explain the origin of a hump in our studied complex system we have to rely on neutron reflection study of Taylor *et al* [70] where they studied the adsorption of the cationic surfactant alkyltrimethylammonium bromide (CTAB)/sodium polystyrene system and found a hump in the surface tension behavior as a function of CTAB concentration and chain length. From their reflectivity data they resolved three different complex structures of their polyelectrolyte/surfactant systems.

The first of these structures is a monolayer of surfactant molecules attached to the polymer backbone and complex is present all the time. The second structure is a bilayer of surfactant molecules attached to the polyelectrolyte and the third structure is surfactant aggregates with the polymer in the bulk. It seems to us that the fluctuation in our interfacial tension data and the observed hump must originate from changes of the amount of these different structures at the interface and their competition with complexes in the bulk. Guzmán [71] has mentioned

that the maxima in the surface tension of these complex systems data is due to insufficient equilibration time.

3.1.7 Surface Activity Comparison:

From figure 5.6 we note that the activity of the polyelectrolyte-surfactant complex at the hump point is greater than free polyelectrolyte with the same concentration of PAACl polyelectrolyte as shown in in figure 5.3 which shows the activity of free PAACl.
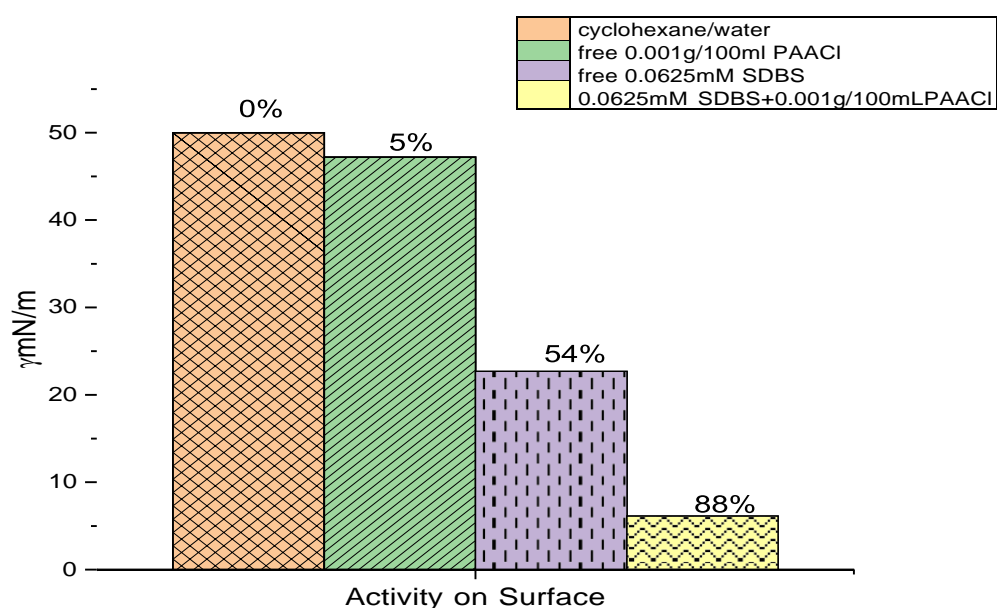
Figure 3.7: Comparison between polyelectrolyte surfactant complex with free surfactant and free polyelectrolyte.

On the other hand, the activity of free anionic surfactant SDBS is less than the activity of the complex with the same concentration of surfactant. Figure 5.7 shows the comparison between free polyelectrolyte, free surfactant and the complex with taking cyclohexane-water interface as a reference. The complex shows the most active sample which decrease interfacial tension from 50 mN/m to about 6 mN/m that's means 88% from water-cyclohexane interfacial tension value.

3.1.8 Interfacial Tension as a Function of Time:

In our study we have equilibrated our samples for 24 hours and studied the interfacial tension as a function of time as shown in *figure 3.8* which shows the interfacial tension of the PAACl/SDBS complex at the cyclohexane/water interface as a function of time and at two different SDBS concentration of 0.065 mM and 0.25 mM. The measurements of interfacial tension are carried out after 24 hours' equilibration time. The interfacial tension in *figure 3.8* saturates after about 20 minutes and stays constants for about 40 minutes.
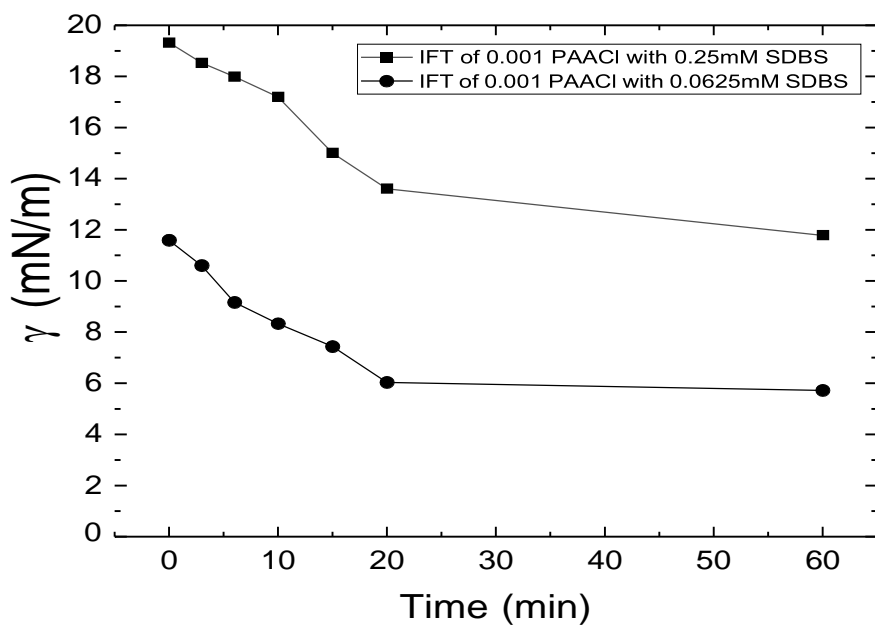
Figure 3.8: Interfacial tension (IFT) of the PAAl/SDBS complex at the cyclohexane interface as a function of time at two different surfactant concentration of 0.25 mM (solid squares) and 0.0625 mM (solid circles)

This shows that the interfacial tension we have measured is indeed an equilibrium one and the observed hump in our interfacial tension graph to be true effect and not due to insufficient time of equilibration.

3.1.9 Critical Aggregation Concentration(CAC):

Figure 3.9 (a) shows the change in PAACl concentration as a function of the concentration of SDBS at the minimum (critical aggregation concentration) of the interfacial tension extracted from *figure 3.6* above. *Figure 3.9 (b)* shows the maximum of the interfacial tension as a function of PAACl concentration extracted from *figure 3.6.*
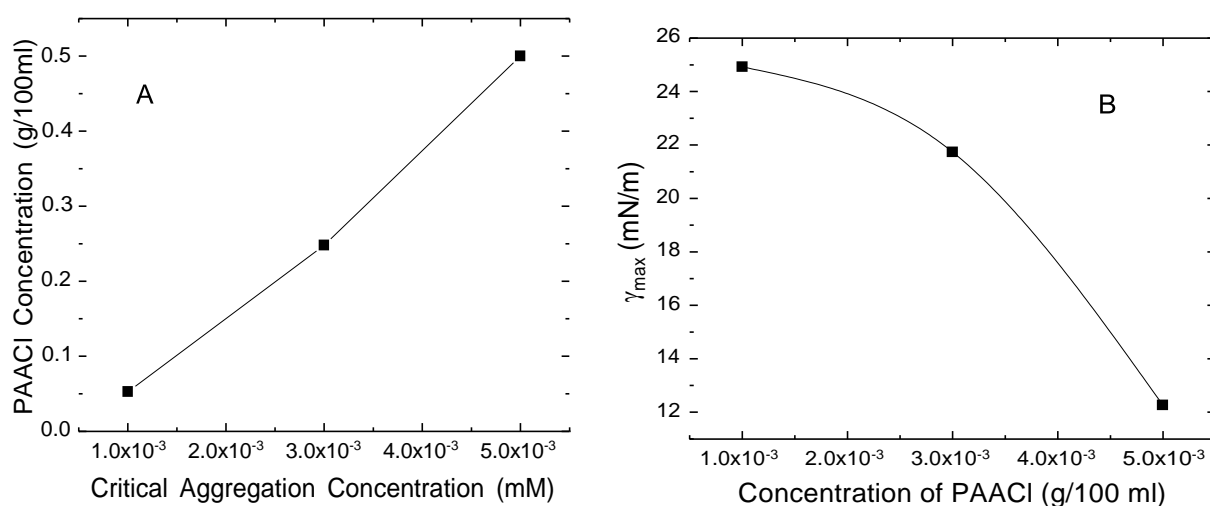
Figure 3.9:(A) PAACl concentration as a function of the concentration at the minimum of interfacial tension (CAC). **(B)** the interfacial tension at the maximum as a function of PAACl concentration.

It is clear form *figure 3.9 (A)* that as the polyelectrolyte concentration increases in solution the critical aggregation concentration (CAC) increase as well because more association between the surfactant molecules and the polyelectrolyte chains occurs. The minimum in the interfacial tension at CAC is due to the presence of a surface complex (associated polyelectrolyte/surfactant molecules). It seems that this complex has high affinity to adsorb

at the interface than the surfactant itself and thus impart high surface activity. In *figure 3.9*

(B), γ_{max} corresponds to a surfactant monolayer at the interface where the polyelectrolyte is

associated with the surfactant micelles in the bulk. The conclusion that can be drawn here

is that the polyelectrolyte/surfactant complex is more interfacial active than the surfactant

itself for this particular system

3.1.10 Interfacial tension of the BAC/NaPSS system:

The interfacial tension of the BAC/NaPSS system at the cyclohexane-water interface for

two different NAPSS amount in solution is shown in *figure5.10* below plotted together with

the interfacial tension of pure BAC solution at the same interface. This system consists of

cationic surfactant and anionic polyelectrolyte. No maxima of minima of the interfacial

tension is observed for this system. Note the very low concentration of the cationic BAC

surfactant. This surfactant is difficult to study because it shows high interfacial activity at

very low concentration. The surprising effect of this system is that the NaPSS upon

association with the surfactant molecules increases the interfacial tension.
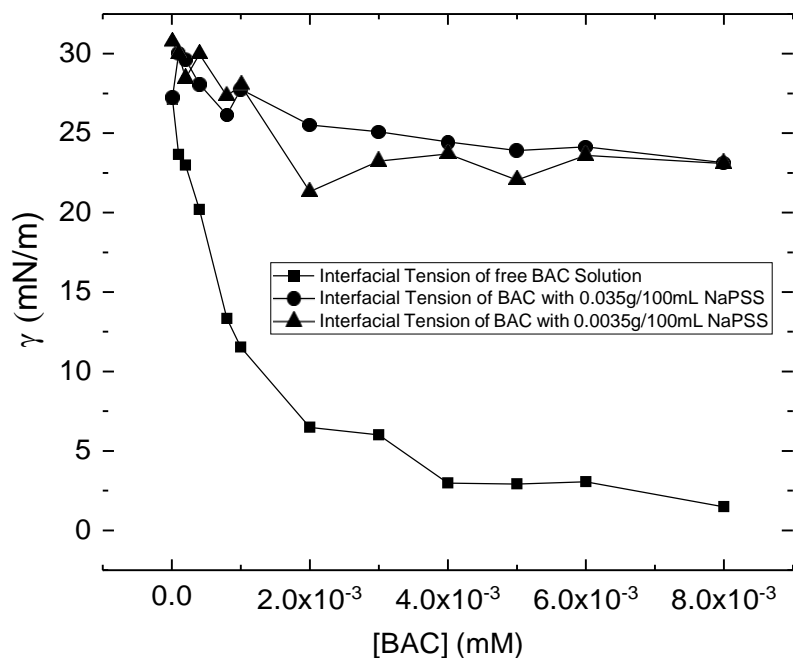
Figure3.10: Interfacial tension of the BAC/NaPSS system at the cyclohexane-water interface as a function of BAC concentration for two different NaPSS amounts of 0.0035 g (solid triangles) and 0.035 g (solid circles) plotted together with the interfacial tension of pure BAC solution (solid squares). The lines are drawn to guide the eye.

This implies that the NaPSS polyelectrolyte drags the surfactant from the interface to the bulk causing less surface activity. These experiments where repeated and the same effect was found. The NaPSS is a polyanion and not interfacial active and therefore stays in the bulk. It seems that because the cationic BAC surfactant shows high surface activity at very low concentration, there is no complete association between its molecules and the NaPSS chains and thus there are not enough surfactant molecules to neutralize the negative charges at the backbone of the anionic polyelectrolyte NaPSS. No such effect was previously reported for

this particular polyelectrolyte/surfactant system and thus the findings here constitute a challenge for neutron and x-ray reflectivity measurements.

3.1.11 Surface Tension of BAC surfactant as a Function of Dye volume addition:
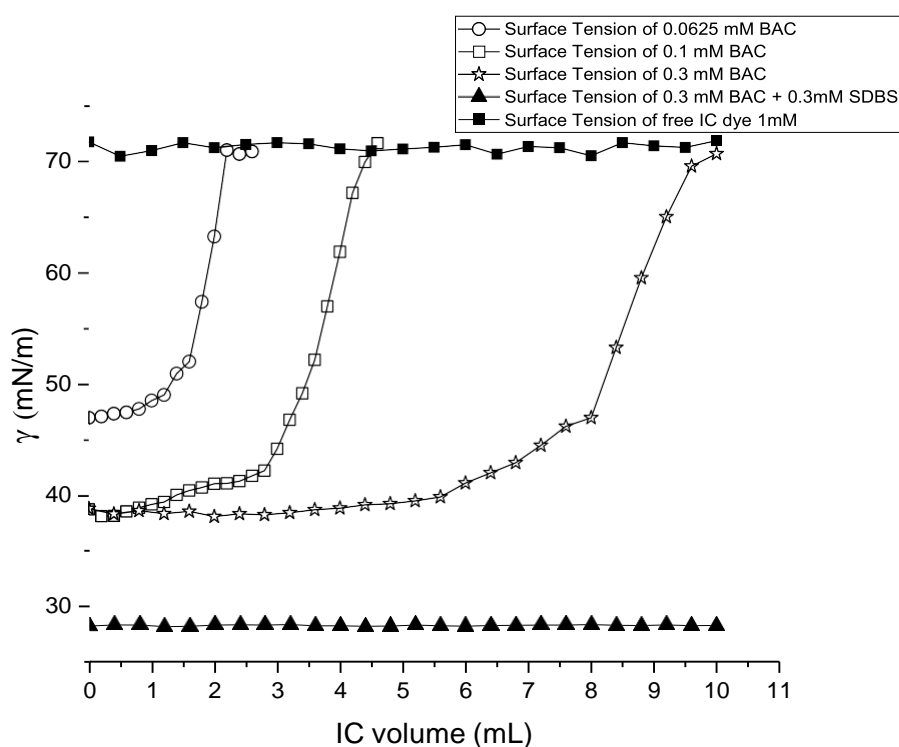
Figure 3.11: surface tension of 0.0625 mM of BAC surfactant as a function of different IC dye volumes with concentration of 1mM addition at water-air interface (open circle), 0.1 mM BAC (open square) , and 0.3 mM BAC (open star), 0.3 mM BAC in presence of 0.3 mM SDBS (solid triangle) , free dye surface tension (solid square).

As shown in *figure 3.11*, the surface tensions of three different systems were measured, first of all, free IC dye surface tension was measured and found to be non-active on the surface as shown in solid square line the addition of dye dose not effect on the surface tensionand still around 71 mN/m, on the other side the surface tension 50 mL of three different BAC concentration (0.0625mM, 0.1mM and 0.3mM) open circle, open square and open star respectively as a function of 1mM dye addition was compared, and found that the anionic IC dye reacted with cationic BAC surfactant to form non-active complex and remove the surfactant from surface toward bulk region which means increasing in the surface tension value and decrease the effect of surfactant on the water air interface, as the dye was added to the solution as the value of surface tension increased until all of surfactant molecules was complexed and surface tension of solution returned to about 72 mN/m, in the addition, the largest concentration form BAC surfactant(0.3mM) consumed the highest amount from IC dye about 10 mL, in the last system(solid triangle) two equal concentrations of oppositely charged surfactant (0.3mM BAC and 0.3mM SDBS) was mixed in the same solution and surface tension was measured as a function of IC addition, there was no change on surface tension reads, which can be interpreted as anionic surfactant dose not reacted with added dye and remained on the surface.

Part 2: Removal of Surfactant from Water using Graphene Oxide Nanoparticles.

3.2.1 Spectrophotometric Determination of BAC Surfactant:

As shown in *figure 3.12*. The absorption spectra of IC and IC-BAC complex was measured. Comparing the two spectra λ_{max} of IC dye was found and was located at 610nm. For IC-BAC complex, λ_{max} was determined to be 564 nm. The blue shift was calculated to be about 46nm, such a great shift was rare in similar systems [72], The findings indicates that the IC-BAC binding is strong in spite of the electrostatic attraction. Nevertheless, ordinary UV spectrophotometry is still unfit for characterization of the IC-BAC complex. Instead, FT-IR was used to give bitter characterization of IC-BAC complex.
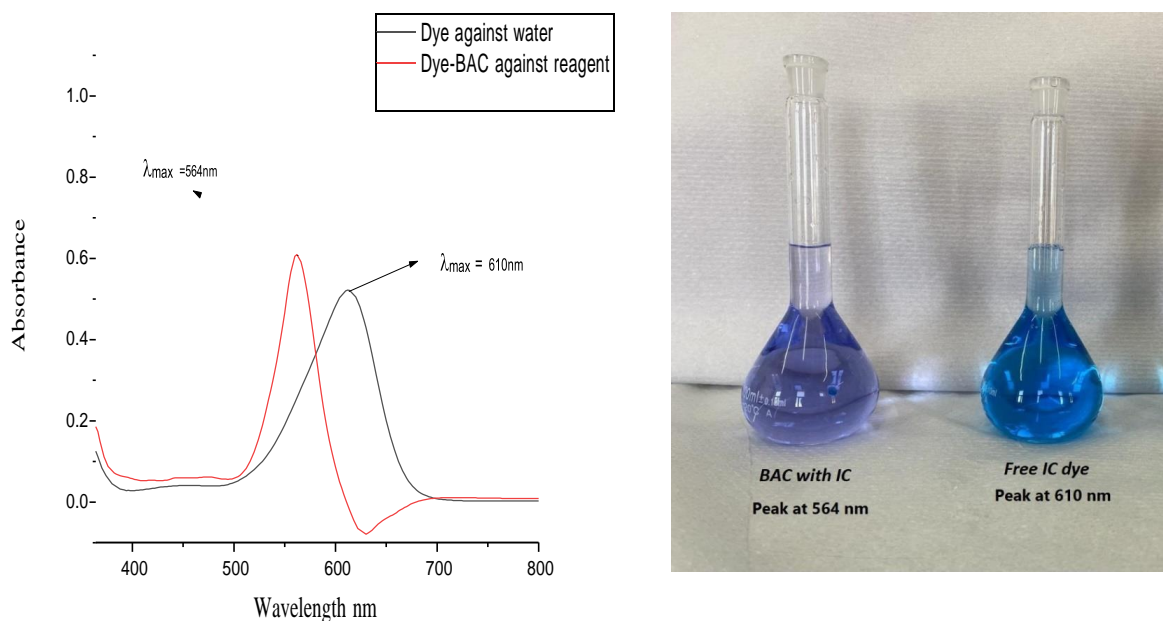
Figure 3.12: Absorption spectra of IC dye compared with IC-BAC solution contains 2mM of BAC, absorption spectra of IC was measured against water, and IC-BAC against reagent (IC dye).

3.2.2 Solid IC-BAC Complex

Figure 3.13A shows step-wise addition of 1mM IC solution over 0.3mM BAC parallel with absorbance measurement of formed complex between IC and BAC. Through the observation and analysis figure 3.13 A the complex reached a breaking point which transform from soluble to isolable in the form of solid aggregation which can be easily filtrated and isolated. From experimental analysis the breaking point occurred when all of surfactant molecules reacted with the added dye molecules, This means that the number of moles of IC added was equivalent to the number of moles of BAC in the solution
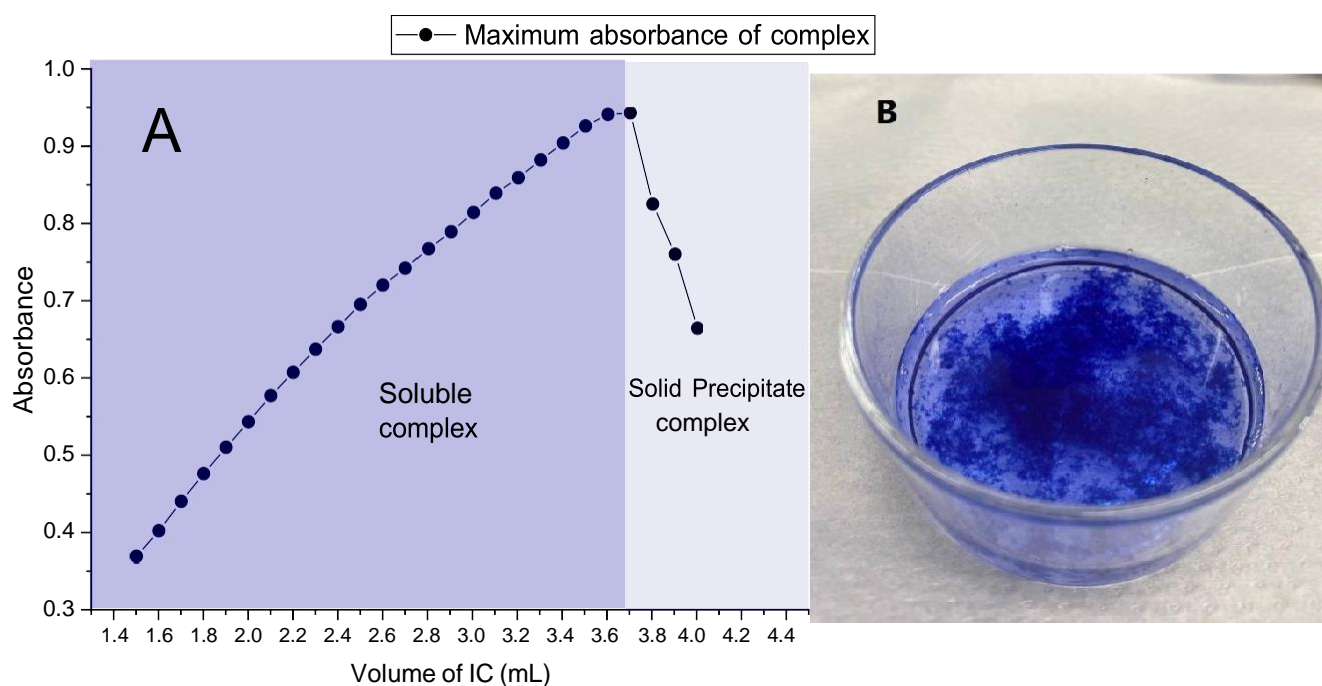
Figure 3.13A: Maximum absorbance 0.3mM of BAC in 25mL as a function of 1mM IC addition,

Figure 3.13B: Solid state of IC-BAC complex separated from the solution.

. For more clarification, 3.7mL of 1mM IC which equal (3.7×10^{-6} mol) of IC was added to 25 mL of 0.3mM BAC which equal ($7.5 \times 10^{-6)}$ mol of BAC, note that the mole of BAC is double that of IC and that was corresponded to theoretical explanation with just about 1.4 % error. This can be explained by each molecule of IC has 2 partial negative, one to each sulfur trioxide, on the other side each BAC molecule contains on 1 partial positive on the ammonium group, so the ratio 2 is IC : 1 BAC.

Two major benefits of this experiment were obtained:

1- Get the solid precipitate for FT-IR analysis

2- Generate calibration curve for BAC determination.

3.2.3 Calibration Curve of the BAC Surfactant:
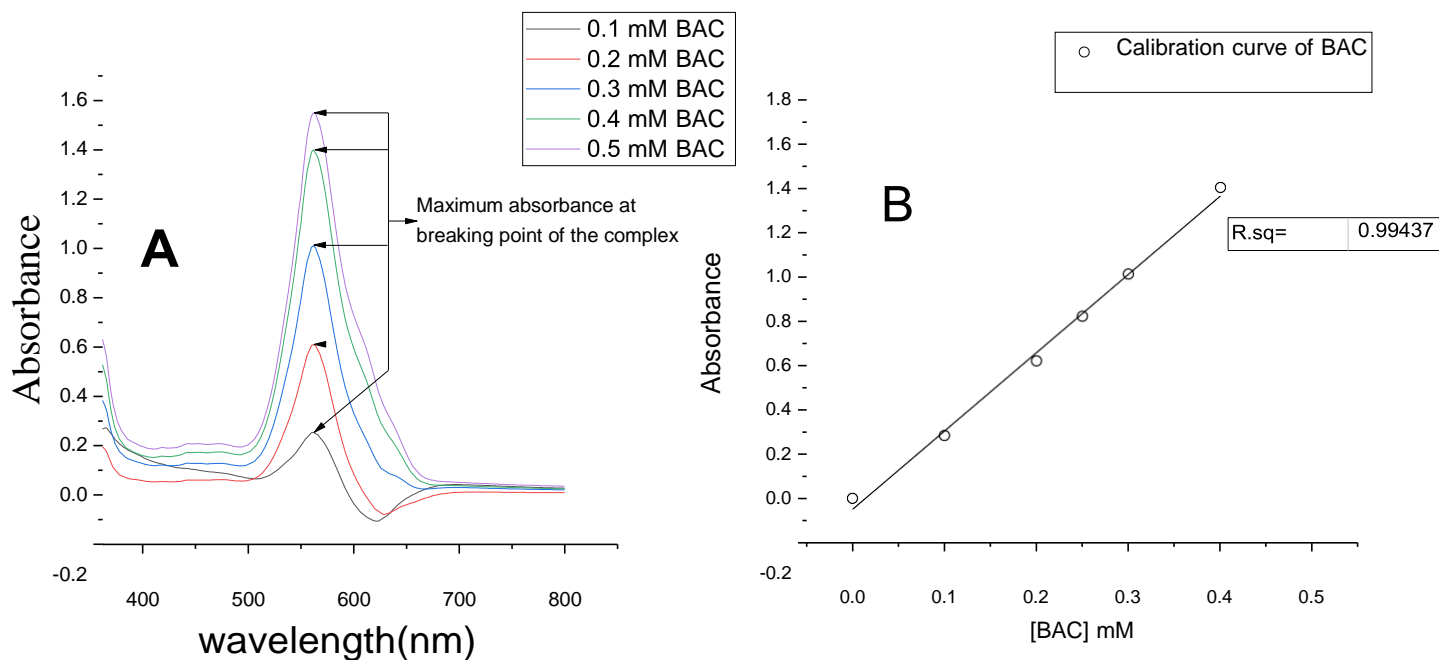
Figure 3.14: A: Absorption spectra at maximum absorbance of different IC-BAC complex concentrations, B: calibration curve of IC-BAC in terms of BAC concentration.

Figure 3.14 shows the absorbance versus concentration of BAC. Each concentration was handled according to the method described in the previous section, so that the UV spectra of IC-BAC complex at range from 380 nm to 800 nm was obtained. By applying this method to the rest of concentrations, the maximum absorbance of several concentrations were collected as shown in *figure 3.14A*. The maximum absorbance of each concentration was used to create the calibration curve as in *figure 3,14B*. This calibration curve was used to determine unknown concentration at equilibrium of BAC surfactant in a range from 0 to 0.5 mM.

The percentage removal (%R) was determined by using equation (3-1)

$$\%R = \frac{Ci - Ce}{Ci} * 100\% \qquad\qquad (3\text{-}1)$$

Where C_i is initial concentration of BAC surfactant in (mM) and C_e is concentration at equilibrium of BAC surfactant in (mM).

Table(3-1) shows the initial concentrations used and equilibrium concentrations obtained from calibration curve depending on maximum absorbance of remains surfactant.

Initial concentration mM (Ci)	Absorbance of remains	Equilibrium Concentration mM (Ce)	Removed BAC mM	%of Removal
4 mM **trial (A)**	1.086	0.321	3.679	91.20%
2mM **trial (A)**	0.248	0.0831	1.916	95.8%
4 mM **trial (B)**	0.983	0.292	3.703	92.7%
2mM **trial(B)**	0.323	0.105	1.895	94.75%
4 mM **Average**	1.034	0.3065	3.7	91.8%
2mM **Average**	0.285	0.094	1.90	95.28%

3.2.4 FT-IR study of IC-BAC complex:
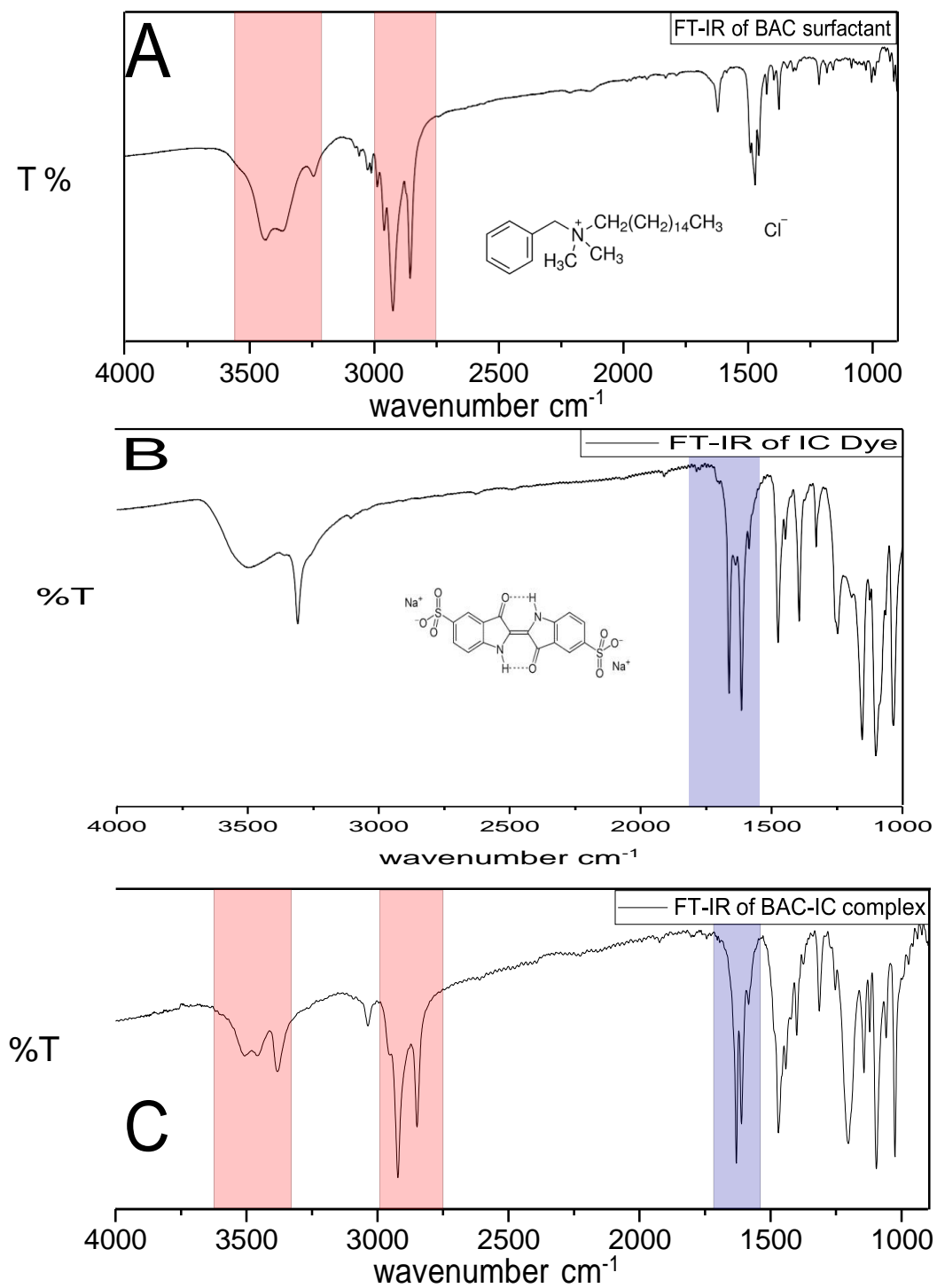
Figure 3.15: FT-IR spectra of **A)** BAC surfactant **B)** IC dye **C)** BAC-IC complex

The spectrum of indigo carmine dye is shown in the first FT-IR spectra, and the values of FT-IR vibrations in this spectra are compatible with previous study on this dye[73].as shown in the spectra, the peat at about 1600 cm-1 corresponding several mods of C=C pond which indicate with blue color in the spectra. This peak also appeared in the spectra of the complex at the same wave length which means binding of indigo carmine and BAC surfactant. In the spectra of BAC surfactant which also match with Sigma Aldrich FT-IR spectra of BAC surfactant[74], the appearance of two strong C-H stretching on about 2923cm-1 and 2850cm-1 in free BAC spectra are also found in complex spectra is another sign to occurrence of complexation between dye and surfactant .

3.2.5 Graphene oxide-surfactant FT-IR study:

FT-IR of graphene oxide was studied and different IR vibrational bands are found in the region $4000cm^{-1}$ to $500 cm^{-1}$. Graphene oxide demonstrate beak at $3426 cm^{-1}$ which represent hydroxyl group, another beak at about $1726 cm^{-1}$ to carbonyl group, $1626 cm^{-1}$ for C=C bond, and $1052 cm^{-1}$ for C-O group. This FT-IR study of graphene oxide is matched with previous studies which carried out graphene oxide [65], in the complex spectra, almost all of graphene oxide beaks appears with extra two beak at $2923cm^{-1}$ and $2850 cm^{-1}$ which referred to C-H stretching of BAC surfactant, the appearance of GO and BAC beaks in the same spectra is an indication to binding between GO and BAC by adsorption.
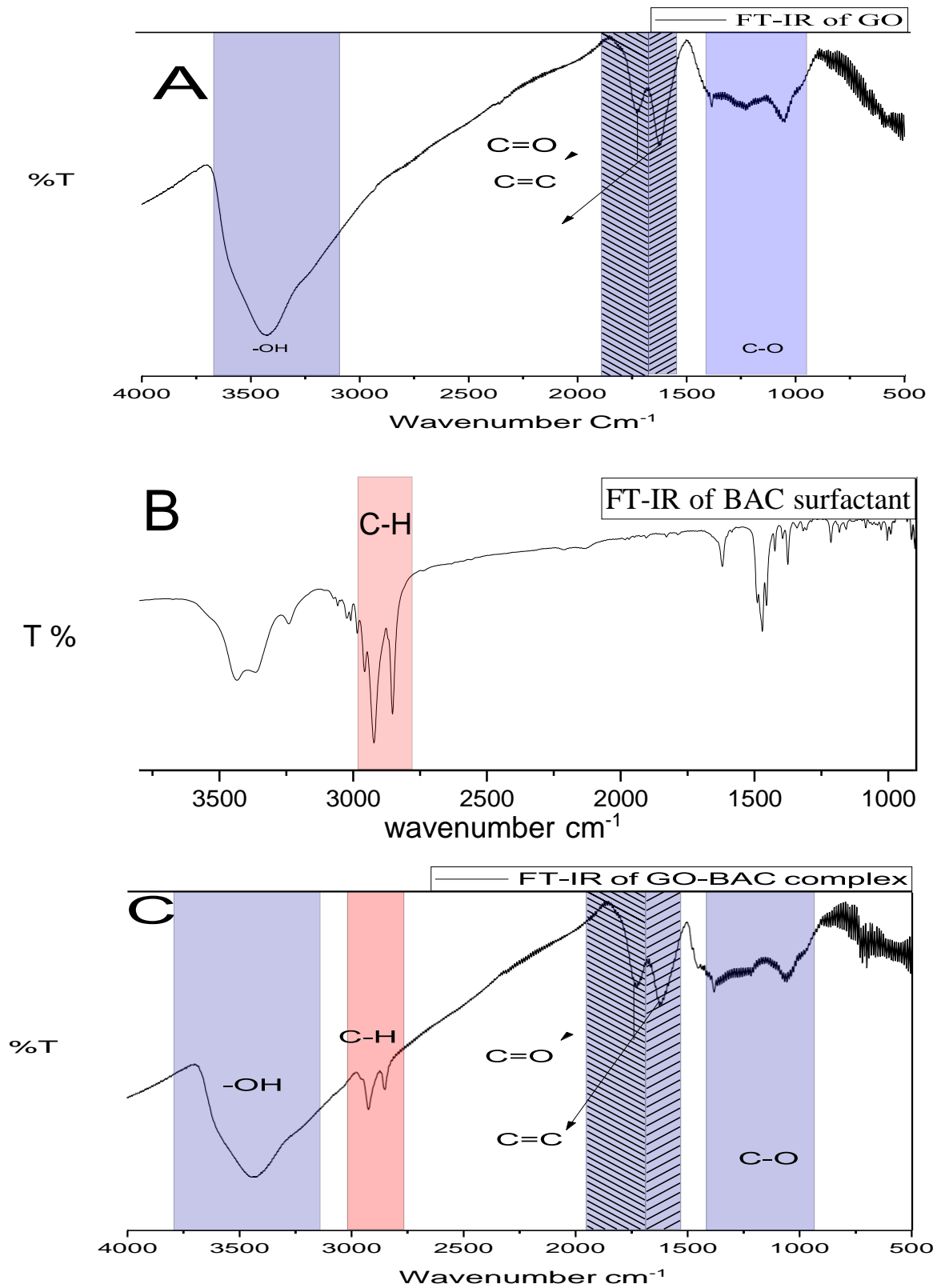
Figure 3.16: FT-IR spectra of **A)** graphene oxide **B)** BAC surfactant **C)** graphene oxide with BAC surfactant.

Chapter Four:

Conclusion &

Recommendations

4.1 Conclusion:

The interaction between surfactant and polyelectrolyte produced a complex with superior surface activity which decrease surface and interfacial tension on liquid outperforming the free surfactant and free polyelectrolyte. Since the tremendous use of surfactant at free state resulted in an increased flux of surfactants in aquatic environment over the past years, the Nano technologically-based and modern society is now interested in graphene oxide (GO) because of its promising properties. The removal of cationic surfactant can be achieved by graphene oxide nanoparticles. This is what was addressed in the second part of this theses by giving promising preliminary result in removing cationic surfactant from water by using graphene oxide nanoparticle's.

4.2 Recommendations:

From our studies we seriously recommend to use plate method in interfacial tension measurements specially at low value of interfacial tension due to its ability to measure low interfacial tension and to avoid breaking of lamila when using ring method. In further studies different types of polyelectrolyte and surfactant can be used.

Graphene oxide also must be carried out to enhance its surface functional groups by different oxidation methods or by coating its surface with different molecules as surfactant or polyelectrolyte to increase active sites and efficiency.

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الملخص

في هذا البحث ؛ تم دراسة تأثير المعقدات الناتجة عن اتحاد المبلمرات مع الجزيئات النشطة على السطح الفاصل بين

الماء والهكسان الحلقي، وتبين ان اتحاد المبلمرات مع المركبات النشطة على السطح لها كفاءة اعلى في تخفيض

التوتر السطحي من المبلمرات او المركبات النشطة على السطح عندما يكونان على شكل حر، وهذه النتجه تعد الاولى

من نوعها من حيث المركبات المستخدمة والسطوح التي تمت الدراسة عليها، وتم اعتماد هذه الفكرة كفكرة اساسية

للبحث.

كفكرة ثانوية ؛ تم تحضير جزيئات الجرافين الثانوية عن طريق الاكسدة والاختزال حيث اظهرت نتائج التحليل

باستخدام FT-IR وجود العديد من المجموعات الوظيفية على سطح اكسيد الجرافين، حيث تم استخدام اكسيد

الجرافين في التخلص من وجود جزيئات الـ(surfactant) التي تحمل شحنة موجبة الموجودة في الاوساط المائية،

وتعتبر النتائج المتحصل عليها نتائج واعدة ويمكن الاعتماد عليها لإلانطلاق في دراسة كاملة للجوانب.

Appendixes

Appendix A: Surface and Interfacial tensions of

Polyelectrolyte/surfactant systems – data analysis

Table-A1: Surface and Interfacial tension of free SDBS surfactant:

[SDBS] mM	Surface tension mN/m	Interfacial Tension mN/m
4	33.496	0
2	33.504	2.579
1	33.692	4.29
0.5	37.983	7.453
0.25	43.646	11.83
0.125	53.534	17.825
0.0625	59.281	22.697
0.03125	64.821	28.012
0.01563	69.069	31.822

Table-A2: Surface tension of free BAC surfactant:

[BAC] mM	Surface tension mN/m
0.00781	59.57
0.01563	57.21
0.03125	52.92
0.0625	47.76
0.125	44.58
0.25	39.51
0.5	36.67
1	36.22
2	36.49
4	36.25
8	36.34

Table-A3: Interfacial Tension of free BAC surfactant:

[BAC] mM	Interfacial tension mN/m
1.00×10^{-5}	27.13
1.00×10^{-4}	23.67
2.00×10^{-4}	22.99
4.00×10^{-4}	20.2
8.00×10^{-4}	13.34
0.001	11.53
0.002	6.48
0.003	6.01
0.004	2.98
0.005	2.92
0.006	3.06

Table-A4: Interfacial tension of PAACl/NaPSS:

[NaPSS] g/100ml	Interfacial tension mN/m	[PAACl] g/100ml	Interfacial tension mN/m
0.01	43.137	0.01	47.237
0.02	43.82	0.02	46.993
0.04	45.115	0.04	45.731
0.06	46.436	0.06	43.126
0.08	44.058	0.08	41.947
0.1	45.919	0.1	40.372
0.15	43.876	0.2	39
0.2	43.957	--	--

Surface and Interfacial tension of PVA:

[PVA] g/100ml	surface tension mN/m	[PVA] g/100ml	Interfacial tension mN/m
0.1	47.767	0.1	13.506
0.05	47.649	0.05	14.885
0.025	44.921	0.025	16.441
0.0125	46.717	0.0125	17.574
0.00625	50.241	0.00625	19.38
0.00313	55.59	0.00313	21.611
0.00156	57.539	0.00156	24.161
7.81×10^{-4}	59.925	7.81×10^{-4}	25.465
3.91×10^{-4}	66.096	3.91×10^{-4}	31.32

: Interfacial Tension PVA as a function of [SDBS]:

[SDBS] mM	Interfacial tension of free SDBS	Interfacial tension of SDBS+0.02gPVA/100ml	Interfacial tension of SDBS+0.2PVAg/100ml
0.01562	31.822	11.55	8.81
0.03125	28.012	9.71	8.51
0.0625	22.697	8.42	8.02
0.125	17.825	7.18	7.23
0.25	11.83	5.78	6.99
0.5	7.453	4.49	5.45
1	4.29	3.5	6.25
2	2.579	0.89	5.33
4	0	0.52	2.68

Table-A7: Interfacial tension of PAACl as a function of [SDBS]:

[SDBS]mM	Interfacial tension of free SDBS	Interfacial tension of SDBS+0.001gPAACl/100ml	Interfacial tension of SDBS+0.003gPAACl/100ml	Interfacial tension of SDBS+0.005gPAACl/100ml
4	1.25	2.47	2.3	2.23
2	2.579	2.84	4.49	4.87
1	4.29	9.2	10.61	12.29
0.5	7.453	15.66	21.61	2.09
0.25	11.83	24.92	3.74	10.69
0.125	17.825	9.8	30.54	25.87
0.0625	22.697	6.15	40.63	31.64
0.03125	28.012	41.88	42.31	41.92
0.01563	31.822	43.47	44.62	41.72

Table-A8: Interfacial Tension as a function of time:

Time (min)	IFT of 0.001gPAACl with 0.25mM SDBS	IFT of 0.001gPAACl with 0.0625mM SDBS
0	19.32	11.59
3	18.53	10.6
6	17.99	9.17
10	17.2	8.33
15	15.01	7.44
20	13.61	6.03
60	11.79	5.72

: Critical aggregation concentration:

[PAACl]g/100ml	Critical Aggrication Concentration (mM)
0.001	0.0528
0.003	0.2478
0.005	0.4997

Table-A9: the maximum of the interfacial tension as a function of PAACl concentration:

[PAACl]g/100ml	Max Interfacial tension mN/m
0.001	24.927
0.003	21.737
0.005	12.27

Table-A10: interfacial tension of the BAC/NaPSS system:

[BAC] mM	Interfacial tension of free BAC	Interfacial tension of BAC+0.035gNaPSS/100ml	Interfacial tension of BAC+0.0035g NaPSS/100ml
1.00×10^{-4}	23.67	30.01	29.98
2.00×10^{-4}	22.99	29.63	28.47
4.00×10^{-4}	20.2	28.07	29.98
8.00×10^{-4}	13.34	26.13	27.35
0.001	11.53	27.76	28.02
0.002	6.48	25.51	21.33
0.003	6.01	25.08	23.25
0.004	2.98	24.44	23.71
0.005	2.92	23.89	22.06
0.006	3.06	24.13	23.61
0.008	1.48	23.13	23.1

Appendix B: Surface tension and spectroscopic analysis of dye/surfactant systems:

Table-B1: Surface tension of free IC dye:

volume of IC dye(ml)	Surface Tension of free IC dye mN/m	volume of IC dye (ml)	Surface Tension of free IC dye mN/m
0	71.753	5.5	71.274
0.5	70.467	6	71.512
1	70.975	6.5	70.652
1.5	71.687	7	71.348
2	71.24	7.5	71.23
2.5	71.537	8	70.516
3	71.695	8.5	71.691
3.5	71.587	9	71.401
4	71.133	9.5	71.262
4.5	70.955	10	71.871
5	71.124	---	---

Table-B2: Surface tension of 50 ml of BAC with 0.3mM concentration as a function of 1mM IC addition:

Volume of IC (ml)	surface tension of IC/0.3mM BAC system	Volume of IC (ml)	surface tension of IC/0.3mM BAC system
0	38.883	5.2	39.56
0.4	38.378	5.6	39.91
0.8	38.686	6	41.16
1.2	38.414	6.4	42.079
1.6	38.623	6.8	42.984
2	38.159	7.2	44.536
2.4	38.402	7.6	46.246
2.8	38.32	8	47.012
3.2	38.497	8.4	53.315
3.6	38.765	8.8	59.561
4	38.914	9.2	65.034
4.4	39.198	9.6	69.576
4.8	39.297	10	70.692

Table-B3: Surface tension of 50 ml of BAC with 0.1mM concentration as a function of

1mM IC addition:

Volume of IC (ml)	surface tension of IC/0.1mM BACsystem	Volume of IC (ml)	surface tesnsion of IC/0.1mM BAC system
0	38.79	2.4	41.333
0.2	38.19	2.6	41.804
0.4	38.214	2.8	42.269
0.6	38.615	3	44.232
0.8	38.954	3.2	46.828
1	39.254	3.4	49.201
1.2	39.464	3.6	52.209
1.4	40.099	3.8	57
1.6	40.486	4	61.902
1.8	40.756	4.2	67.189
2	41.096	4.4	69.963
2.2	41.128	4.6	71.652

Table-B5: Surface tension of 3mM BAC/3mM SDBS mixture as a function of 1mM IC addition:

Volume of IC (ml)	surface tension of IC/0.3mM BAC+0.3mM SDBS system	Volume of IC (ml)	surface tension of IC/0.3mM BAC+0.3mM SDBS system
0	28.21	5.2	28.3
0.4	28.31	5.6	28.23
0.8	28.29	6	28.2
1.2	28.14	6.4	28.25
1.6	28.18	6.8	28.28
2	28.29	7.2	28.29
2.4	28.32	7.6	28.3
2.8	28.29	8	28.36
3.2	28.36	8.4	28.28
3.6	28.23	8.8	28.25
4	28.23	9.2	28.31
4.4	28.19	9.6	28.24
4.8	28.21	10	28.27

Table-B6: Surface tension of 50 ml of BAC with 0.0625mM concentration as a function of 1mM IC addition:

Volume of IC (ml)	surface tension of IC/0.0625mM BAC system
0	47.012
0.2	47.125
0.4	47.38
0.6	47.5
0.8	47.809
1	48.55
1.2	49.064
1.4	50.978
1.6	52.058
1.8	57.411
2	63.272
2.2	71.031
2.4	70.67
2.6	70.89

Table-B7: Absorbance of IC-BAC complex as a function of addition 1mM of IC over 0.3mM of BAC:

volume of IC (ml)	Absorbance	volume of IC(ml)	Absorbance
1.5	0.368	2.8	0.766
1.6	0.401	2.9	0.788
1.7	0.439	3	0.813
1.8	0.475	3.1	0.838
1.9	0.509	3.2	0.858
2	0.542	3.3	0.881
2.1	0.576	3.4	0.903
2.2	0.606	3.5	0.925
2.3	0.636	3.6	0.94
2.4	0.665	3.7	0.942
2.5	0.694	3.8	0.824
2.6	0.719	3.9	0.759
2.7	0.741	4	0.663