Aggregation of Long Chain Anionic Surfactants

Suraj Mishra

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Author:	Suraj Mishra
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Supervisor (Arcada):	Mariann Holmberg
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Abstract:

Surfactants are chemical organic compounds tend to enrich strongly at interfaces which plays a vital role in both fundamental and applied sciences. They are amphiphilic in nature. Hydrophobic and hydrophilic parts are two main parameters in a surfactant molecule. Surface active compound gives a reduction in surface tension when it comes in contact with aqueous solution, which is the main fundamental property of surfactants. During the aggregation process the hydrophobic and hydrophilic part comes together as a monomer and forms a spherical shaped structure termed as micelles. Micelles have been a great interest in the field of bioscience. Critical micelle concentration of surfactant is an important term in surface chemistry, which is the concentration of solution above which all the surfactant monomers end to form micelles. This concentration provides a valuable guidance in comparing the detergency of surface active compounds. Micelles, surface tension, and critical micelle concentration are correlated terms with each other and can all be discussed together.

Surface tensions of different ionic liquids were measured in the Laboratory of Analytical Chemistry at the Department of Chemistry (University of Helsinki). Contact angle meter (CAM) was used for the measurement of surface tension. Fitting of curve method was applied to determine critical micelle concentration (CMC) value.

The value of CMC for all the ionic liquids was obtained as it was expected. Aggregation and surface property of newly synthesized ionic liquid was known by showing the strong surfactant property.

Keywords:	Surfactants, Micelles, Ionic liquids, Surface tension, CMC
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ACRONYMS AND ABBREVIATIONS

CAM	Contact angle meter
CMC	Critical micelle concentration
IL	Ionic liquid
RT	Room temperature
SDS	Sodium dodecyle sulfate
ST	Surface tension

1 Introduction

Currently the environmental awareness and the optimization of current energy technologies are so evidently emphasized, the unique characteristics features of surfactants and ionic liquids have drawn the attention of scientific communities and chemical industries around the world. The high potential displayed by these ionic liquids reveals applicability in different areas of chemistry, petrochemical and nuclear industry. In addition to this, these substances have some benefits regarding preservation of environment by stimulating the practice of green chemistry. Furthermore, in the field of heat transfer there is high demand of new heat transfer fluids that has the capability of replacing the existing environmentally harmful ones with properties that can result in maximum possible energy efficiency and contribution to the healthy and sustainable applications in different fields. Last but not least, production and rough management of different toxic chemicals that have been producing from different industries around the globe has unbalanced the life of water animals and hence putting them into danger and also welcoming different unwanted diseases. So we are not only focusing into the emerging applications of surfactants and ionic liquids but also the management techniques to preserve life cycles of different animals.

2 Background

Surfactants are known to play a vital role in several processes of interest in both fundamental and applied sciences. They are chemical organic compounds which tend to enrich strongly at interfaces. An important group of surfactants are amphiphilic molecules consisting of hydrophobic and hydrophilic parts. During aggregation of surfactants in aqueous solution the hydrophobic part, the tail, prefers an apolar environment towards an aqueous solution whereas hydrophilic part, the head, prefers to be in contact with aqueous solution. This is the main fundamental property of surfactant that makes them surface active. During the accumulation of monomers within the surfactant forming a colloidal structure is called as micelles. The critical micelle concentration (CMC) is the concentration of solution above which the monomeric surfactants end to form micelles. Another important parameter, crucial for aggregation, is the temperature. In order for the aggregation to take place, the temperature must be higher than the so-called Kraft point (temperature), which is the minimum temperature at which surfactants form micelles.

Surface tension of fluids plays a vital role in calculation of CMCs of surfactants. It is a property of liquid that causes it to act like an elastic membrane. The strength of surface tension of liquid depends upon the attraction force between the molecular particles within the liquid and with the particles of solid, liquid and gas with which it comes in contact. The angle that a liquid creates with a solid surface when both materials come in contact is referred as contact angle. The concentration of surfactant molecules in the solution, surface tensions of solution and the contact angle can all be discussed together.

3 Objectives

Following are the main objectives of this thesis;

i. To determine the CMC of different surface active compounds. The aggregation of sodium dodecyle sulfate (SDS) will be used as a bench mark. Specific focus will be on the determination of the CMC of novel ionic liquids, synthesized in the Laboratory of Organic Chemistry at the Department of Chemistry (University of Helsinki). The methodologies adopted rely on changes in the fluorescence, surface tension, or conductivity of solutions upon aggregation.

ii. To study novel ionic liquids, with specific focus on the impact of the ionic strength, pH, and type of solution on the aggregation of the ionic liquids. The effect of added organic solvents on the aggregation will be studied as well.

4 Literature review

5 Surfactants

5.1 Definition of surfactant

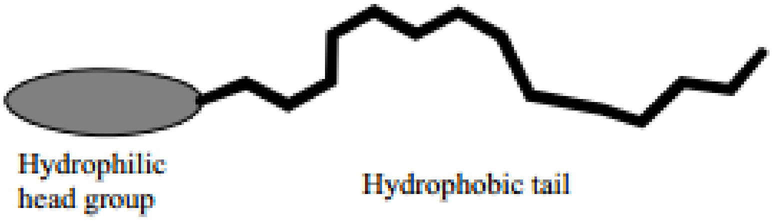
Surfactant is the contemporary name of surface active agents. In other words, they are characterized by its tendency to adsorb at surfaces and interfaces. They are organic compounds having molecules which have an ability to modify interface properties by lowering the surface or interfacial tension. However, this is not very different quality. Most water soluble organic compounds gives a reduction in surface and interfacial tension when it comes in reaction with aqueous solution but the effect is normally much less than that of surfactant. The term `surface´ and `interface´ denotes air phase and a boundary line between any two immiscible phases respectively. There exist five different interfaces altogether:

Solid-vapor *Surface*
Solid-liquid
Solid-solid
Liquid-vapor *Surface*
Liquid-solid [2]

The adsorbing phenomenon of surfactants at interfaces is to lower the free energy of that phase boundary. The amount of work necessary to expand the interface is equal to the interfacial free energy per unit area. Thus the surface tension of any liquid is equivalent to the interfacial free energy per unit area of the boundary between the liquid and air above it. When the boundary is covered with surfactant molecules the amount of work to expand the interface is reduced and hence the surface tension. The number of surfactant molecule packing at interfaces is directly proportional to the reduction in surface tension. The concentration of surfactant molecules at a boundary depends upon the structure of surfactant and the nature of two phases that meet at interfaces. In summary, the stronger the tendency to accumulate at interfaces, the better the surfactant. The most familiar use for surfactants are; soaps, laundry detergents, dishwashing liquids, and shampoos.

5.2 General structural feature

Surfactants are *amphiphilic* in nature. It has a Greek origin *amphi* meaning "*both"* and *phil* meaning "*like"*; that is, surfactants like both polar and nonpolar environment. They possesses fundamental characteristic molecular structural group that has very strong attraction for a solvent called *lipophilic* together with a group which has less attraction for a solvent called *lipophobic* group. The terms *hydrophilic* and *hydrophobic* respectively are normally used when the solvent is water, which is usually the case. The hydrophilic part contains solubilizing group such as; sulfate, sulfonate, and ethoxylate whereas the hydrophobic group contains hydrocarbon chains. Figure 2 shows the schematic illustration of surfactant monomer representing hydrophilic head group and hydrophobic tail group. [2]



[2]

Figure 1. Schematic illustration of a surfactant showing the head and tail groups.

When molecule with amphiphilic structure comes in contact with solvent, the hydrophobic group may alter the structure of a solvent by increasing the free energy of the system. When this incident occurs then it minimizes the contact between the hydrophobic groups and solvent. Usually when the solvent is water, the hydrophobic groups alter the structure of water by breaking the hydrogen bond. As a result of this alternation, some of the surfactant molecules are disqualified to the interfaces by orienting the hydrophobic groups towards, so as to minimize the contact with water molecules. The surfactant molecule with their hydrophobic groups facing towards the air forms a single layer and covers the surface of water. Since hydrophobic groups and air are nonpolar in nature, this decreases the dissimilarity between the two phases contacting each other at surface and hence decreases the surface tension of the water. On the other hand, the surfactant will not be expelled out from the solvent due to the presence of hydrophilic groups.

In this way, the amphiphilic structure of surfactant not only causes the reduction of surface tension of water and concentration of surfactant at interfaces but also orienting the hydrophilic groups towards an aqueous medium and hydrophobic groups oriented away from it.

5.3 Classification of surfactant

The hydrophilic group of a surfactant is an ionic or highly polar group whereas the hydrophobic group is usually a long chain hydrocarbon residue. According to the nature of hydrophilic group, surfactants are classified into four categories:

i.	Anionic	Having negative charge ions
ii.	Cationic	Having positive charge ions
iii.	Zwitterionic	Having both positive and negative charge ions
iv.	Nonionic	Without any charges

5.4 Surfactants are plentiful in nature

Due to the popular perception that natural is by definition and always better for the environment than synthetic ones. Natural surfactants are mostly referred as polar lipids, which are available in all living organisms. In biological system, surface active compounds functions in a same way as in the technical system: to overcome solubility problems, as emulsifiers, as dispersants, to modify surfaces and so on. Bile salts found in blood are extreme solubilizing agents of hydrophobic components. On the other hand, microorganisms are also efficient producers of surface active compounds. [4]

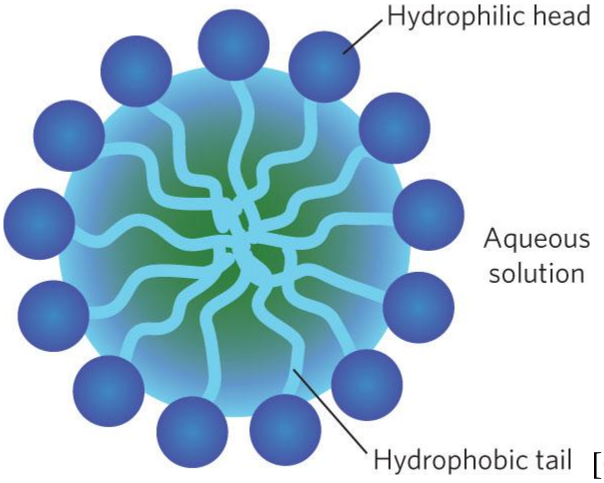
5.5 Environmental effects of surfactants

Surfactants are termed as `performance´ chemicals as they are used to perform some particular function in the product or system rather than other organic chemicals that are usually used to produce another chemical. Since the surfactants are used in processes or products, they have an impact in environment; people are concern about their effect, their biodegradability in the environment and toxicity to marine life in particular. As surfactants are necessary products worldwide as cleaning agents, their usage in a large quantities means that their waste and potential environmental pollutions are high. All surfactants may not be toxic but their usage in large volume with high concentration may act as agents for releasing toxic pollutants. There are plenty of compounds that can be used as surface active agents which are usually classified by their ionic behavior in aqueous solutions. There are many sources of surfactants that are directly or indirectly discharged into natural water and landfill. Surfactant are used as cleaning agents and therefore found in outlets from sewage systems whereas industrial sources include detergent formulation and textile productions. They are also used in agriculture as different forms of pesticides.

Due to the hydrophilic nature of surfactant molecule, they tend to be soluble in water but the solubility depends upon the specific chemicals and their structure. And hence surfactants are easily transferred to water resources through various media and it is toxicity to marine organisms. On the other hand, some cationic surfactants are strongly absorbed by clays. Significant absorption of some surfactant can be found in organic river sediments which are then directly harmful to water animals and human being as well. However, surfactants in these modern days are biodegradable under conditions of efficient sewage treatment but the degradation highly depends upon the structure of hydrophobic group present in the surfactant. [21]

5.6 Micelle formation by surfactants

Micelles have been a great interest in the field of organic and bio-chemistry. The monomers in the surfactant solution aggregates to form a liquid colloidal structure, which is referred as micelles. As described above in the general structural feature, surfactant has two molecular structural group called as; hydrophobic and hydrophilic part. During the aggregation process of micelles, the hydrophobic tail faces opposite to the water phase (combines in interface) and hydrophilic head faces towards the water phase. When the process continues it forms a colloidal structure. As the concentration of the surfactant solution increases, it becomes energetically favorable for individual monomers to combine together to form micelles. [7] Figure 2 shows the schematic illustration of spherical micelle of surfactant molecule in aqueous solution showing hydrophobic tail and hydrophilic head part.

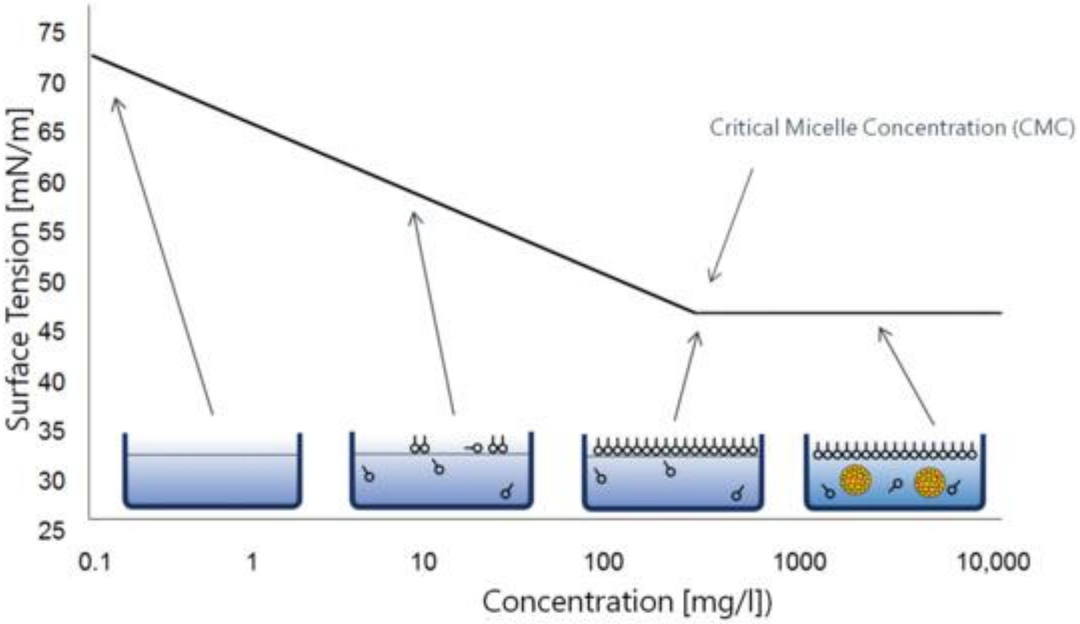


[6]

Figure 2. A schematic figure of a spherical micelle of surfactant molecules in aqueous solution.

5.7 Critical micelle concentration (CMC)

Critical micelle concentration (CMC) is defined as the concentration of surface active compounds above which micelle forms and all the additional surfactant added to the system will transformed into micelles spontaneously. This is an important feature of surfactant. During the micelle formation within the surfactant solution, the surface tension of liquid changes rapidly when the concentration of solution increases and when it reaches the CMC the surface tension remains relatively constant or decreases with a lower slope.



[8]

Figure 3. Surface tension of a surfactant solution with increasing concentration.

5.8 Determination of CMC and factors affecting CMC

Basically, the CMC is measured by intersecting two straight lines through a graphical representation of measured property versus concentration of solution. However, there are different methods for the determination of CMC for water soluble compounds. As for example; electrical conductivity, NMR chemical shifts, tensiometry, self diffusion coefficients, fluorescence intensity, and so on. During this thesis work, I have used tensiometry method for the determination of surface tension and hence the CMC. In this method, we measure the surface tension of surfactant with series of concentration and by analyzing the graphical relationship between the concentration and obtained surface tension; we can calculate CMC of surfactant. There are certain factors which affects the CMC of water soluble compounds, which are listed below;

i. Structure of surfactant i.e. the hydrophobic group and hydrophilic group
ii. Electrolyte
iii. Organic additives
iv. Presence of second liquid phase
v. Temperature

Different methods are available for the calculation of critical micelle concentration (CMC) of water soluble compounds. In this thesis, fitting of two straight lines from the obtained curve was used to determine the CMC of ionic liquids. The graph was plotted between the surface tension value and the concentration of ionic liquids. It was then broken into two nearly straight lines and the equation for the two straight lines was obtained. By solving the obtained equations, the value for CMC was obtained. A simple example of calculating the CMC is shown below in Figure 4, which shows the graphical representation of surface tension and concentration. It is clear in the graph that there can be two straight lines and are colored differently. So, in order to determine where exactly the breaking point is, we need to break the curve into two lines as shown in Figure 5 in order to find out the slope, in other word the breaking point.

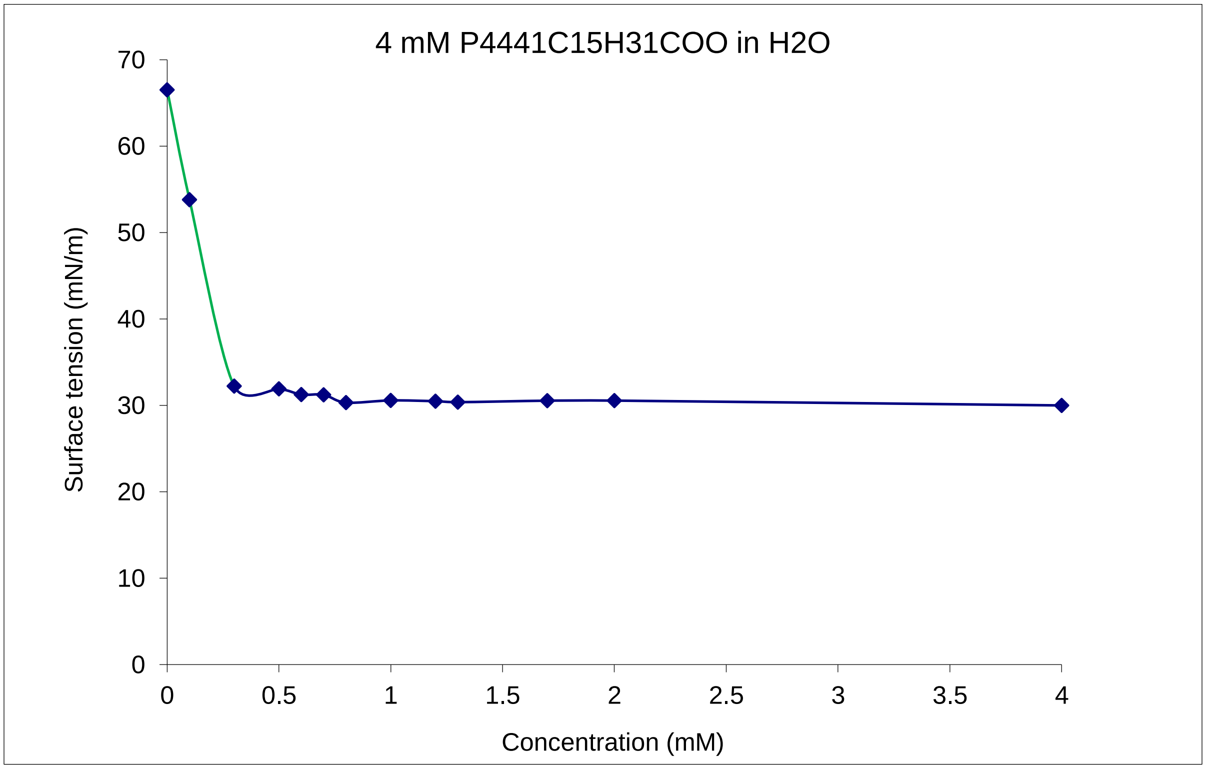
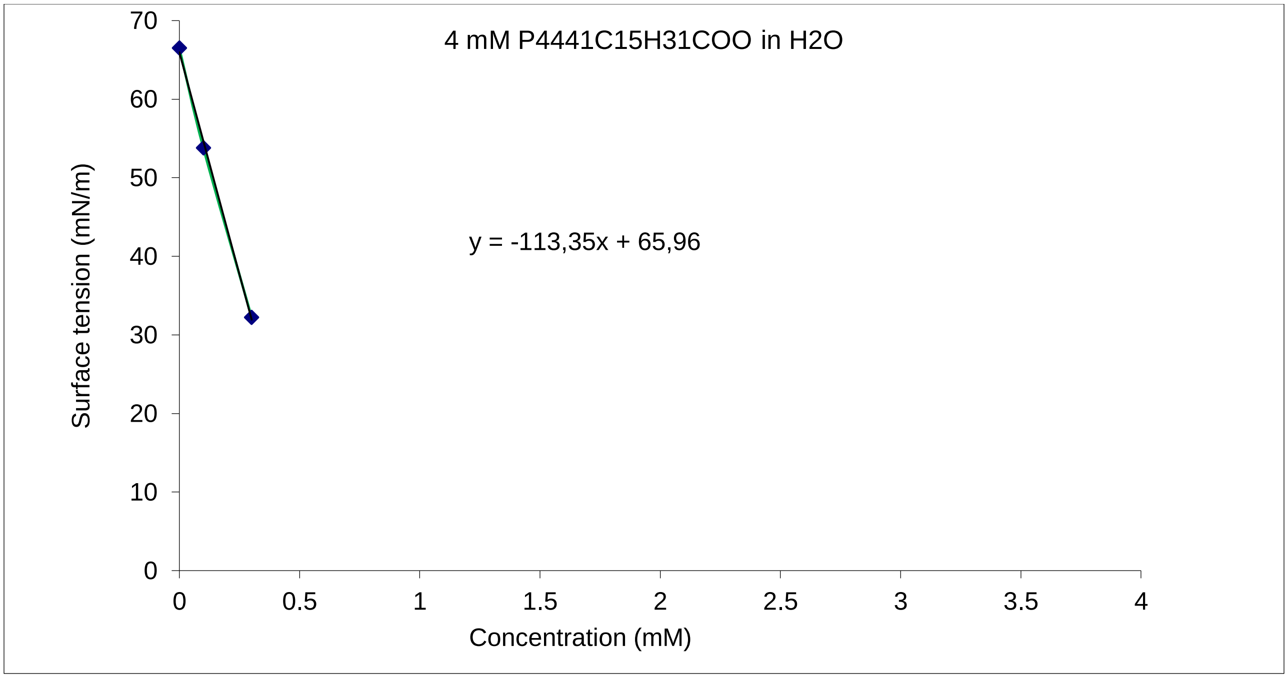


Figure 4. Graphical representation of surface tension and concentration to understand the breaking point.



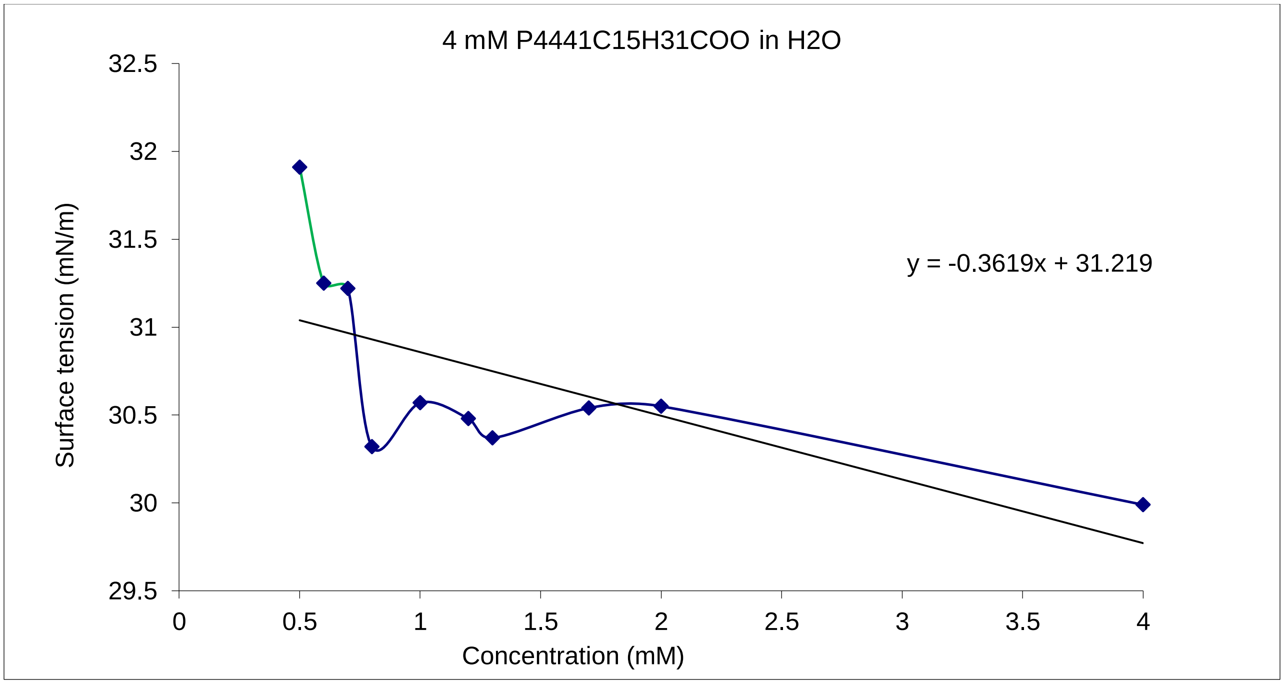


Figure 5. Breaking of curve into two straight lines

The equations for two lines were obtained which we can see in the above two graphs. In the equation the `y´ represents the surface tension value and `x´ represents the concentration value. So now we need to find the value of x which is the breaking point, in other words critical micelle concentration. To find this we need to solve these two equations.

$$y = -113.35x + 65.96 \qquad (1)$$

$$y = -0.3619x + 31.219 \qquad (2)$$

Hence, solving the equations will result in a value of $x = 0.31$, which in this case is the critical micelle concentration given in mM.

5.9 Surface and interfacial tension

Surface tension is an important natural property of liquids that highly influences the ecosystem. It is an elastic tendency of liquids to adhere at surfaces. There is an attraction between the molecules in liquid. The interaction of molecules in the liquid is balanced by the equal force of attraction in all direction. However, the molecules at surfaces of a liquid experiences little unbalance between the attraction forces. An example of adhering liquid drops at surfaces is shown in figure 6.

Surface tension is the cause of cohesive forces between liquid molecules. It results a net zero force when each and every internal molecules pull each other. But the molecules at surfaces do not have similar atoms on all sides and thus they are pulled inwards and try to cohere more strongly with those they are associated with around the surface. This creates some internal pressure and forces liquid surface to minimize its area. In this way, they create a surface layer which makes an object to move difficult through the surface rather than when it is totally immersed. This is the case when water is in contact with air. But the same phenomenon applies to those different liquids that do not mix each other and it is termed as interfacial tension.

On the other hand, surface tension can also be studied in terms of energy. As the internal molecules attracts each other, resulting a zero net force, the energy of molecules inside the liquid is reduced. But the boundary molecules do not have enough molecules in all the direction and hence there is much less attraction force, which results them having in a higher energy state. For the liquid to minimize its energy state, the boundary molecules must be minimized. And hence, less number of molecules in the boundary will results in a minimum surface area. The SI unit of surface tension is N/m. But in this thesis, mN/m has been used.


[24]

Figure 6. Water drops on the surface due to surface tension.

6 Application of surfactants

Surfactant lies in the heart of interfacial chemistry. Surfactant plays vital role in various sectors. It has an ability to radically alter the surface and inter face properties and thereby transforming themselves into micelles.[19] Surfactants are used together with polymers in wide range of applications. The formulation of lower molecular weight surfactant in combination with polymer which may or may not be highly surface active which provides high stability and rheological phenomenon in different specific applications. Surfactant reduces surface tension when it comes in contact with aqueous solutions and hence it has been widely used as detergent products and cleaning agents. It has many extensive practical applications and scientific interest due to their nature and properties.[9] Some of the important potential applications are listed below;

i. Surfactant as enhancers for percutaneous absorption
ii. Surfactants as flocculating agents
iii. Surfactants in mouth washes
iv. Surfactants in respiratory distress therapy
v. Surfactants in suppository bases
vi. Surfactants in suspension aerosols
vii. Surfactants in water based aerosols
viii. Surfactants for contact lens cleaning
ix. Surfactants in hard gelatin capsules
x. Surfactant as emulsifying agents
xi. Surfactants as cerumen removing solutions
xii. Surfactant influencing drug absorption
xiii. Surfactant in drug absorption from rectal suppositories
xiv. Surfactant used in transdermal penetration of drugs
xv. Surfactants in microbiology and biochemistry

7 Ionic liquid (IL)

Ionic liquids are organic solvents having low melting temperatures and thermal stability up to high temperature. More commonly, ionic liquids are liquid at room temperature. IL consist group of solvents that have very distinct chemical and physical characteristics that makes them suitable for many applications. It has high solubility for both polar and non-polar organic and inorganic substances presenting interesting solvation and coordination properties that depend on the nature of ions. In addition to this, they have low vapor pressure and hence ILs has become good alternative source for green solvents of potential commercial interest. Some examples of ionic liquids are; tributyltetradecylphosphonium chloride ($[P_{14444}]Cl$), tributylhexadecylphosphonium bromide ($[P_{16444}]Br$), tetrabutylphosphonium chloride ($[P_{4444}]Cl$), triisobutylmethylphosphonium tosylate ($[P_{14444}]OTs$), and so on. Ionic liquids has already been applied in many chemical reactions, such as polymerization, esterification and electrochemical synthesis, which helps for the fast reaction process, high conversion rate and many other activities. [10, 13-16]

During this thesis work I have worked with several ionic liquids and studied about their surface tension reduction in water soluble compounds and did mathematical calculation of their critical micelle concentrations (CMC).

8 Properties of Ionic liquids

Ionic liquids are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. They have very important properties in physics and chemistry such as, viscosity, density, melting point, and thermal stability. The physicochemical properties of ionic liquids can be altered by adding impurities such as organic solvents, chloride ions, and water.[11] Some important properties of ionic liquid are discussed below;

Ionic liquids have different physico-chemical properties regarding melting point, densities, thermal stability, viscosity, solubility, and vapor pressure. Melting point is one of the most important properties of ionic liquids. This is the most significant property of ionic liquid that can directly be correlated with the structure and composition. The cation group has more visible impact on the melting point of ionic liquids. The lower symmetry cation decreases the melting point of ionic liquids. Also the melting point of ionic liquid reduces when the size of anions increases [11-12]. Density of ionic liquid is related to the volume of present anions and cations. Normally ionic liquids are denser than water. The N-alkyl chain of cation is the main factor on determining the densities of ionic liquids. The larger the volume of cations and hence the smaller density of ionic liquids. Anions also have effects on density, when the volume of anion increases, so does the density [12]. Most of the ionic liquids are stable at 400^0C and above it. The thermal decomposition of ionic liquids mostly depends upon the nature of anions and it is inversely proportional to the hydrophilicity of anions [11].

Basically ionic liquids are high viscous chemical substances. That is why it is less suitable for solvent media during a chemical reaction or for any other applications. Viscosity of ionic liquids changes drastically upon addition of solvent. Most of the ionic liquids are quite good solvents in many chemical reactions. But some of the ionic liquids that were used during the experiment were not quite fast soluble in water and needed some heat. However, the solubility of ionic liquids is connected with the properties of cations and anions. The vapor pressure of ionic liquid is quite low even at higher temperature in vacuum.

9 Applications of Ionic Liquids

Ionic liquids have unique properties and unlimited structural combinations with great potential applications in different fields. They have received great interest because of their unique properties as liquids. Because of high ion conductivity and nonvolatile nature of ionic liquids which is an important property of electrolyte solutions, they are used in energy devices. Ionic liquids are more advanced and safe source for electrolyte solutions because of its non flammability property, which is of great advantage as safety is becoming more valuable issues nowadays. As ionic liquids are only composed of ions showing very high ionic conductivity, non flammability, and non volatility these are emerging practical materials in the field of electrochemistry. Most of the energy devices in motor vehicles and in many other field can accidently explode or burst into flames, ionic liquids can be a good option as it is very safe liquid with many new open possibilities. Ionic liquids are versatile material so there are many significant and unpredicted applications. [17] Their unique properties and unlimited structural combinations give ionic liquids great potential for applications in many fields such as electrolytes, lubricants, solvents in organic reactions, bio processing, cellulose dissolution, wood extraction, and so on. Some other potential application fields of ionic liquids are listed below;

i. Chemical industry
ii. Batteries
iii. Pharmaceuticals
iv. Food and bio-products
v. Cellulose processing
vi. Dispersants
vii. Solar thermal energy
viii. Waste recycling
ix. Nuclear fuel reprocessing
x. Algae processing
xi. Fundamental research

10 Experimental Section

The experimental section includes about the surface tension studies and critical micelle concentration calculation of three different ionic liquids. All the ionic liquids were synthesized at the organic laboratory of University of Helsinki and all the materials and instruments that were used during the whole experiment were from the chemistry department of University of Helsinki. Measurement of surface tension and calculation of critical micelle concentration values and procedures are explained in three different stages and results, discussions and conclusion are drawn in combination of all.

10.1 Materials

The studied ILs comprised tributylmethyl myristic acid (P4441C13H27COO; M =444.71 g/mol), tributylmethyl palmitic acid (P4441C15H31COO; M=472.76 g/mol), and tributylmethyl steric acid (P4441C17H35COO; M=500.82 g/mol) (the general structural feature is shown below in fig 7, 8, and 9 respectively), H_2O, buffer, pipettes, pipette tips, micro test tubes, shaker, ultrasonic theater, heater, round bottom flask, beaker, microgram, dry air, acetone, methanol, contact angle meter (CAM).

i. P4441C13H27COO

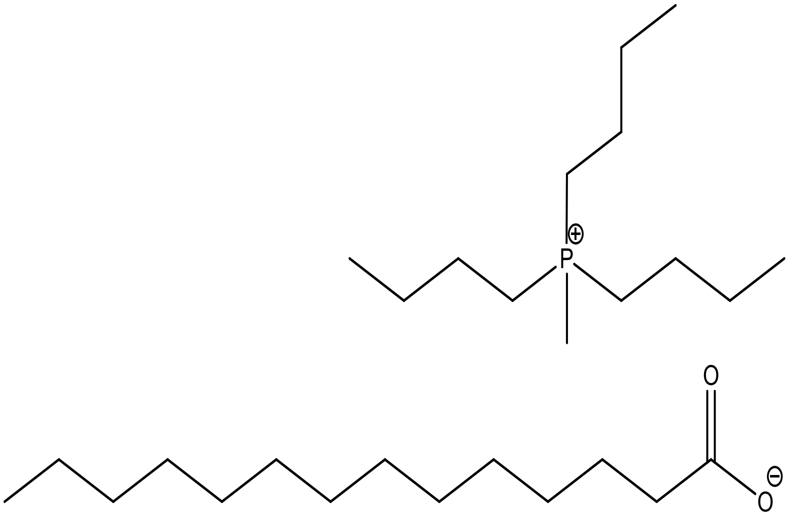


Figure 7. General structure of tributylmethyl myristic acid (P4441C13H27COO).

ii. P4441C15H31COO

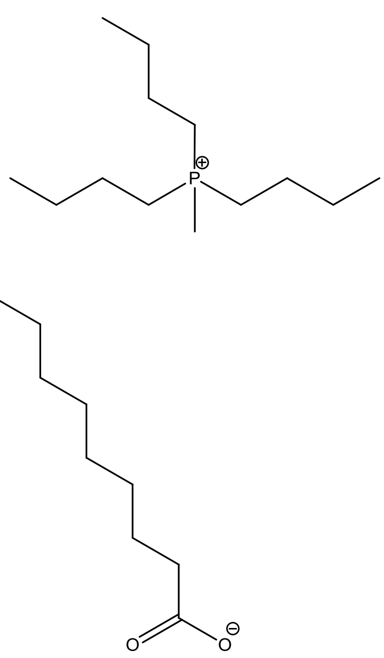


Figure 8. General structure of tributylmethyl palmitic acid (P4441C15H31COO).

iii. P4441C17H35COO

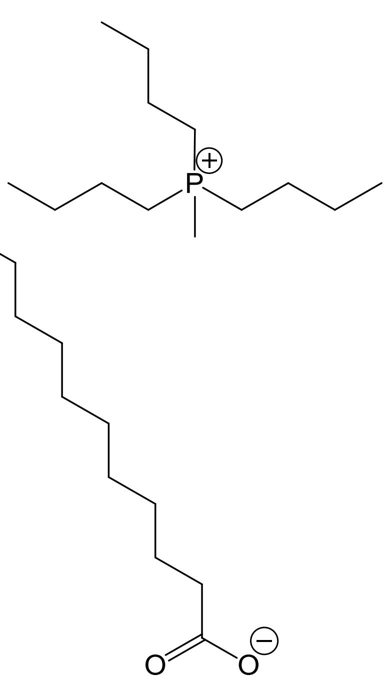


Figure 9. General structure of tributylmethyl steric acid (P4441C17H35COO).

10.2 Procedure

Surface tension of different ionic liquids (all are surface active compounds, surfactants) with water and buffer were measured at different concentrations. However, in this thesis only three ionic liquids are included and the surface tension was measured at different concentrations in water. Samples were prepared with water as a solvent in different concentration of ionic liquids. Procedure on how the samples were prepared and the different data for the calculations are mentioned below separately.

After the samples were prepared, then the surface tension was measured with the contact angle meter (CAM). CAM is a computer controlled and user programmable video based instrument specially designed for the measurement of surface and interfacial tension, contact angles, and surface free energy of solids. It includes a video camera, an adjustable sample stage, and a LED light source. Details on how to measure the surface tension and all the steps on the whole process are included as an extra attachment on the last pages of this thesis, where all the necessary steps are presented in details.

Preparation of IL solutions

Preparation of 8 mM P4441C13H27COO in H_2O

10 mL of 8 mM P4441C13H27COO (M = 444.7167 g/mol) stock solution was prepared by dissolving of appropriate amount (0.03558 g, calculated according eq. (1)) of IL in H_2O.

$m = c * V * M$……… (1) [25]

In equation (1), m stands for the mass (g) of the IL, c is the concentration (mol/l) of the stock solution, V is the volume, and M is the molar weight (g/mol) of the ionic liquid. The ionic liquid was dissolved and stock solution was shaken for 1 minute. The IL stock solution was degased using ultrasonic bath for 15 min and kept in dark at room temperature (RT).

P4441C13H27COO ionic liquid samples (1 mL each) for pendant drop surface tension measurements (Table 1) have been prepared by mixing of calculated amount (eq. (2)) of IL and H_2O.

$c_1 V_1 = c_2 V_2$……… (2) [25]

Table 1. Volumes of P4441C13H27COO and water in accordance with P4441C13H27COO concentration

P4441C13H27COO concentration (mM)	**P4441C13H27COO in H_2O (µL)**	**H_2O (µL)**
0.00	0	1000
0.50	62.5	937.5
1.00	125	875
1.40	175	825
2.00	250	750
2.40	300	700
3.00	375	625
3.40	425	575
4.00	500	500
5.00	625	375
6.00	750	250
8.00	1000	0

Preparation of 4 mM P4441C15H31COO in H2O

c = 4 mM = 0.004 mol/L
V = 10 mL = 0.01 L
M = 472.77 g/mol
m =?
m= c*V*M……… (1) [25]

m = 0.004 mol/L * 0.01 L * 472.77 g/mol = **0.01891 g**
Hence the required mass of P4441C15H31COO is 0.01891 g.

Procedure

10 mL of 4 mM P4441C15H31COO (M=472.76 g/mol) stock solution was prepared by dissolving of appropriate amount (0.01891 g, calculated according eq. (1)) of IL in H_2O. The ionic liquid was dissolved and stock solution was shaked for 1 minute. The IL stock solution was degased using ultrasonic bath for 15 min and kept in dark at room temperature (RT). P4441C15H31COO ionic liquid samples (1 mL each) for pendant drop surface tension measurements (Table 3) have been prepared by mixing of calculated amount (eq. (2)) of IL and H_2O.

$c_1 V_1 = c_2 V_2$……… (2) [25]

Table 2. Volumes of P4441C15H31COO and water in accordance with P4441C15H31COO concentration

P4441C15H31COO concentration (mM)	P4441C15H31COO in H_2O (µL)	H_2O (µL)
0.00	0	1000
0.10	25	975
0.20	50	950
0.30	75	925
0.40	100	900
0.50	125	875
0.60	150	850
0.70	175	825
0.80	200	800
1.00	250	750
1.20	300	700
1.30	325	675
2.00	500	500

Preparation of 2 mM P4441C17H35COO in H2O

c = 2 mM = 0.002 mol/L

V = 10 mL = 0.01 L

M = 500.8234 g/mol

m =?

m = c * V * M……… (1) [25]

m = 0.002 mol/L * 0.01 L * 500.8234 g/mol = **0.01002 g**

Hence the required mass of P4441C15H31COO is 0.01002 g.

Procedure

10 mL of 4 mM P4441C17H35COO (M=500.82 g/mol) stock solution was prepared by dissolving of appropriate amount (0.01002 g, calculated according eq. (1)) of IL in H_2O. The ionic liquid was dissolved and stock solution was shaked for 1 minute. The IL stock solution was degased using ultrasonic bath for 15 min and kept in dark at room temperature (RT).

P4441C17H35COO ionic liquid samples (1 mL each) for pendant drop surface tension measurements (Table 5) have been prepared by mixing of calculated amount (eq. (2)) of IL and H_2O.

$c_1 V_1 = c_2 V_2$……… (2) [25]

Table 3. Volumes of P4441C17H35COO and water in accordance with P4441C17H35COO concentration

P4441C17H35COO concentration (mM)	P4441C15H31COO in H_2O (µL)	H_2O (µL)
0.00	0	1000
0.10	50	950
0.30	150	850
0.40	200	800
0.50	250	750
0.60	300	700
0.70	350	650
0.90	450	550
1.00	500	500
1.30	650	350
1.50	750	250
1.70	850	150
2.00	1000	0

11 Results and Discussions

Measurements of surface tension

Surface tension was measured of four different drops of liquid of each sample, capturing twenty frames in twenty seconds. The obtained data for surface tension measurement including concentration of each ionic liquid are presented in tables 4, 5, and 6 below along with the figures of graphical representation of mean surface tension versus concentration of ionic liquid.

Surface tension for P4441C13H27COO

Data is shown in table 4 according to concentration of P4441C13H27COO and the schematic presentation of the concentration of the IL as a function of the surface tension is shown in Figure 10.

Table 4. Surface tension measurements of P4441C13H27COO ionic liquid

P4441C13H27COO concentration (mM)	**Surface tension (mN/m)**				**Mean surface tension (mN/m)**
0.00	65.66	65.09	65.16	65.00	**65.23**
0.50	42.52	41.93	41.34	43.87	**42.41**
1.00	36.54	37.71	36.85	36.71	**36.95**
1.40	29.11	28.71	28.52	28.67	**28.75**
2.00	25.79	25.92	25.84	25.97	**25.88**
2.40	25.72	25.65	25.60	25.73	**25.68**
3.00	26.09	26.24	26.16	26.21	**26.17**
3.40	26.17	25.93	26.01	26.17	**26.07**
4.00	26.77	26.70	26.57	26.35	**26.60**
5.00	27.71	27.75	27.47	27.60	**27.63**
6.00	28.18	28.26	28.35	28.19	**28.25**
8.00	26.93	27.00	27.06	26.85	**26.96**

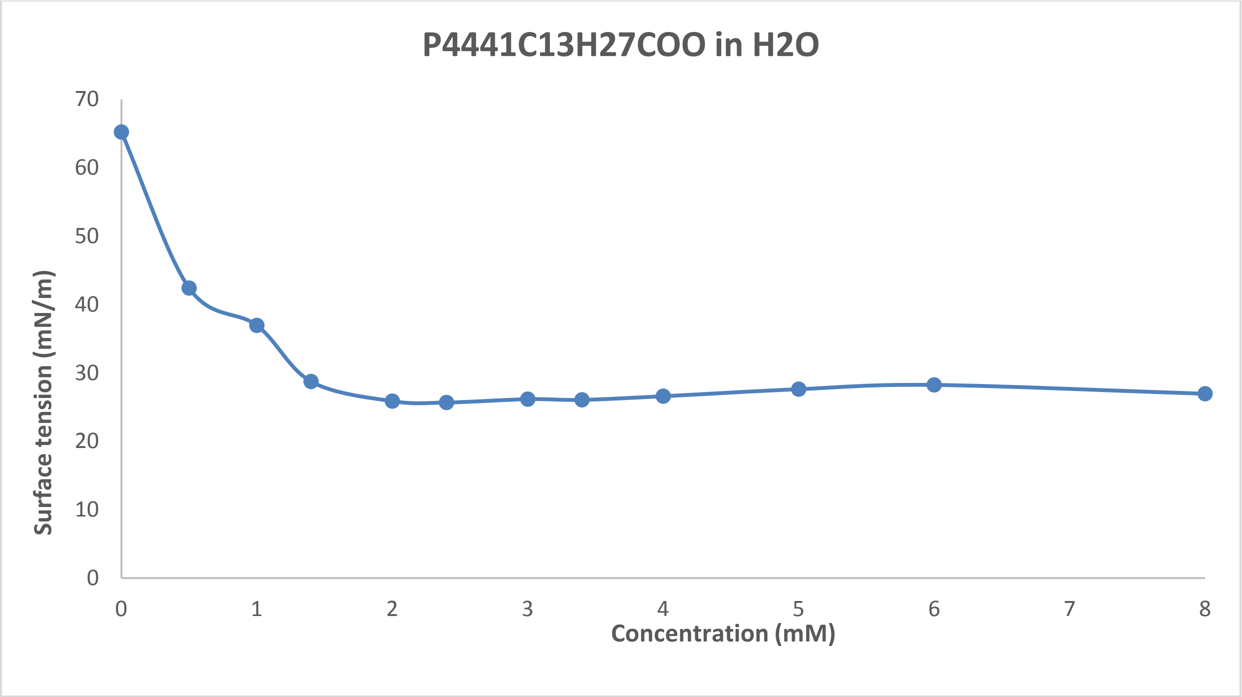


Figure 10. Graphical representation of surface tension and concentration of P4441C13H27COO

Calculation of CMC for P4441C13H27COO

For the calculation of critical micelle concentration fitting curve method is used as discussed in the method of calculating CMC and hence the value for x (CMC) is then calculated by solving two obtained equations.

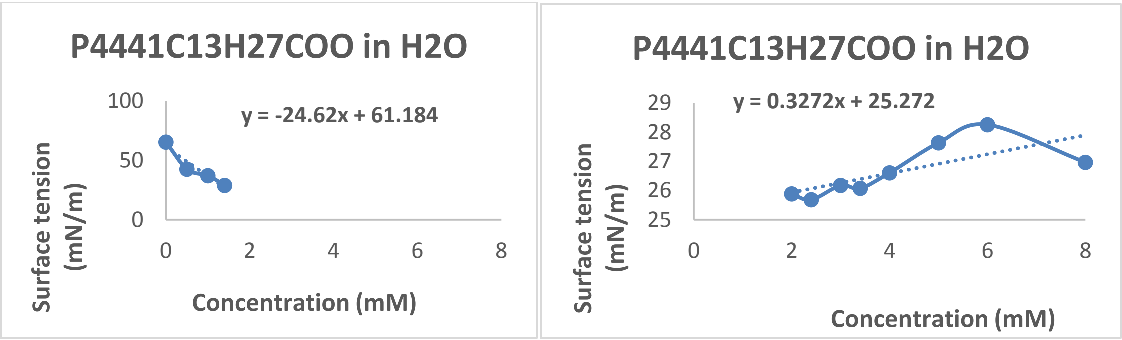


Figure 11. Fitting curve lines for CMC of P4441C13H27COO

Now, solving the two obtained equations;

$y = -24.62x + 61.184$

$y = 0.3272x + 25.272$

$x = 1.45$

Hence the critical micelle concentration for ionic liquid P4441C13H27COO is calculated to be **1.45 mM**.

Surface tension for P4441C15H31COO

Data is shown in table 5 according to concentration of P4441C15H31COO and the schematic presentation of the concentration of the IL as a function of the surface tension is shown in Figure 12.

Table 5. Surface tension measurements of P4441C15H31COO ionic liquid

P4441C15H31COO concentration (mM)	**Surface tension (mN/m)**				**Mean surface tension (mN/m)**
0.00	66.25	66.05	66.15	66.11	**66.14**
0.10	50.37	51.01	50.52	51.13	**50.76**
0.20	40.31	40.41	41.09	40.05	**40.45**
0.30	34.69	35.27	35.43	35.28	**35.18**
0.40	31.13	31.77	32.40	32.87	**32.04**
0.50	30.65	30.65	31.13	31.07	**30.88**
0.60	30.33	31.09	30.74	30.81	**30.74**
0.70	30.87	31.06	30.66	31.06	**30.90**
0.80	30.79	30.74	30.70	30.69	**30.73**
1.00	30.26	30.42	30.67	30.76	**30.53**
1.20	30.17	30.47	30.62	30.69	**30.49**
1.30	30.42	30.61	30.58	30.56	**30.54**
2.00	30.28	30.22	30.18	30.13	**30.20**

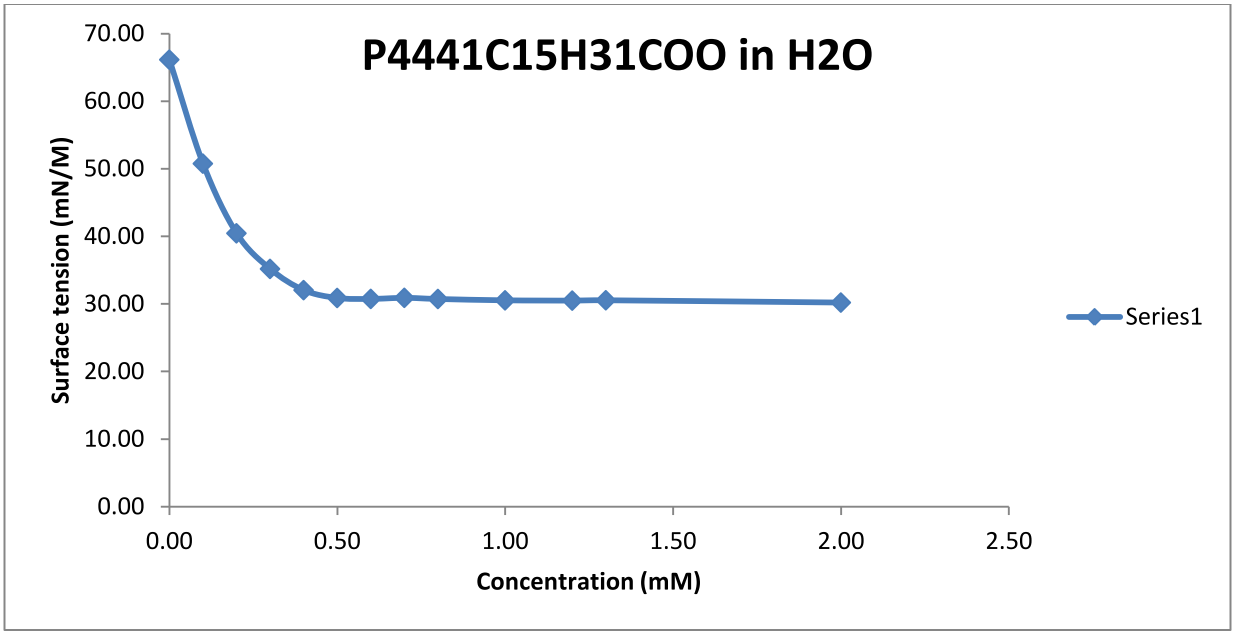


Figure 12. Graphical representation of concentration and surface tension of P4441C15H31COO

Calculation of CMC for P4441C15H31COO

For the calculation of CMC, fitting of two straight lines is used and then the value for CMC is calculated by solving the obtained equations of two lines.

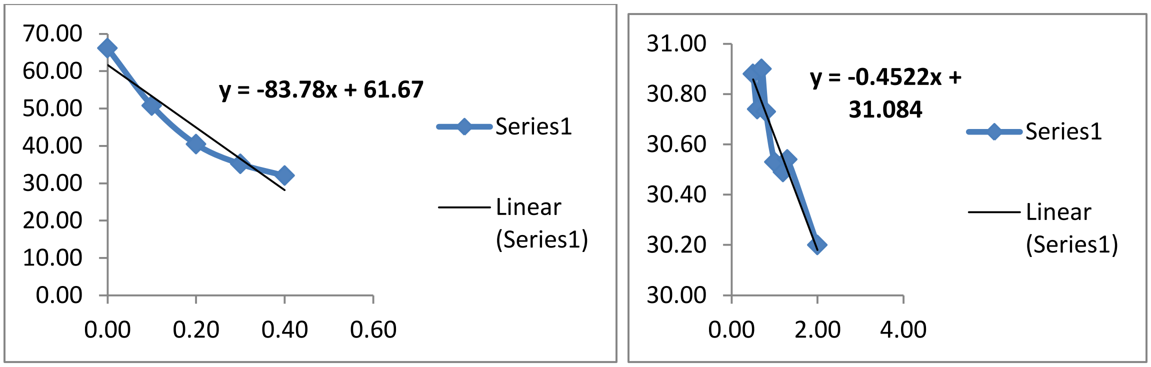


Figure 13. Fitting curve lines for CMC of ionic liquid P4441C15H31COO

$y = -83.78x + 61.67$

$y = -0.4522x + 31.084$

$x = 0.38$ mM

Hence, the critical micelle concentration for ionic liquid P4441C15H31COO is calculated to be **0.38 mM** when soluble in water.

Surface tension for P4441C17H35COO

Data is shown in table 6 according to concentration of P4441C17H35COO and the schematic presentation of the concentration of the IL as a function of the surface tension is shown in Figure 14.

Table 6. Surface tension measurements of P4441C17H35COO ionic liquid

P4441C17H35COO concentration (mM)	**Surface tension (mN/m)**				**Mean surface tension (mN/m)**
0.00	66.25	66.05	66.15	66.11	**66.14**
0.10	62.97	61.91	62.20	62.22	**62.32**
0.30	40.93	41.18	41.89	40.99	**41.25**
0.40	39.25	39.68	38.94	39.48	**39.34**
0.50	37.08	37.62	37.85	37.88	**37.61**
0.60	37.29	36.77	36.83	36.58	**36.87**
0.70	35.57	36.06	36.41	36.67	**36.98**
0.90	35.97	36.04	36.73	36.05	**36.20**
1.00	35.87	35.88	35.69	36.26	**35.92**
1.30	34.59	35.11	35.35	35.81	**35.43**
1.50	35.19	35.56	35.74	35.94	**35.60**
1.70	34.97	35.35	35.65	35.51	**35.37**
2.00	35.46	35.58	35.55	35.34	**35.48**

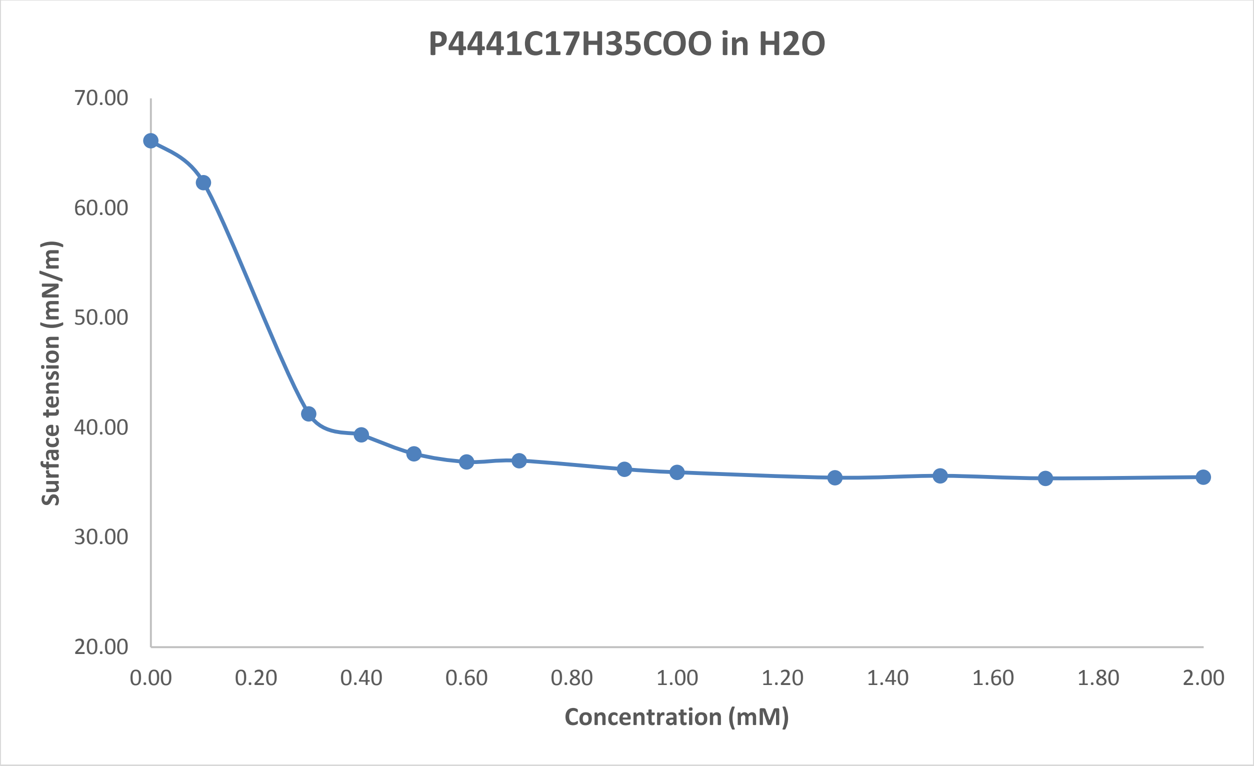


Figure 14. Graphical representation of concentration and surface tension of P4441C17H35COO

Calculation of CMC for P4441C17H35COO

For the calculation of CMC, fitting line method was used and then the value for CMC is calculated by solving the obtained equations of two lines.

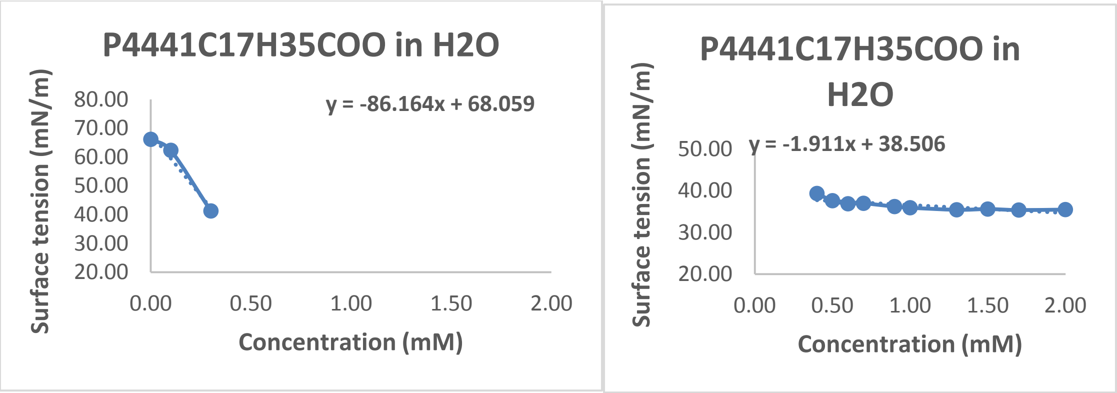


Figure 15. Fitting curve lines for CMC of ionic liquid P4441C17H35COO

$y = -86.164x + 68.059$

$y = -1.911x + 38.506$

$x = 0.35$

Hence the critical micelle concentration for ionic liquid P4441C17H35COO is calculated to be **0.35 mM** in water.

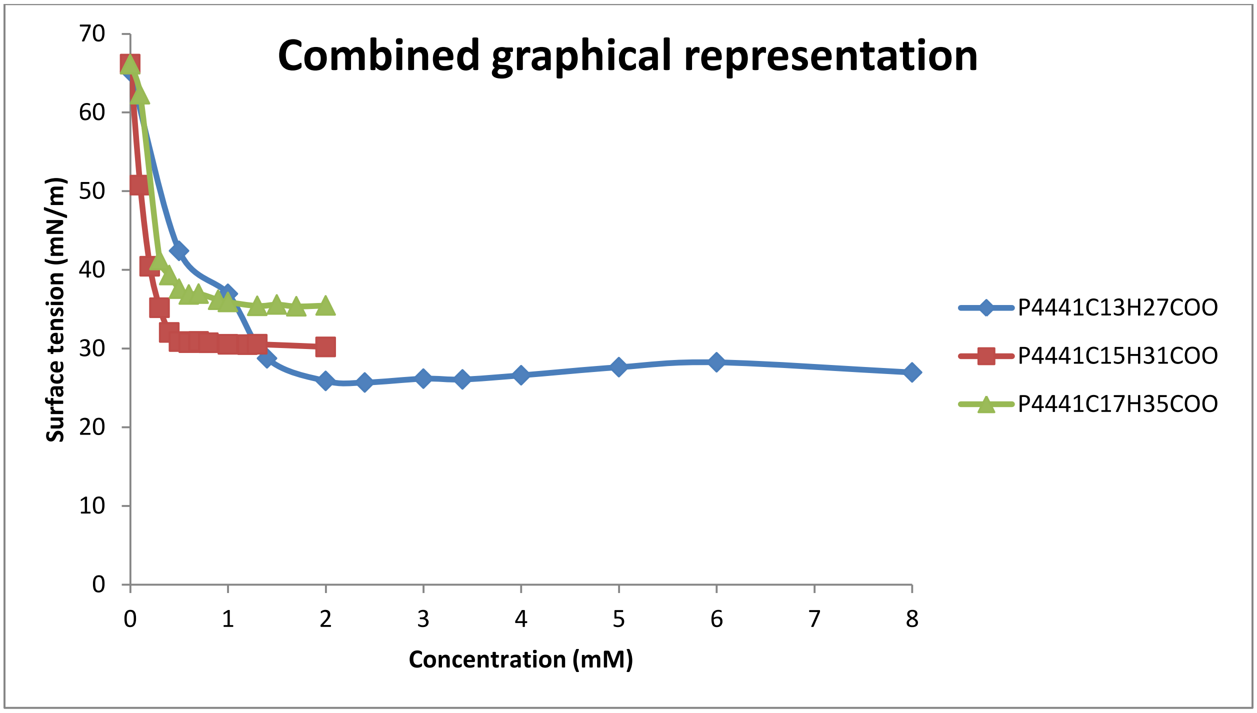


Figure 16. Graphical representation surface tensions and concentrations of all ionic liquids.

As shown in the graph above, the surface tension for ionic liquids P4441C15H31COO and P4441C17H35COO were measured at the different concentrations ranging from 0 mM to 2 mM and for ionic liquid P4441C13H27COO the concentration range was used from 0 mM to 8 mM. The surface tension for water was obtained to be around 66 mM in each case. Surface tension of ionic liquids P4441C15COO and P4441C17H35COO was decreased up to around 0.5 mM concentrations and after that the surface tension remained constant with a very slight change. However, the surface tensions for the ionic liquid P441C15H31COO compared to ionic liquid P4441C17H35COO was obtained to be little less at around same concentrations. And the critical micelle concentration for P4441C15H31COO was obtained to be 0.38 mM whereas, for P44410C17H35COO it was 0.35 mM.

In the case of ionic liquid P4441C13H27COO, surface tensions were measured up to 8 mM concentration. The graph shows that the concentration below 1.4 mM, surface tensions were little higher than those of P4441C15H31COO and P4441C17H35COO measurements. But after the concentration 1.4 mM the surface tension values were slightly constant although there were some fluctuations. And finally the critical micelle concentration for P4441C13H27COO was obtained to be 1.45 mM.

The obtained CMC result of ionic liquid P4441C13H27COO 1.45 mM shows that this surfactant has strong impact or efficiency at 1.45 mM concentration. In other words less surfactant is needed to form micelles at this concentration. However the surface tension data of P4441C13H27COO shows that there might be slight fluctuation in forming micelles on increasing the concentration. On the other hand, in the case of ionic liquids P4441C15H31COO and P4441C17H35COO the CMC value was obtained at 0.38 mM and 0.35 mM respectively, nearly the same range of 0.36 mM (average value). This value shows that the ionic liquid P4441C17H35COO has more surfactant efficiency than that of ionic liquid P4441C15H31COO.

12 Conclusion

Surface tensions of different surface active compounds were measured and the values for CMCs were calculated. The measurement of surface tension was done at different concentrations of three different ionic liquids with water as a solvent through contact angle meter method. The values of surface tension obtained from contact angle meter were quite realistic and the process is well established. The method also compares the data that was obtained from fluorescence and conductivity method from different research and hence concludes the results. The effect of temperature upon solubility of ionic liquids with water was studied as well.

Three different ionic liquids which were newly synthesized in the Laboratory of Organic Chemistry at the Department of Chemistry (University of Helsinki) were analyzed through the surface tension measurement of possibly having their great potential in the preservation of marine life which naturally contributes for the better environment. Hence the surface properties of these ionic liquids were tasted by determining surface tension at different concentration ranges and thereby calculating CMCs.

Fitting of curve method was quite convenient for the determination of CMC for all ionic liquids through surface tension measurement. The method used was reliable and quite simple. The CMC values for all ionic liquids were obtained at low concentration level, which indicates that less surfactant is needed to saturate interfaces and to form micelles because of showing strong surfactant efficiency. On the other hand, the value of CMC provides a strong guideline for comparing different surface active compounds.

Hence, the obtained data shows that using a contact angle meter for determining the surface tension of surfactants, in order to achieve information about the aggregation of surfactants is a well-working methodology. In this work the CMCs of several ILs were determined, which is of great importance for getting a deeper understanding of their impact on the environment.

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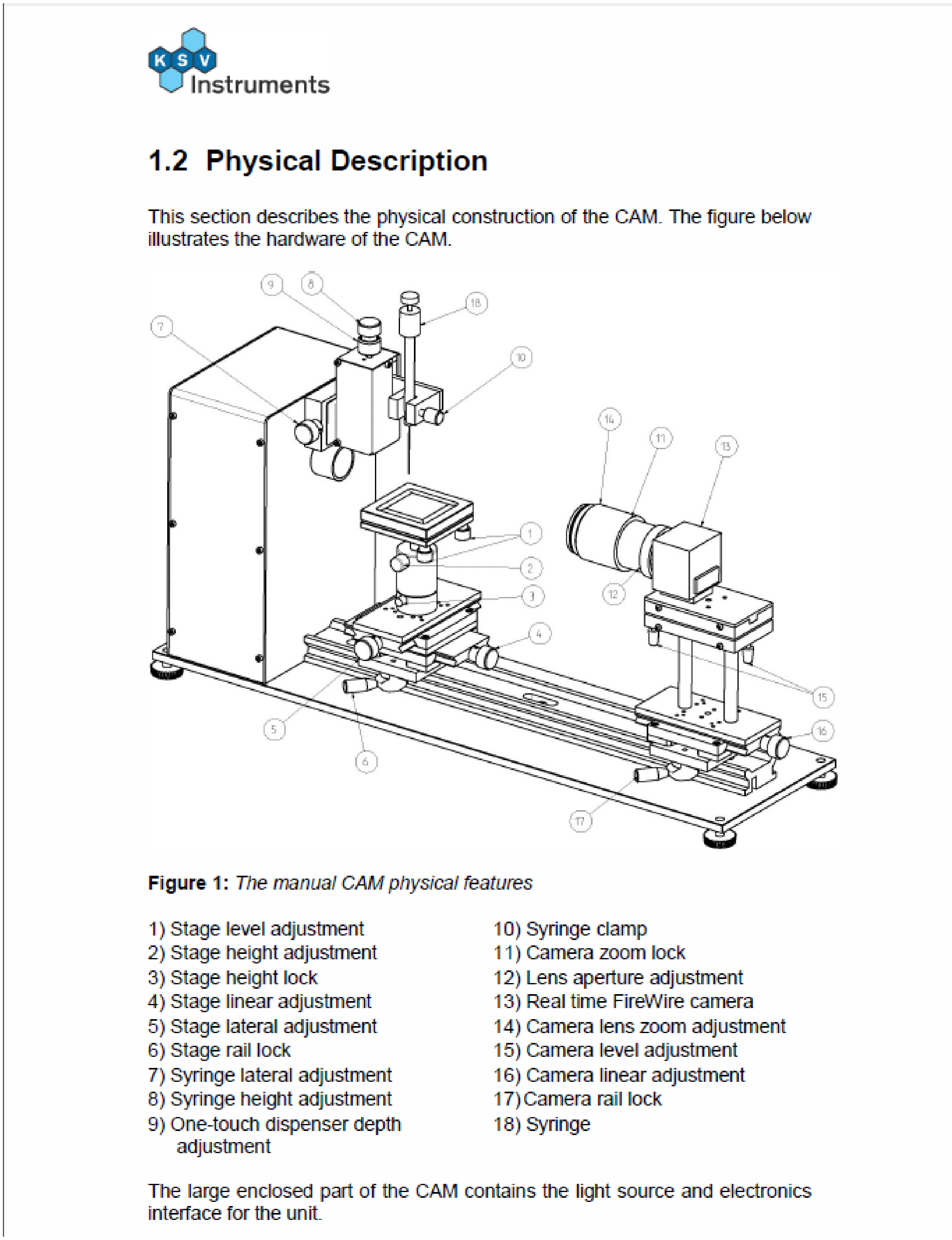
14 Appendix

Instruction manual for measurement of surface tension



KSV Instruments

1.2 Physical Description

This section describes the physical construction of the CAM. The figure below illustrates the hardware of the CAM.

Figure 1: *The manual CAM physical features*

1) Stage level adjustment
2) Stage height adjustment
3) Stage height lock
4) Stage linear adjustment
5) Stage lateral adjustment
6) Stage rail lock
7) Syringe lateral adjustment
8) Syringe height adjustment
9) One-touch dispenser depth adjustment
10) Syringe clamp
11) Camera zoom lock
12) Lens aperture adjustment
13) Real time FireWire camera
14) Camera lens zoom adjustment
15) Camera level adjustment
16) Camera linear adjustment
17) Camera rail lock
18) Syringe

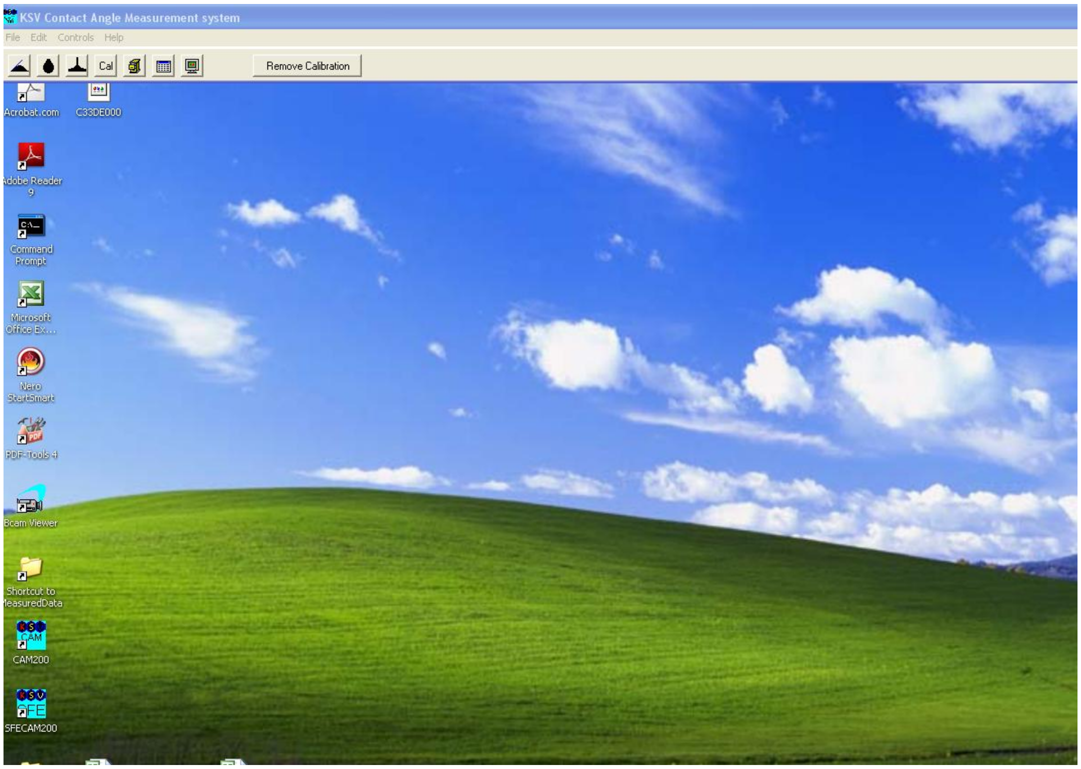
The large enclosed part of the CAM contains the light source and electronics interface for the unit.

Surface tension

Surface tension is a property of a liquid surface that causes it to act like a stretched elastic membrane. The strength of membrane depends upon the attraction force among the particles of the liquid itself and with the particles of the gas, solid, or liquid with which it comes in contact.

Steps of operating CAM 200 for surface tension measurement

- Before you start measuring the surface tension, it is important to **clean the needle with acetone and methanol** respectively from **both inside and outside**. Later on, the needle should be **cleaned with water from inside**.
- Always start measuring from the **lowest concentration sample**, before you measure always remember to **wash the syringe and needle,** little bit with the new concentration sample.
- Turn on the light of camera and open the software (CAM 200).



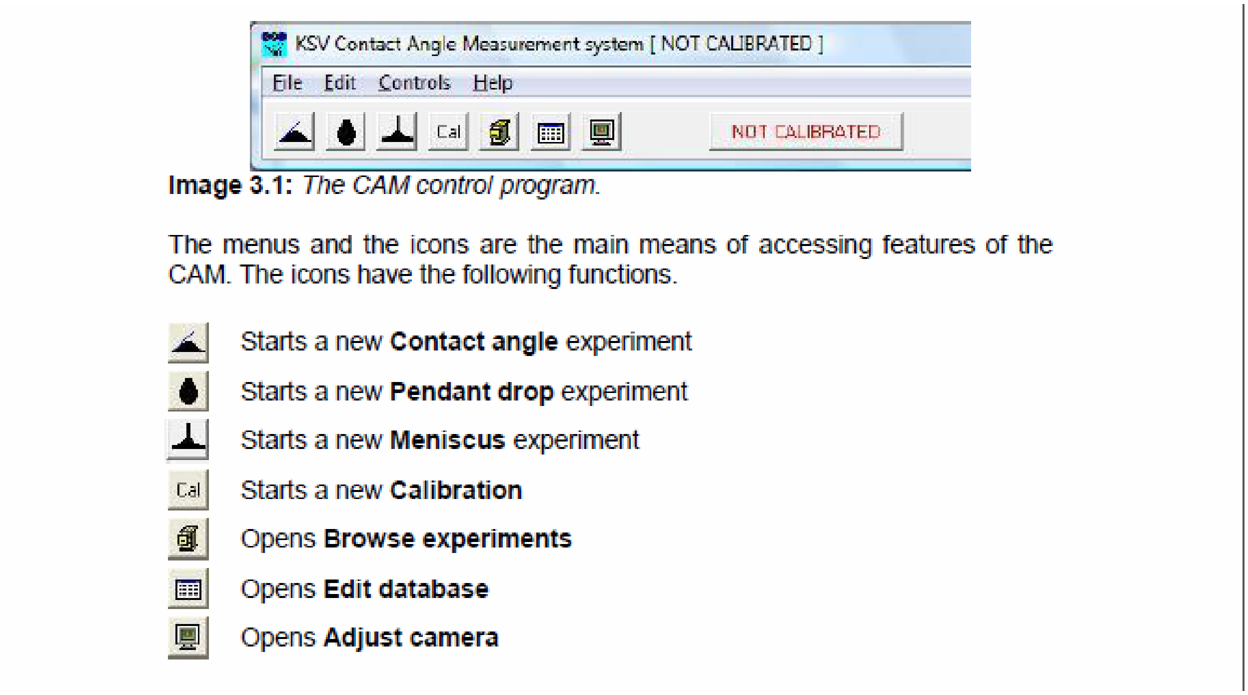
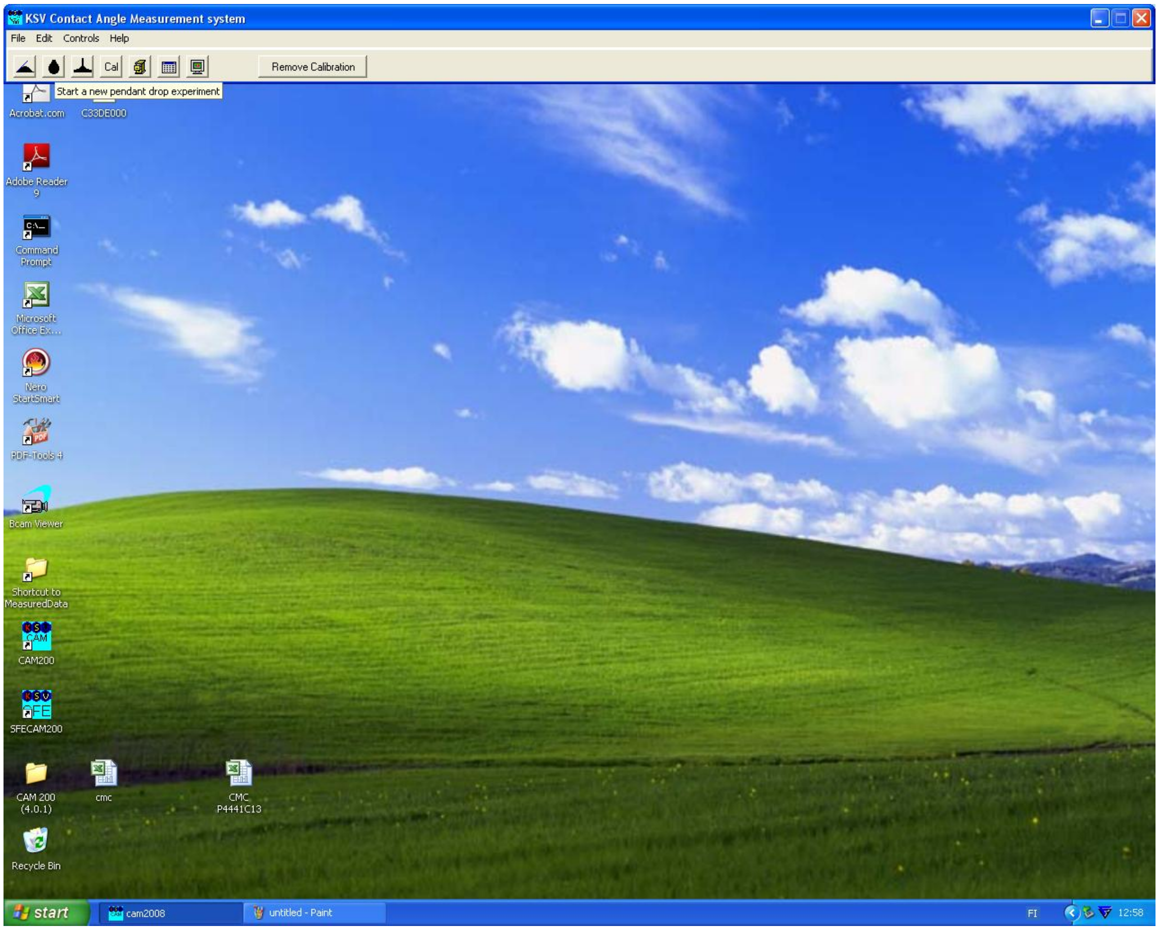


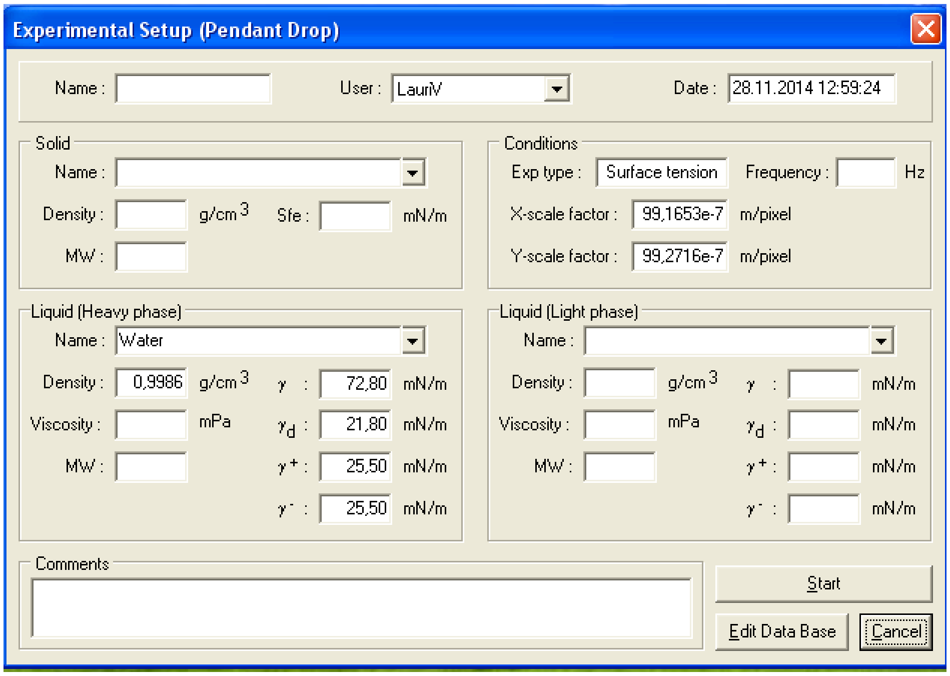
Image 3.1: *The CAM control program.*

The menus and the icons are the main means of accessing features of the CAM. The icons have the following functions.

Starts a new **Contact angle** experiment
Starts a new **Pendant drop** experiment
Starts a new **Meniscus** experiment
Starts a new **Calibration**
Opens **Browse experiments**
Opens **Edit database**
Opens **Adjust camera**

- Click on **Pendant drop** experiment button.




Experimental Setup (Pendant Drop)

Name :
User : LauriV
Date : 28.11.2014 12:59:24

Solid
Name :
Density : g/cm ^{3}
Sfe : mN/m
MW :

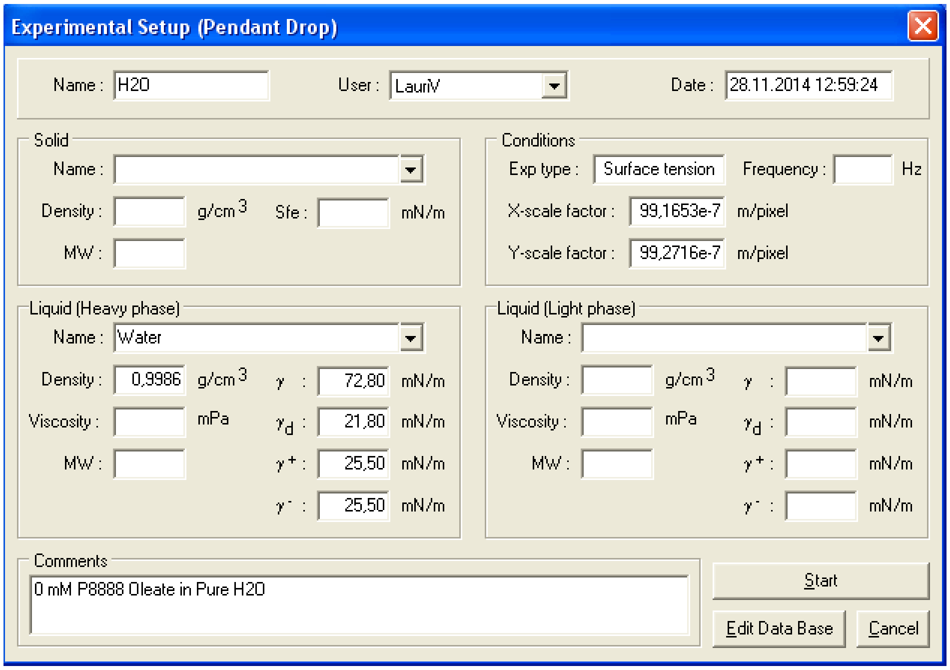
Conditions
Exp type : Surface tension
Frequency : Hz
X-scale factor : 99,1653e-7 m/pixel
Y-scale factor : 99,2716e-7 m/pixel

Liquid (Heavy phase)
Name : Water
Density : 0,9986 g/cm ^{3}
Viscosity : mPa
MW :
γ : 72,80 mN/m
γ_d : 21,80 mN/m
γ^+ : 25,50 mN/m
γ^- : 25,50 mN/m

Liquid (Light phase)
Name :
Density : g/cm ^{3}
Viscosity : mPa
MW :
γ : mN/m
γ_d : mN/m
γ^+ : mN/m
γ^- : mN/m

Comments

- Write the **Name** of the liquid of which you are going to measure surface tension, this way you can find your measurement in future easily. Put some comment about the solute concentration and solvent name in **Comments** box.



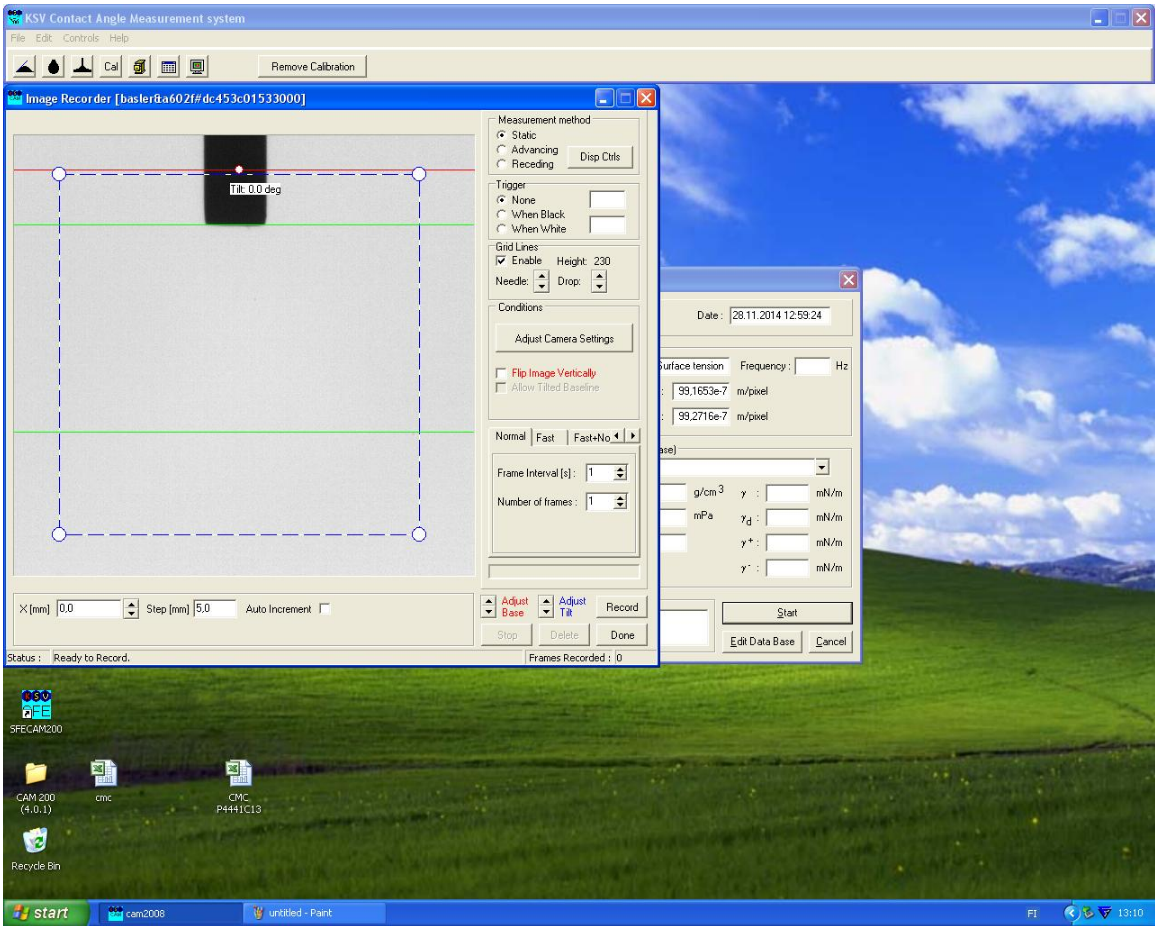
Name : H2O
User : LauriV
Date : 28.11.2014 12:59:24

Conditions
Exp type : Surface tension
X-scale factor : 99,1653e-7 m/pixel
Y-scale factor : 99,2716e-7 m/pixel

Liquid (Heavy phase)
Name : Water
Density : 0,9986 g/cm 3
γ : 72,80 mN/m
γ_d : 21,80 mN/m
γ^+ : 25,50 mN/m
γ^- : 25,50 mN/m

Comments
0 mM P8888 Oleate in Pure H2O

- Click on **Start** button.



Measurement method: ● Static ○ Advancing ○ Receding

Trigger: ● None ○ When Black ○ When White

Grid Lines: ☑ Enable Height: 230

Needle: Drop:

Conditions: ☐ Flip Image Vertically ☐ Allow Tilted Baseline

Normal | Fast | Fast+No

Frame Interval [s] : 1

Number of frames : 1

X [mm] 0,0 Step [mm] 5,0 Auto Increment ☐

Status : Ready to Record.

Frames Recorded : 0

Date : 28.11.2014 12:59:24

Surface tension Frequency : Hz

: 99,1653e-7 m/pixel

: 99,2716e-7 m/pixel

g/cm 3 mPa

γ : mN/m

γ_d : mN/m

γ^+ : mN/m

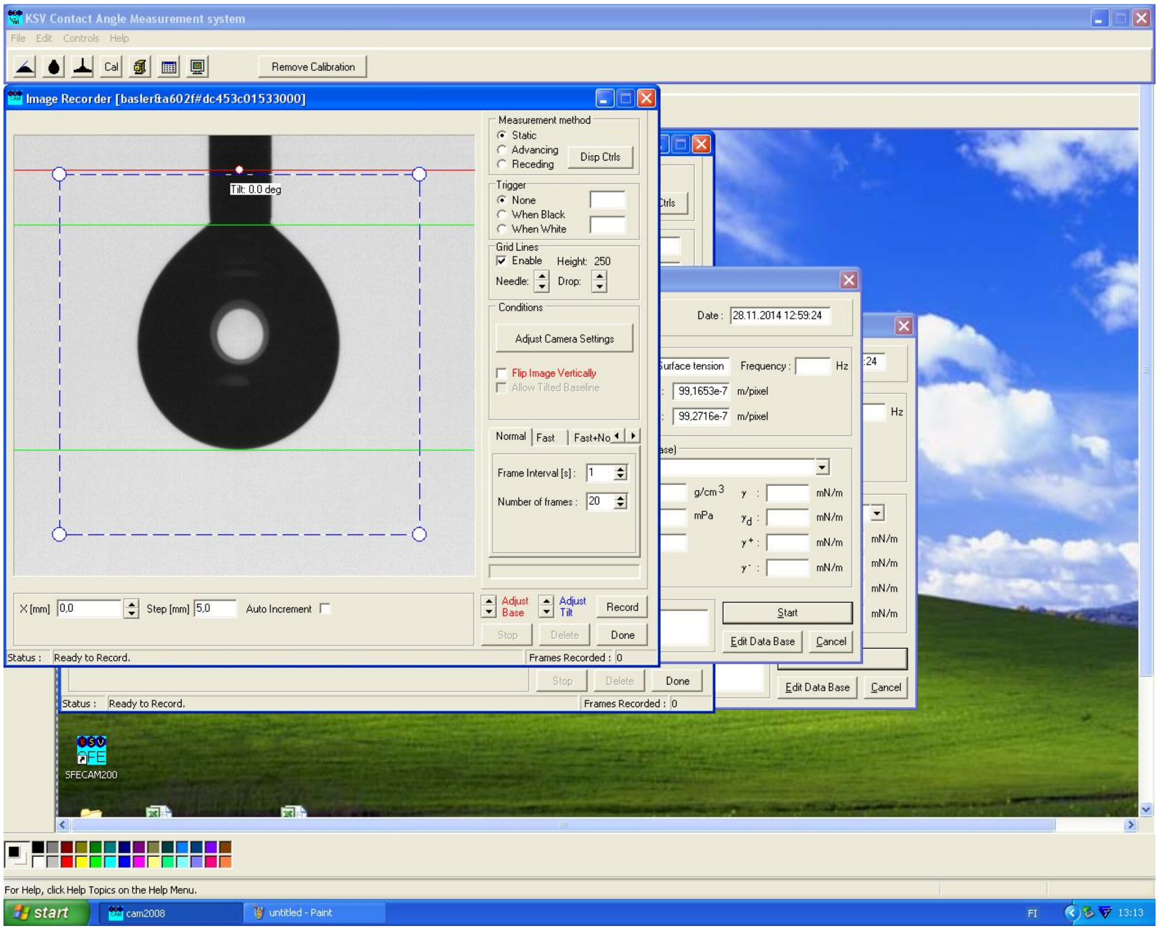
γ^- : mN/m

- Adjust the tip of needle and the green line as shown above, you can change the distance between two lines to manage the maximum size of the drop.

- The **Frame Interval** is time in seconds **(s)** and it is meaning how much time does it takes to capture one frame of the drop. Adjust it to **1**.

- **Number of Frames** is the total number of picture going to taken. Adjust it to **20**. So it takes 20 seconds to capture 20 frames.

- Make the drop gently and try to adjust it as shown below;



Tilt: 0.0 deg

Measurement method: ● Static ○ Advancing ○ Receding

Trigger: ● None ○ When Black ○ When White

Grid Lines: ☑ Enable Height: 250

Needle: Drop:

☐ Flip Image Vertically

☐ Allow Tilted Baseline

Frame Interval [s]: 1

Number of frames: 20

X [mm] 0,0 Step [mm] 5,0 Auto Increment ☐

Status: Ready to Record. Frames Recorded: 0

Date: 28.11.2014 12:59:24

Surface tension Frequency: Hz

99,1653e-7 m/pixel

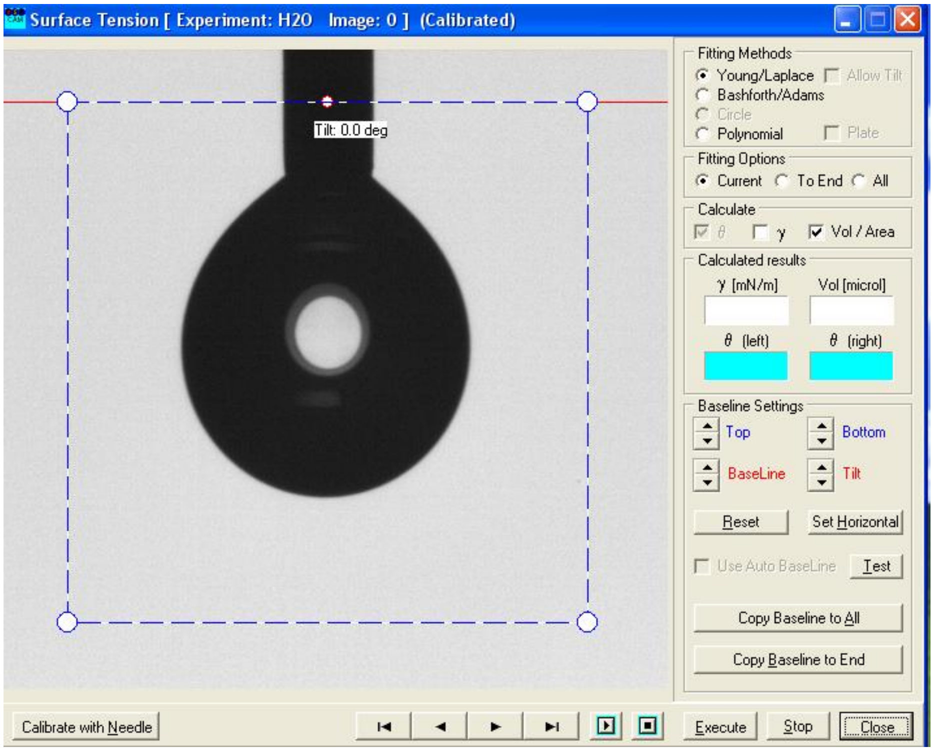
99,2716e-7 m/pixel

g/cm3 mPa γ: mN/m γ_d: mN/m γ^+: mN/m γ^-: mN/m

- Click on **Record** button to record images.

- Do the same measurement for several drops; let’s say **4** drops.

- After you have recorded it for 4 times, click **Done** button.



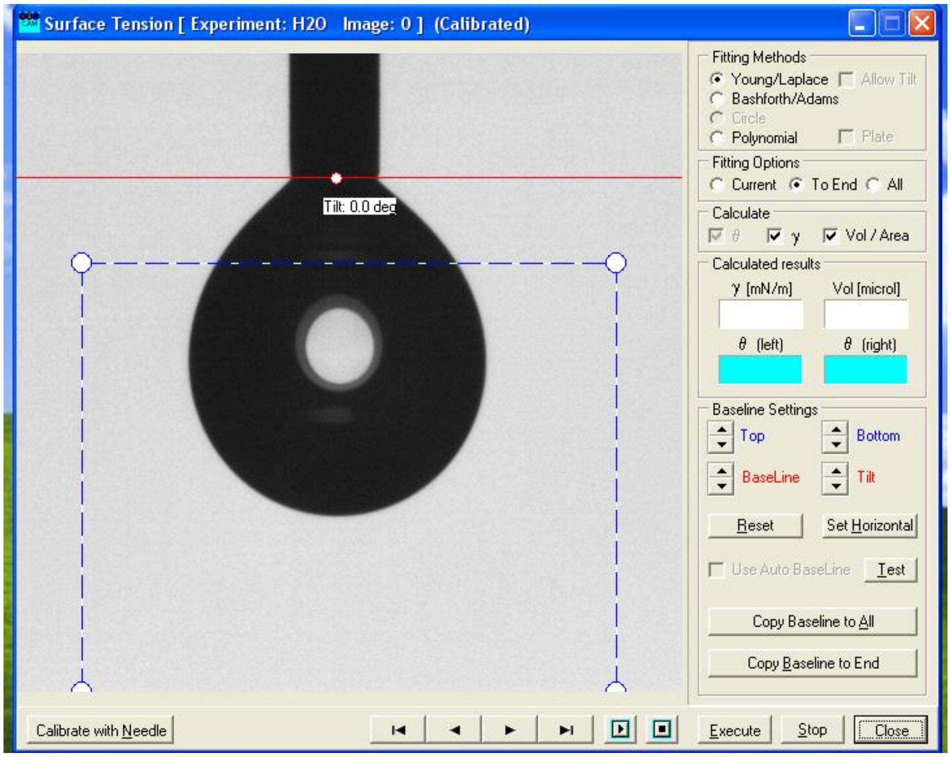
Surface Tension [Experiment: H2O Image: 0] (Calibrated)

Fitting Methods
● Young/Laplace ☐ Allow Tilt
○ Bashforth/Adams
○ Circle
○ Polynomial ☐ Plate

Fitting Options
● Current ○ To End ○ All

Calculate
☑ θ ☐ γ ☑ Vol / Area

- Make the fitting options **To End,** select calculate **ү (surface tension)** and adjust the tip of needle and curve fitting as shown below;



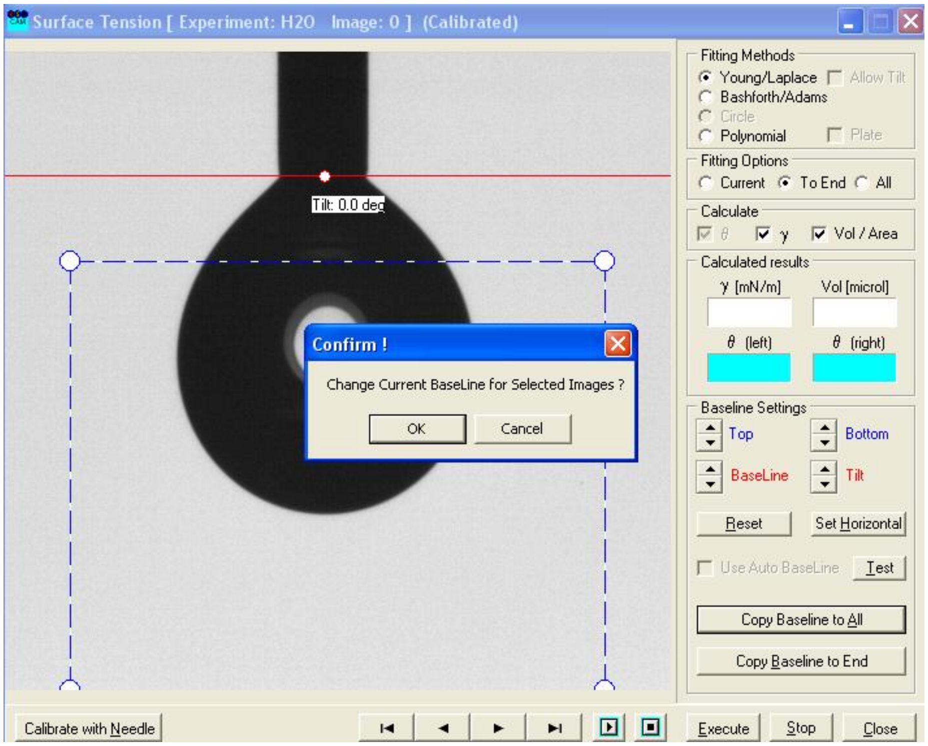
Surface Tension [Experiment: H2O Image: 0] (Calibrated)

Fitting Methods
● Young/Laplace ☐ Allow Tilt
○ Bashforth/Adams
○ Circle
○ Polynomial ☐ Plate

Fitting Options
○ Current ● To End ○ All

Calculate
☑ θ ☑ γ ☑ Vol / Area

- Click on **Copy Baseline to All**.



Surface Tension [Experiment: H2O Image: 0] (Calibrated)

Confirm !

Change Current BaseLine for Selected Images ?

Fitting Methods
● Young/Laplace ☐ Allow Tilt
○ Bashforth/Adams
○ Circle
○ Polynomial ☐ Plate

Fitting Options
○ Current ● To End ○ All

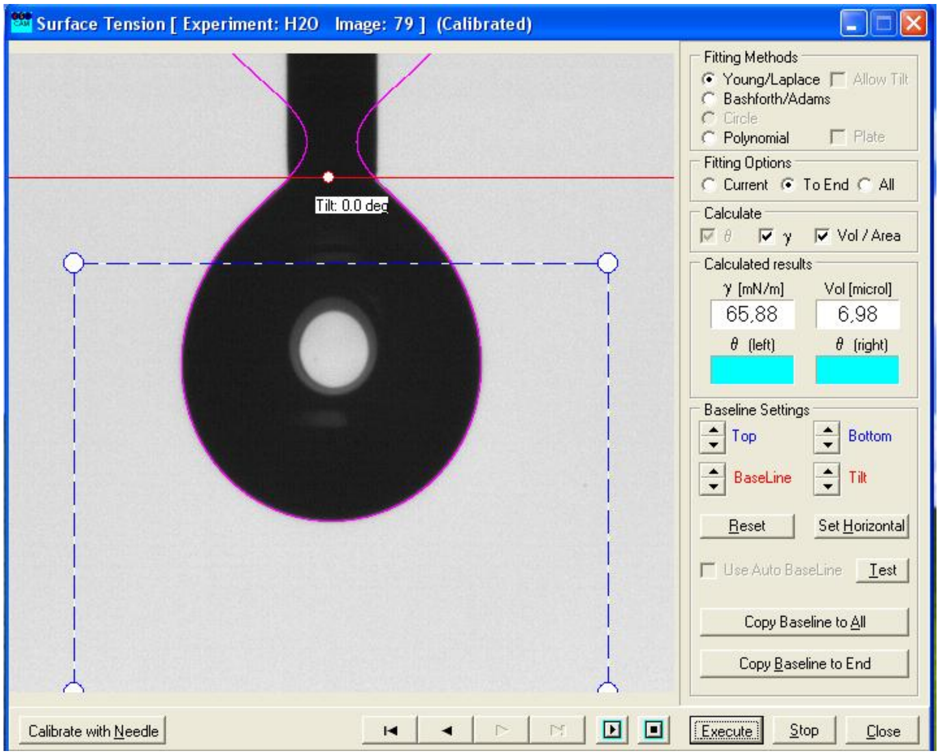
Calculate
☑ θ ☑ γ ☑ Vol / Area

Calculated results
γ [mN/m] Vol [microl]
θ (left) θ (right)

Baseline Settings

☐ Use Auto BaseLine

- Click **Ok** and then **Execute**.
- Wait for **80 seconds**; it automatically calculates the surface tension value and **click Close** button.


Surface Tension [Experiment: H2O Image: 79] (Calibrated)

Fitting Methods

● Young/Laplace ☐ Allow Tilt

○ Bashforth/Adams

○ Circle

○ Polynomial ☐ Plate

Fitting Options

○ Current ● To End ○ All

Calculate

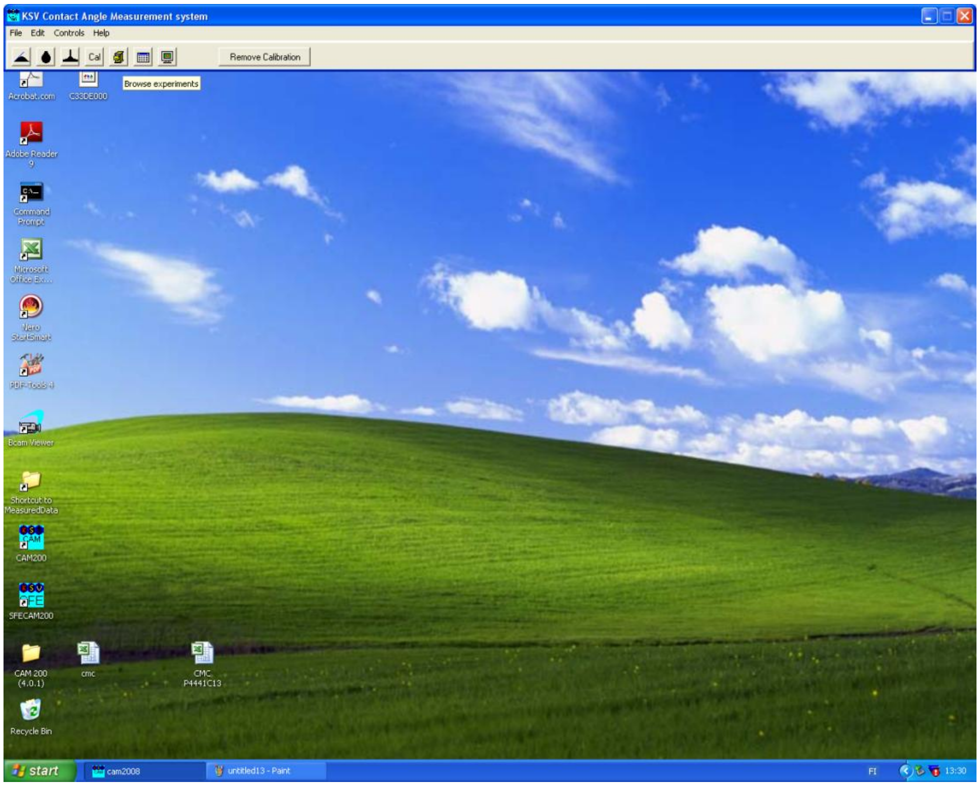
☑ θ ☑ γ ☑ Vol / Area

Calculated results

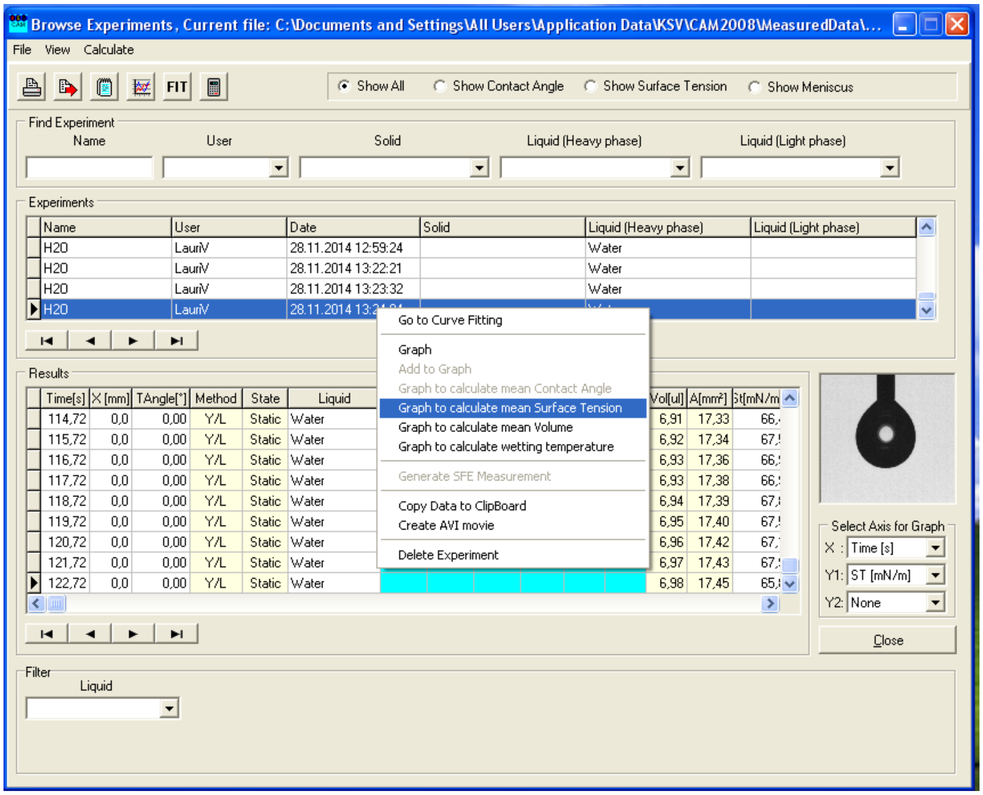
γ [mN/m]	Vol [microl]
65,88	6,98
θ (left)	θ (right)

Baseline Settings

☐ Use Auto BaseLine



- Click on **Browse Experiments**.



Select Axis for Graph

X : Time [s]

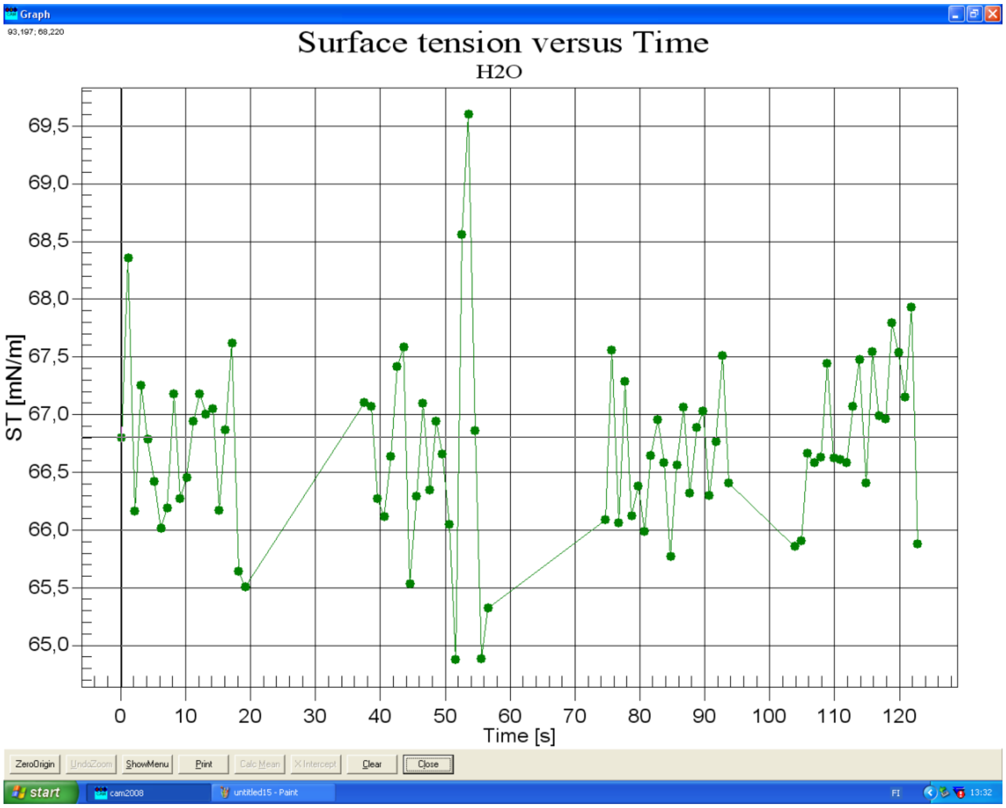
Y1: ST [mN/m]

Y2: None

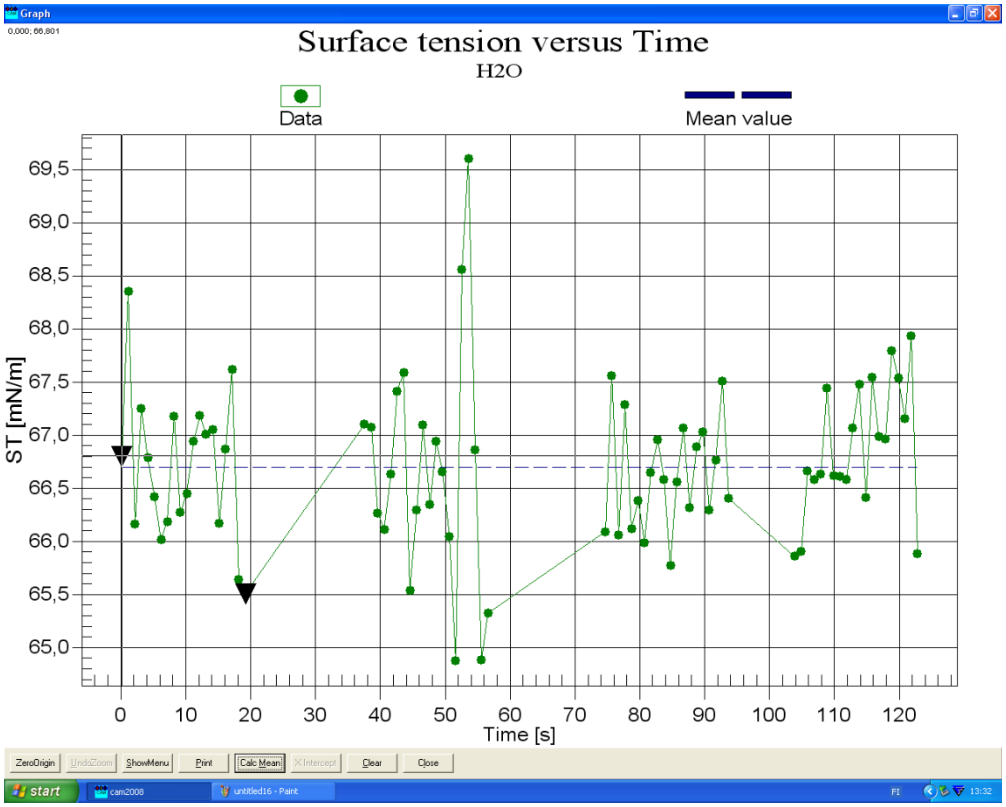
Name	User	Date	Solid	Liquid (Heavy phase)	Liquid (Light phase)
H20	LauriV	28.11.2014 12:59:24		Water	
H20	LauriV	28.11.2014 13:22:21		Water	
H20	LauriV	28.11.2014 13:23:32		Water	
H20	LauriV	28.11.2014 13:2			

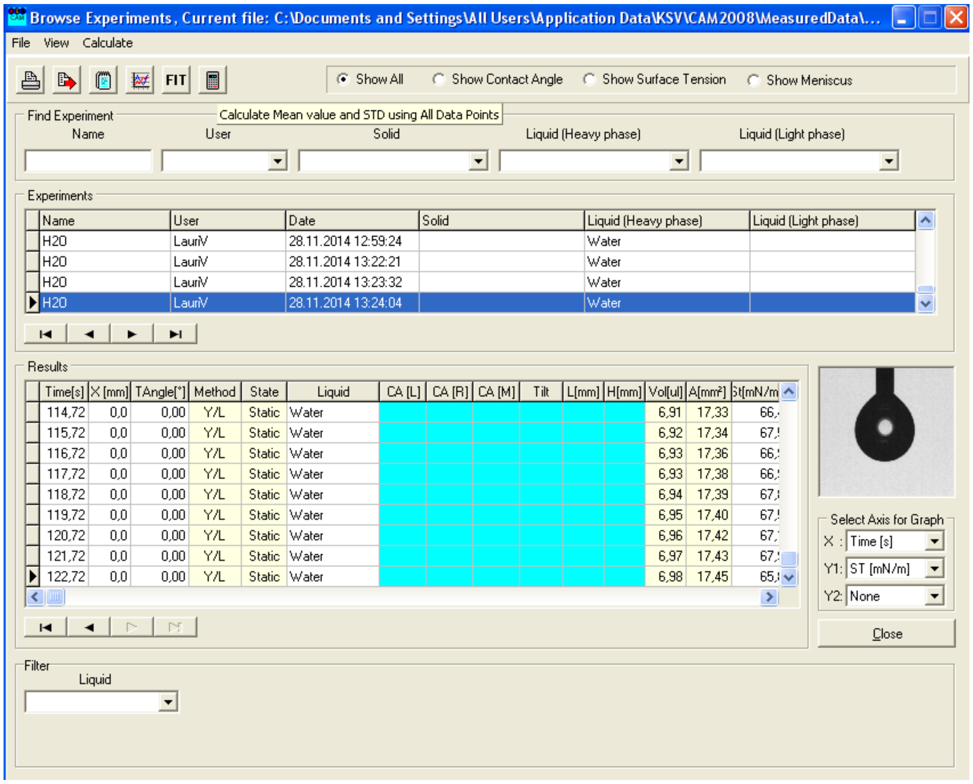
Time[s]	X [mm]	TAngle[°]	Method	State	Liquid	Vol[ul]	A[mm²]	St[mN/m
114,72	0,0	0,00	Y/L	Static	Water	6,91	17,33	66,
115,72	0,0	0,00	Y/L	Static	Water	6,92	17,34	67,
116,72	0,0	0,00	Y/L	Static	Water	6,93	17,36	66,
117,72	0,0	0,00	Y/L	Static	Water	6,93	17,38	66,
118,72	0,0	0,00	Y/L	Static	Water	6,94	17,39	67,
119,72	0,0	0,00	Y/L	Static	Water	6,95	17,40	67,
120,72	0,0	0,00	Y/L	Static	Water	6,96	17,42	67,
121,72	0,0	0,00	Y/L	Static	Water	6,97	17,43	67,
122,72	0,0	0,00	Y/L	Static	Water	6,98	17,45	65,

- Right click on selected area and click on **Graph to Calculate Mean Surface Tension**.



- Select the two points (Start-end) of each drop by double clicking and click **Cal Mean**.





● Show All ○ Show Contact Angle ○ Show Surface Tension ○ Show Meniscus

Find Experiment

Name	User	Solid	Liquid (Heavy phase)	Liquid (Light phase)

Experiments

Name	User	Date	Solid	Liquid (Heavy phase)	Liquid (Light phase)
H20	LauriV	28.11.2014 12:59:24		Water	
H20	LauriV	28.11.2014 13:22:21		Water	
H20	LauriV	28.11.2014 13:23:32		Water	
H20	LauriV	28.11.2014 13:24:04		Water	

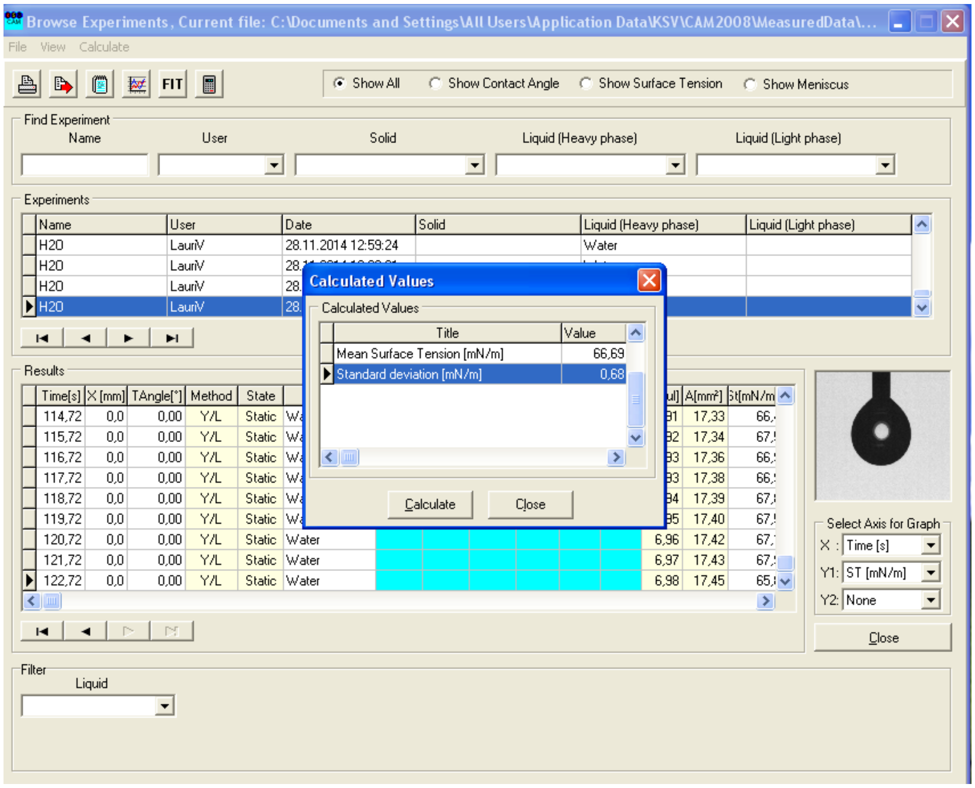
Results

Time[s]	X [mm]	TAngle[°]	Method	State	Liquid	CA [L]	CA [R]	CA [M]	Tilt	L[mm]	H[mm]	Vol[ul]	A[mm²]	St[mN/m
114,72	0,0	0,00	Y/L	Static	Water							6,91	17,33	66,
115,72	0,0	0,00	Y/L	Static	Water							6,92	17,34	67,
116,72	0,0	0,00	Y/L	Static	Water							6,93	17,36	66,
117,72	0,0	0,00	Y/L	Static	Water							6,93	17,38	66,
118,72	0,0	0,00	Y/L	Static	Water							6,94	17,39	67,
119,72	0,0	0,00	Y/L	Static	Water							6,95	17,40	67,
120,72	0,0	0,00	Y/L	Static	Water							6,96	17,42	67,
121,72	0,0	0,00	Y/L	Static	Water							6,97	17,43	67,
122,72	0,0	0,00	Y/L	Static	Water							6,98	17,45	65,

Select Axis for Graph
X : Time [s]
Y1: ST [mN/m]
Y2: None

Filter
Liquid

- Click on **Calculator** as shown above to get the value for surface tension.

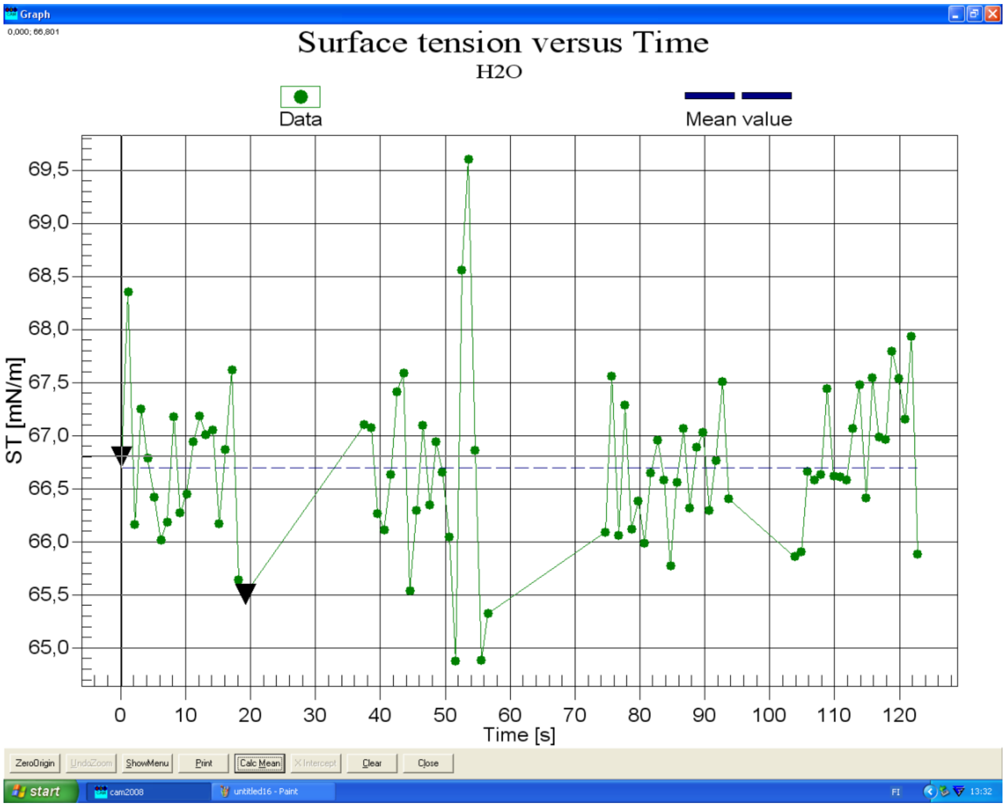

Browse Experiments, Current file: C:\Documents and Settings\All Users\Application Data\KSV\CAM2008\MeasuredData\...

Calculated Values

Title	Value
Mean Surface Tension [mN/m]	66,69
Standard deviation [mN/m]	0,68

Select Axis for Graph
X : Time [s]
Y1: ST [mN/m]
Y2: None

- Repeat the same process for each drop to calculate the surface tensions.
- Finally calculate the mean value as shown below;



- Note all the individual drop´s mean surface tension and a single mean surface tension for all drops to calculate the critical micelle concentration by plotting graph between obtained surface tension measurements and concentrations.

- Remember to clean the needle and syringe after finishing all the measurements and the contact angle meter should be handled gently and safely in order not to break the calibration. Last but not least, cover the needle and camera part with plastic bags.