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***Effect of Temperature and Added Salts on the Adsorption of
Selected Polyelectrolyte at the Surface of Water***

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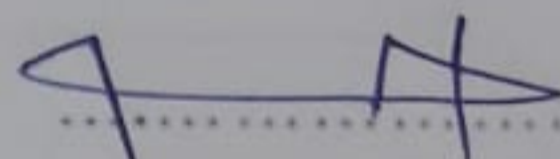
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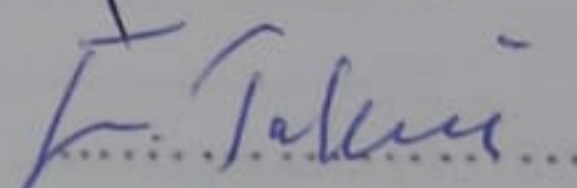
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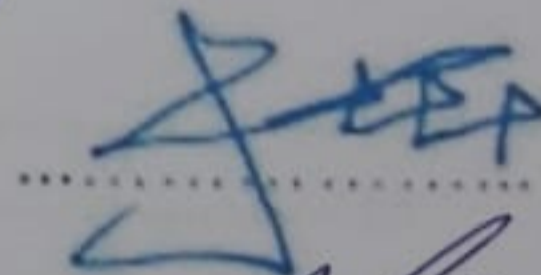




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Abstract

Surface tensions of aqueous solutions of oppositely charged sodium poly(styrene sulfonate)/benzyltrimethylhexadecyl ammonium chloride and sodium poly(styrene sulfonate)/polyallylamine hydrochloride have been measured by the Wilhelmy plate method as a function of temperature and addition of NaCl and CaCl₂ salts. The surface activity of the pure polyelectrolytes is very low. Upon mixing the polyelectrolyte with the oppositely charged surfactant, benzyltrimethylhexadecyl ammonium chloride, complexation takes place which showed significant surface activity. The same trend was found when the polyelectrolyte was mixed with the oppositely charged polyelectrolyte polyallylamine hydrochloride. The surface tension of the polyelectrolyte/surfactant mixture is lower than that of the pure surfactant but only at low concentrations of the polyelectrolyte (~ 0.1 g /100 ml). At relatively higher concentrations it is higher due to diminishing of the complexation process and thus the surface activity. It is found that the complexation process between either the polyelectrolyte/surfactant or the polyanion/polycation is enhanced by increasing temperature or addition of salts. The surface excess entropy was calculated from the temperature dependence of the surface tension to get more insight into the ordering at the surface. A downward peak was observed in the behavior of the surface tension as a function of the poly(styrene sulfonate) for the case of the polyanion/polycation mixture at equal amounts (0.1 g/100ml) of the two polyelectrolytes. This peak may indicate that the complexation process is at its maximum and therefore the surface activity is at its maximum value. Finally, it has to be mentioned that studies on the surface activity of the complex formed from the polyanion/polycation mixture are lacking and thus a major part of this study is absolutely needed.

Chapter 1

1. Introduction

1.1 Interfacial Tension

Interfacial tension is defined as the force of attraction between the molecules at the interface. The SI units of interfacial tension are milli-Newtons per meter (mN/m) or mJ/m^2 [1]. When the interface is between a liquid and a gas, it is called surface tension, and for the solid-gas interface, it refers to surface free energy.

Molecules in the liquid possess the cohesive forces; these forces exist between the particles and down to the joint liquid with all neighboring atoms. At the surface they have no neighboring atoms above and exhibit stronger attractive forces up to their nearest neighbors on the surface. This intermolecular attractive force at the surface is called surface tension.

When these forces are between like molecules, they are referred to as cohesive forces. For example, the molecules of a water droplet are held together by cohesive forces. When the attractive forces are between different molecules, they are said to be adhesive forces. An example is the adhesion forces between water molecules and the walls of the glass tube, which lead to an upward turning meniscus at the walls of the vessel and contribute to capillary action [2-4].

Surface tension plays a significant role in many natural phenomena, such as capillary action, the shape of droplets and the formation of capillary waves at liquid surfaces. Figure 1. shows a schematic sketch of atomic or molecular bonding at the surface and in the bulk.

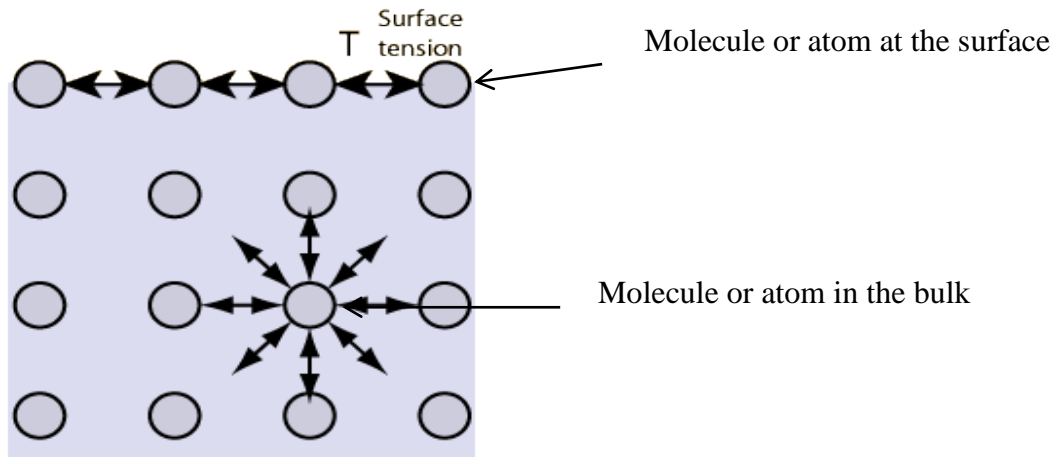


Fig. 1.1 Schematic sketch of atomic or molecular bonding at the surface and in the bulk

1.2 Polyelectrolytes

Polyelectrolytes are macromolecules that carry many ionizable groups attached to their polymeric backbone. The combination of large molar masses and high charge densities gives these molecules distinctive physicochemical properties different from that of both simple electrolytes and uncharged polymers. The ionizable groups can dissociate in polar solvents such as water that leave charged polymer chains and counter ions as shown in Fig.2.

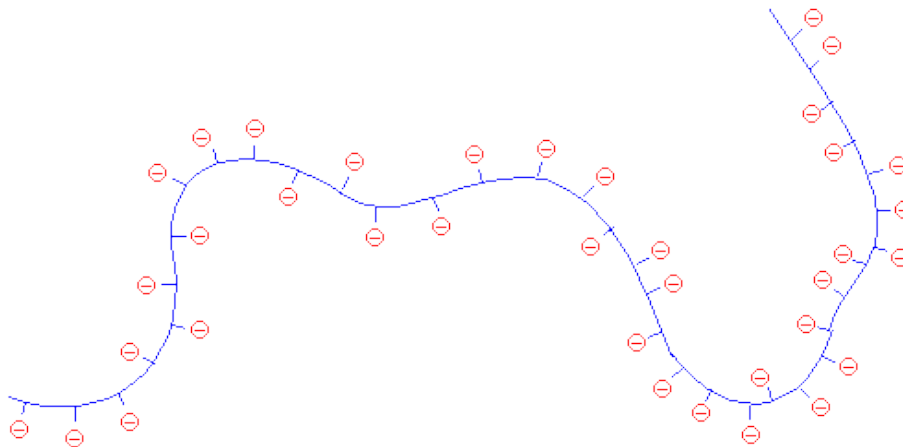


Fig.1.2. Schematic diagram of a polyelectrolyte. The solid line represents the polymer backbone and the groups with negative charges are represented by circles with (-) signs

1.2.1 Types of Polyelectrolytes

Polyelectrolytes are classified into various types according to different criteria. Based on their origin they are classified as natural (biological), inorganic minerals and synthetic polyelectrolytes. Natural or biological polyelectrolytes include proteins, nucleic acids, pectins, sialic acid. Examples of inorganic polyelectrolytes are polyphosphates, silicates and tungstates. Synthetic polyelectrolytes include polyacrylic acid, polystyrene sulfonate, polyallylamine, carboxymethyl cellulose and their salts. Another classification is related to the nature of ionic groups attached to polymeric backbone. If it is negative the polymer is called a polyanion or simply anionic polyelectrolyte. If the charge is positive then it is called polycation or simply cationic polyelectrolyte. A polymer that contains both negative and positive groups on its backbone is called polyampholyte or ampholytic molecule [5-6].

1.2.2 Interfacial Tension of Polyelectrolytes

The adsorption of polyelectrolytes onto surfaces and interfaces is very important in many technologies. Examples including adsorption of electrolytes onto colloid surfaces which plays essential role in the stabilization of emulsions in food, photographic, and pharmaceutical industries. Adsorption of biological polyelectrolytes is a major step in many biochemical processes. Understanding these processes is of interest to control both contaminations in biotechnology processes and biocompatibility in biomedical applications [7]. Moreover, the adsorption of synthetic polyelectrolytes is of great importance to various applied industrial problems. Because of its water solubility, these polymers are environmentally friendly and can be used in biological systems or in personal care products, and these fields are promising and largely open. Adsorption properties of charged polymers are specified to control specific characteristics of these products, which depend on the stability of the suspension and emulsions and on ability to change surface properties by adsorption. In general, applications depend on either attached charge chains on a solid surface, or locating them on the liquid / liquid or liquid / air interface [8].

A common condition of adsorption of polyelectrolytes on the surface has shown that the adsorbed layers can be thin, with the chain lying on the surface, or can be more flat, with the chains forming loops and nested ends between the adsorption trains in the configuration "pseudo brush [9-10].

This conformation of chains depends mostly on the charging part of the polymer and the charge of the surface of the substrate, and depends on the force of electrical attraction between the chain and the surface and its effects on strong deceleration. This is attributed to extremely high strength in electrical attraction.

Neutral surface condition is somewhat different from charged surfaces since the electrostatic part of interaction with the surface is repulsive and there is a drain layer (a depletion layer). This is usually the case for the free surface of a polyelectrolyte solution where no adsorption is known to happen and the interfacial properties remain [11].

From a fundamental point of view, it is important to investigate how the conformation of a polyelectrolyte is changed near an interface and the factors, which control the conformation such as the adsorbed amount, and the distribution of counter ions [12-14]. In this regard, it is important to investigate the physiochemical properties of polyelectrolytes at surfaces and interfaces and surface tension is one of the important properties among these.

1.2.3 Applications of Polyelectrolytes

Polyelectrolytes have many applications in different fields, such as water treatment as flocculation agents, ceramic slurries as dispersant agents, and concrete mixtures as super-plasticizers. Polyelectrolytes had also been utilized in fields of catalysis, organic synthesis, extraction, electrochemical processes and separation technology. Many shampoos, soaps, and cosmetics contain polyelectrolytes. Certain polyelectrolytes are also added to food products as food coatings and release agents. Some examples are pectin (polygalacturonic acid), alginates (alginic acid), and carboxymethyl cellulose, of which the last one is of natural origin [15-17].

Polyelectrolyte interact with surfactants in solutions to generate systems that are used in many industrial, pharmaceutical and technological applications such as food, medicine and nanotechnological products [18].

1.3 Introduction to Surfactants

The term surfactant comes from an active surface agent. Surfactant is a chemical substance that changes the interfacial properties by adsorption to the boundary between two

immiscible phases [19]. They are amphiphilic molecules that have both hydrophobic (soluble in lipids, or oils) and hydrophilic parts (water-soluble), and are thus adsorbed onto the air-water interface. They tie themselves so that the hydrophobic part is in the air and the hydrophilic part is in the water as shown in Fig. 1.3. This will cause a decrease in surface or interfacial tensions [20-21]. Surfactants can act as moisturizers, emulsifiers, foaming agents, and dispersants.

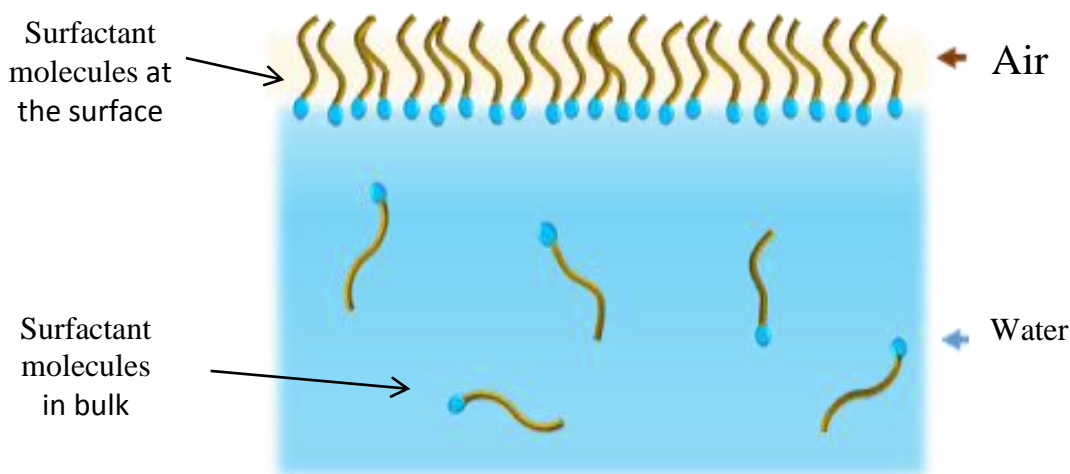


Fig. 1.3 Schematic diagram of surfactant molecules in solvent.

When surfactants molecules are adsorbed on the surface they break cohesive forces between the water molecules. The intermolecular forces between surfactant and water molecules are much lower than between water molecules themselves, which cause reduction in surface tension. The reason for this behavior is that the surfactant molecule contains two structurally distinct parts; hydrophilic head and hydrophobic tail. The hydrophilic head is polar or ionic group that prefer contact with water while the hydrophobic tail which is a hydrocarbon -such as fluorocarbon or siloxane- do not mix well with water. The opposing forces cause small parts of the particles to migrate to the air/water interface and arrange themselves as a single-layer (monolayer). This process is referred to as adsorption. When the surfactant concentration is high, the molecules find an alternative way to minimize their unfavorable contact by aggregation in the bulk solution, where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding aqueous phase. This process is called micelle formation or self-association. The latter is very important because the behavior of this combined

structure composed of many surfactant molecules is qualitatively different from the behavior of free, non-discrete molecules. The point at which micelles are formed is called Critical Micelle Concentration (CMC), shown in Fig. 1.4. [22-23].

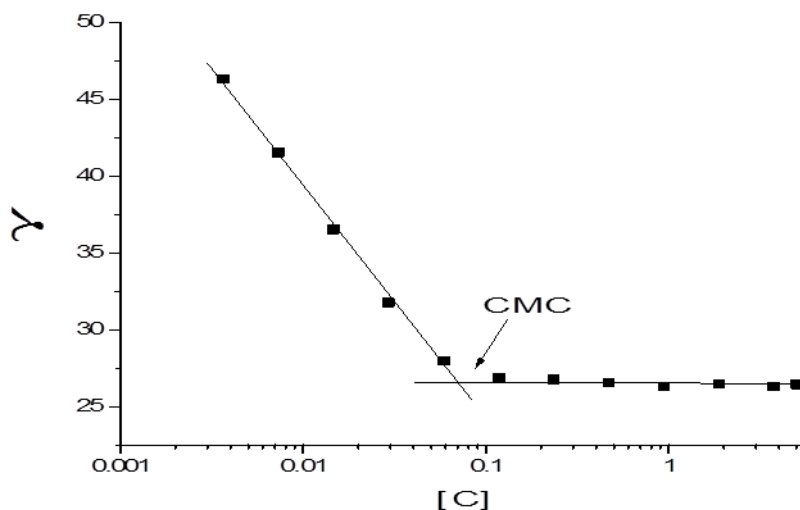


Fig. 1.4. Schematic plot of surface tension (γ) versus surfactant concentration (C). The arrow indicates the CMC point of the surfactant.

1.3.1 Types of Surfactants

Surfactants are classified according to the nature of the hydrophilic part, and the composition of the polarity of the head group. The classification consists of four types: anionic, cationic, zwitterionic and nonionic [24]. The main features of these classifications will be given in the following sections:

1.3.1.1 Anionic Surfactants

The head of an anionic surfactant is negatively charged and this head is commonly neutralized by an alkali metal cation. The members of this group have the highest cleansing power, good wetting properties but moderate disinfectant properties. Soaps with the general formula (RCOO^-Na^+), alkyl sulphates ($\text{RSO}_4^-\text{Na}^+$) and alkyl benzene sulphonates ($\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$) are some of the well known examples of this type of surfactants. Anionic surfactants are the most widely used in industrial practices due to their

excellent cleaning properties and moderate cost and they include laundering detergent, dishwashing liquids and shampoos [25].

1.3.1.2 Cationic Surfactants

The head-group of cationic surfactant has positive charge. Most of these surfactants are stable in a wide range pH. Due to poor detergency and higher cost, cationic surfactants are not widely used in industry. Some of well-known cationic surfactants are salts of long chain amines (RNH_3^+X^-), quaternary ammonium salts $[\text{RN}(\text{CH}_3)_3^+\text{X}^-]$. Common uses of cationic surfactants are in ore floatation, textile industries, pesticides applications, adhesion, corrosion inhibition and preparation of cosmetics [26].

1.3.1.3 Non-Ionic Surfactants

These surfactants are the second most widely used surfactants in industry. They do not have any electrical charges so they may have very little or no electrical interaction between the head groups. Most of non-ionic surfactants are available as viscous liquids. They are lower foaming and less affected by water hardness ions [27]. The most commonly used non-ionic surfactants are alkyl ethoxylate $[\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$ acting as excellent emulsifier and used as greasy stain removal. The polyoxopropylene glycols are used as dispersing agents for pigments and paints, foam-control agents and for removing scales of boilers. Poloxyethylene mercaptans $[\text{RS}(\text{C}_2\text{H}_4\text{O})_n\text{H}]$. They are used in textile detergents, metal cleaning and wetting agents [28]. Sorbitan esters as nonionic surfactants are edible and used as emulsifying agents in the preparation of emulsions, ice creams, beverages, desserts, confectionary products in addition to pharmaceutical and cosmetic products.

1.3.1.4 Zwitterion Surfactants

Are characterized by a molecular structure containing two different functional groups, with anionic and cationic characters respectively. The long chain amino acids ($\text{RNH}_2^+\text{CH}_2\text{COO}^-$) and phospholipids are examples of natural zwitterion substances while botanies ($\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$) or sulfobetaines ($\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$) are examples of synthetic surfactants. Most of these surfactants are able to behave as cationic or anionic surfactants depending on the pH of the medium. They are extensively used in liquid cleansers, moisturizing body wash, shower gel, shaving products, shampoo, toothpastes,

detergent for contact lenses. The wide utilization of these surfactants is related to their good cleansing power, low toxicity, antibacterial properties, excellent resistance to hard water, and excellent compatibility with various kinds of surfactants at different pH values [29].

1.3.2 Applications of Surfactants

Surface active agents are among the most versatile products of the chemical industry. They are used in every industrial area ranging from household detergents to drilling muds and food items to pharmaceuticals.

Surface active agents play an important role as cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents in many practical applications and products such as cosmetics and personal care products, food products, agriculture, including: paints, emulsions adhesives, inks, biocides (sanitizers), shampoos, toothpastes, firefighting (foams), detergents, insecticides and herbicides, textiles and fibers, deinking of recycled papers, and ski waxes [30-31].

1.4 Measurement of Surface and Interfacial Tension

There are several techniques to measure the surface and interfacial tensions of liquids. The main techniques will be discussed briefly in the following sections.

1.4.1 Capillary Rise Method

Capillary rise is a fundamental phenomenon existing in many natural processes and human activities. The experimental method based on capillary rise is widely used for porous media characterization (i.e. pore radius, contact angle, free surface energy) and an illustration of this method is given in Fig. 1.5.

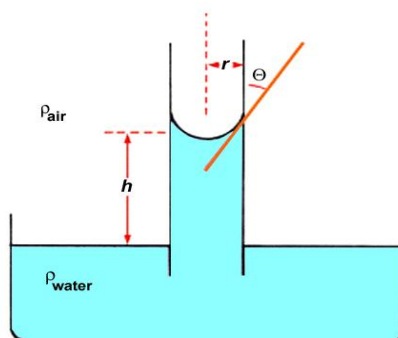


Fig. 1.5. Rise of water meniscus in a glass capillary

In capillary rise method a glass capillary is cleaned and immersed into a liquid or solution. In the case of water or aqueous solutions as the force of adhesion between the liquid molecules and the capillary wall is greater than the cohesion forces between liquid molecules, the liquid will rise up in the capillary. The height at which the liquid raised inside the capillary is related to the surface tension by the equation:

$$\gamma = \frac{\rho g h r}{2 \cos \theta} \quad (1 - 1)$$

Where γ is the surface tension, ρ the density of the liquid, h is highest of liquid meniscus in the capillary, g is the gravity acceleration, and θ is the contact angle between liquid meniscus and glass capillary [32-33].

If the contact angle θ is very small ($\theta \approx 0$) then $\cos \theta \approx 1$ and thus the surface tension can be easily calculated from equation (1 - 2) below.

$$\gamma = \frac{1}{2} \rho g h r \quad (1 - 2)$$

1.4.2 Du Noüy Ring Method

A sketch of the method is shown in Fig. 1.6. In this method a platinum-iridium ring is immersed in the liquid so that the ring will be under the surface of the liquid. The ring will be pulled carefully until it reaches the surface of the liquid. The force necessary to detach a platinum iridium ring is measured and is proportional to the surface or interfacial tension as:

$$\gamma = \frac{F}{L \cos \theta} \quad (1 - 3)$$

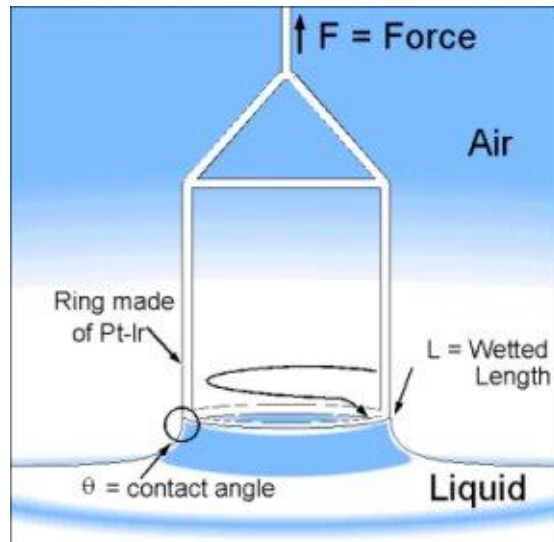


Fig.1.6. A schematic sketch of Du Noüy ring method used for measuring the surface and interfacial tension of liquids

Where γ is the surface tension, l is wetted length, and θ is the contact angle between liquid surface and the platinum ring.

Du Noüy ring method is convenient and has the advantage of obtaining a fair degree of accuracy even with simple experimental procedure. It becomes more complicated when a higher degree of accuracy is sought. The essentials of the procedure are a ring, capable of being wetted by the liquid whose surface tension is to be measured, suspended horizontally in the flat surface of the liquid, and some device to measure the force necessary to separate ring and liquid [34-35].

1.4.3 Wilhelmy Plate Method

Consists of plate (glass or platinum) attached to a suitable balance. The plate is immersed in liquid, and the liquid container is gradually lowered. A sketch of the method is shown in Fig. 1.7. The reading on the balance immediately prior to detachment is noted.

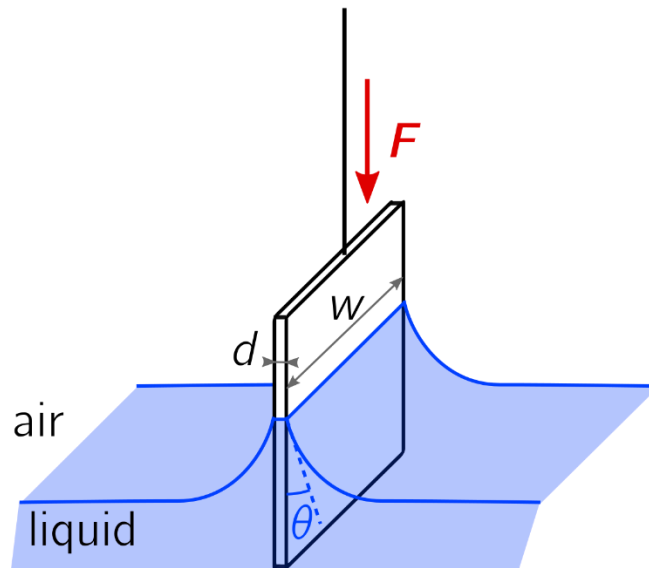


Fig. 1.7. A schematic sketch of Wilhelmy plate method used for measuring the surface and the interfacial tension of liquids.

One major difference between ring and plate methods is the way in which the measurement is carried out. The ring moves through the interface whereas the plate is static at the interface. Therefore, there is no ‘artificial’ disturbance of the interface and no increase in the time to reach equilibrium when using the plate method. Any time dependent effects are true effects and hence the plate is the recommended geometry for studying time dependent characteristic [36-37].

1.5 Polyelectrolyte Complexes

Complex formation is observed when two oppositely charged species are mixed.

Polyelectrolyte complexes can be roughly divided into two types [38]:

The first type is a complex formed of two differently charged polyelectrolytes like cationic and anionic polyelectrolytes.

The second type is a complex of polyelectrolyte and surfactant (anionic polyelectrolytes and cationic surfactants or cationic polyelectrolytes and anionic surfactants).

1.5.1 Oppositely Charged Polyelectrolytes Complex (PEC)

Polyelectrolyte complexes have unique physicochemical properties with high biocompatibility. These are the association complexes formed by the strong electrostatic interaction between two oppositely charged polyelectrolytes. Mixing solutions of polyanions and polycations leads to spontaneous formation of interpolymer complexes and releases of the counterions.

Complex formation can take place between polyacids and polybases, and also between their neutralized metal and halogenide salts [38]. The process of forming a complex is considered as a cooperative process between electrostatic and hydrophobic forces. This process basically involves three steps as show in Fig. 1.8. The first step is the primary complex formation and Coulomb forces are responsible. The second step is the formation process within intracomplexes. This step includes formation of new bonds and/or the correction of the distortions of the polymer chains. The final step is the intercomplex aggregation process, which involves the aggregation of secondary complexes fundamentally through hydrophobic interactions [39-40].

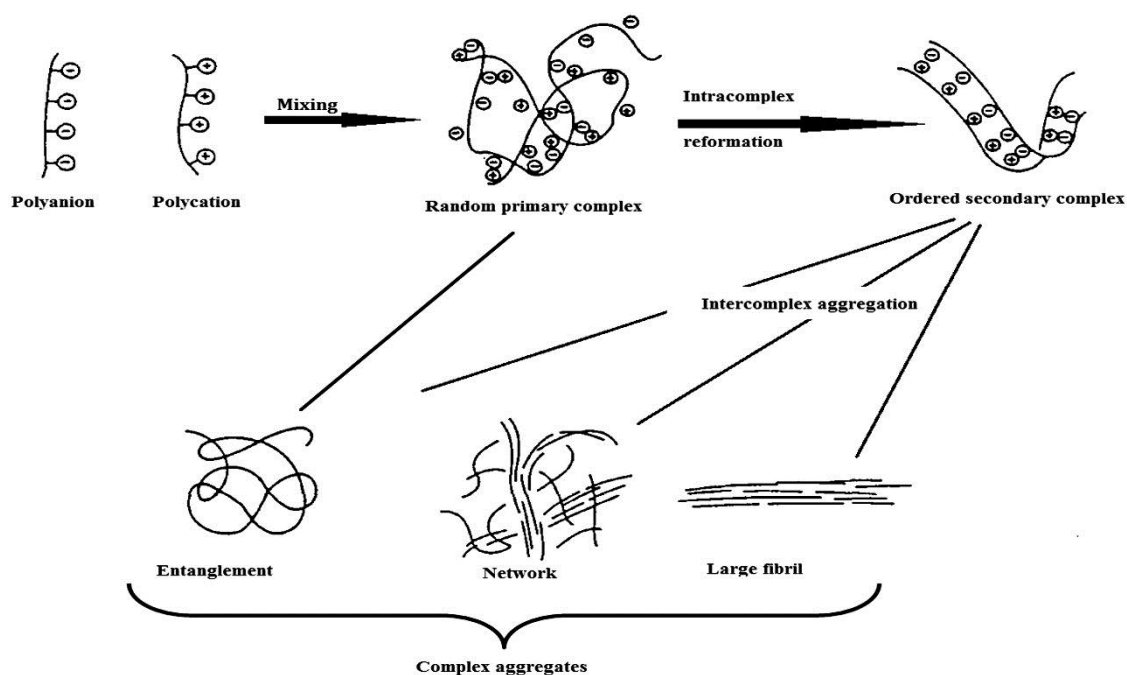


Fig.1.8. Schematic diagram of polyelectrolyte complexes formation

A number of parameters are known to influence the formation of PECs. These are ion site, charge density, polyelectrolyte concentration, pH, ionic strength, type of solvent and temperature. Several workers evaluated the factors effecting the formation of polyelectrolyte complexes with different polymeric blends [41].

The occurrence of PECs often goes along with a phase separation, resulting either in two liquid phases or in a precipitate. The polymer-rich liquid phase which may appear as droplets is called a coacervate and dispersed in the polymer-deficient aqueous phase. Coacervates retain large amounts of water, giving rise to an extremely low interfacial tension between the coacervate phase and the coexisting supernatant phase [42-44].

1.5.2 Polyelectrolyte and Surfactant Complex (PE-Surfs)

The behavior of the polyelectrolyte in the solution is dependent on the balance between hydrophobic and hydrophilic interactions of the polymeric parts, and these interactions are governed either among them or with the solvent. Similarly, surfactant aggregates in the solution are controlled by hydrophobic or ionic reactions. Thus, aqueous solutions containing polyelectrolyte / surfactant mixtures offer a large variety of behaviors. This becomes richer when the surfactant and the polyelectrolyte bear opposite electrical charges [45-47].

There are two basic forces that control the stability of polyelectrolyte and surfactant complexes:

1. Electrostatic forces
2. Hydrophobic forces.

The electrostatic interaction is due to the numerical attraction between the oppositely charged ions and the resultant release of counter ions. Thus, polyelectrolyte and surfactant complexes lead to a significant increase in entropy. The electrostatic interaction depends largely on the density of the charge. Hydrophobic forces are caused by a large gain in entropy by draining the unfavorable water molecules surrounding the hydrophobic areas during the binding process [18,48,49].

1.6 Introduction to Poly(styrene sulfonates)

Polystyrene sulfonates are polymers derived from polystyrene by the addition of sulfonate functional groups as show in Fig. 1.10. They are used to remove ions such as potassium, calcium, and sodium from solutions in technical or medical applications.

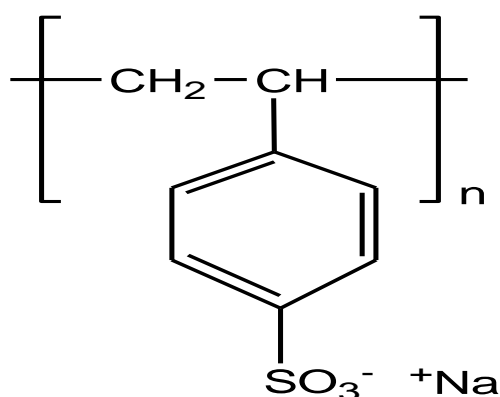


Fig.1.10. Structural formula of Polystyrene sulfonates polyelectrolyte (NaPSS)

In general, a hydrophobic interaction has been approved to explain a variety of solution and interfacial phenomena observed in NaPSS systems. The balance between electrostatic (due to segmental charge density) and hydrophobic (presumably originating from the backbone) these forces has been determinant of NaPSS behavior [50].

Three reason for the differences of the activity of NaPSS at the water air interface. The first one is the degree of sulfonation (DS), which may lead to an erroneous interpretation of the source of hydrophobicity of the molecule. In the case of a high degree of molecule sulphate (usually in the range above 80%), hydrophobicity has been attributed to the remaining unvaccinated aromatic fragments in the molecule. Secondly, the method of synthesis of the NaPSS molecule may be the main determinant of its structure and consequently its properties [51].

Finally, commercial samples of NaPSS could contain ionic impurities with various types of potential impurities like surface active agents or inorganic salts such as Na_2SO_4 . The presence of these impurities may have a strong effect on the polyelectrolyte properties such

as viscosity, osmotic pressure, surface tension and removing them from commercial sample is essential [50,52].

1.6.1 Purification of NaPSS Sample

The removal of ionic impurities from NaPSS polyelectrolyte solution is not possible by conventional solution and precipitation technique; for such a system dialysis or ion exchange method is necessary.

1.6.1.1 Dialysis of Commercial NaPSS Sample.

Dialysis of NaPSS Sample has been carried out by Sen et al. [53], in which NaPSS solution was taken in a sealed semipermeable membrane (cellulose acetate) and placed in distilled water. The dialyzate (out the membrane), was replaced from time to time (each replacement of water is referred as cycle) with new distilled water. The conductivity and UV absorbance of the dialyzate was measured at the end of each cycle. This was repeated until both the conductivity and UV absorbance of the dialyzate were practically equal to that of distilled water. The NaPSS solution in the membrane was finally evaporated to dryness in oven at $110 \pm 5^\circ\text{C}$ to its white solid form and the sample is referred to as D-NaPSS). The original sample is referred to as UD-NaPSS [53].

1.6.1.2 Ion Exchange Method.

Ion-exchange-based purification constitutes a step for removal of possible ionic impurities from the commercial NaPSS sample. The procedure was proposed by Reddy and Marinsky [54]. The solution of NaPSS was eluted through the anionic resin (Amberlite IRA 400C in hydroxide form) column for 4-5 cycles. The final elutant was passed through cationic resin (Amberlite 200 in acid form, with five times weight equivalent of polyions) column, also for 4-5 cycles. Finally, the resulting acid form of NaPSS was neutralized with NaOH solution quantitatively. The final solution was evaporated to dryness in oven at $110 \pm 5^\circ\text{C}$ to its solid form. All the resins were washed until they were free from acid or alkali.

Sen et al. measured the surface tension of UD-NaPSS and D-NaPSS sample of NaPSS and the result is shown in Fig. 1.11 [53]. In the same figure similar data from the literature on NaPSS are also shown for comparison [7,12,55]. However as can be seen from Fig. 1.11, at higher polymer concentrations, the D-NaPSS sample displayed almost no surface activity, whereas the UD-NaPSS sample showed a moderate surface activity. The surface

tension exhibited by D-NaPSS sample is almost similar to that from the work of Theodoly et al. [12].

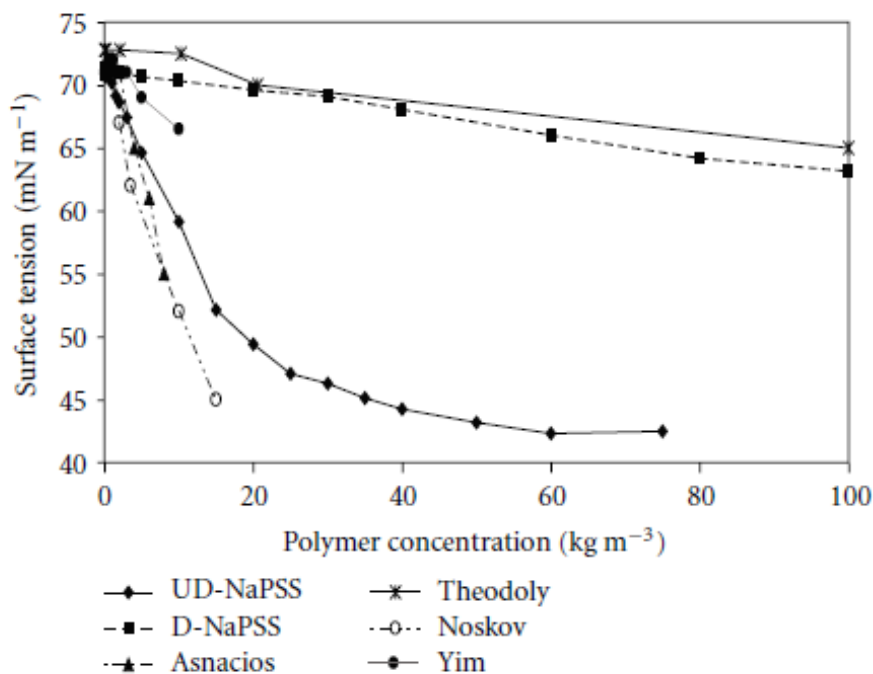


Fig.1.11. Surface tension of NaPSS solutions. The underlying symbols indicate the key to each result.

1.6.2 Application of Sodium Polystyrene Sulfonate

Sodium polystyrene sulfonate (NaPSS) has been extensively used as a model polyelectrolyte system [51]. It also has a wide variety of applications such as flocculation, personal care products [12] and in drug industry. One of the important applications involves its use as a drug during kidney failure. The oral dose for an adult is up to 30 g / day [53].

The adsorption of sodium polystyrene sulfonate (NaPSS) polyelectrolyte onto surfaces is important in many technologies. It plays a central role in the stabilization of emulsions in food, photographic, paint, water purification, flotation separations, oil recovery, and pharmaceutical industries [7]. In this work, commercially dialysed sample of NaPSS has been used.

Purpose and Methodology of the study

Unlike previous studies, where the surface tension of the polyelectrolyte/surfactant mixtures was measured as a function of surfactant concentration, here the surface tension of these mixtures will be studied as a function of the polyelectrolyte concentration and the measured surface tensions will be compared to that of pure surfactant solutions. In this way the effect of the complexation process on the measured surface tension will be more clear since the concentration of the polyelectrolyte at which the effect is maximum will be easily controlled. In addition the effects of temperature and added salts have never been studied on these systems. The temperature parameter is an important one since the surface excess entropy can be calculated from these types of measurements. The latter is an extremely important thermodynamic parameter that was neglected in previous studies. These factors and parameters will be carefully studied and analyzed in this study.

Studies on the surface tension and surface properties of the polyanion/polycation coacervate mixtures are lacking and almost all of the previous studies have concentrated on the bulk properties of these coacervates. Here the surface tension of the Sodium Poly(styrene sulfonate)/polyallylamine Hydrochloride coacervate at the water/air interface will be measured both as a function of temperature and added salts of varying valency. The work here will help us understand the compositions at which the complexation process is at maximum and will lead to better understanding of the effects of this complexation process on the surface tensions of aqueous solutions. The temperature measurements will give us an idea about the ordering of the these complexes at the surface and whether increasing the temperature will enhance or diminish the complexation process. Addition of salts will lead to better understanding of the effects of the screening process on the complexation process and whether changing the valency of the cation has any effect whatsoever.

The fulfilment the objectives of the study will be achieved by:

1. Study the effect of varying concentration of Sodium Poly(styrene sulfonate) on the surface tension of aqueous solutions of Poly(styrene sulfonate) /Benzyltrimethylhexadecyl-ammonium Chloride complexes.
2. Elucidate the behaviour of Sodium Poly(styrene sulfonate)/polyallylamine Hydrochloride coacervate at the water/air interface.

3. Study the effect of temperature on the complexation process of the above-mentioned mixtures by studying their surface tension as a function of temperature.
4. Study the effect of added salts of varying cation valency on the complexation process of these coacervates by studying their surface tension as a function of salt molarity.
5. Calculate the surface excess entropy (an important thermodynamic parameter) to get an idea about ordering of these coacervates at the surface.

Chapter 2

Materials and Experimental Techniques

2.1 Materials

2.1.1 Polyelectrolytes

1. The main material used was sodium poly styrene sulfonate (NaPSS) which was obtained from Sigma-Aldrich with purity of 99.8%. It is an organic compound with the molecular formula $(C_8H_7NaO_3S)_n$. It has an average molar mass of about 70,000. The anionic polyelectrolyte is a white to light yellow crystal.
2. Poly(allylamine hydrochloride) PAA HCl with an average molar mass of ~17,500 and was obtained from Sigma-Aldrich. The cationic polyelectrolyte is white crystal. The structural formula of SDBS is shown in Fig. 2.1.

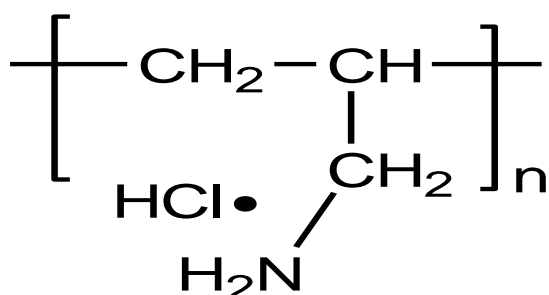


Fig.2.1. Structural formula of Poly(allylamine hydrochloride)(PAA HCl).

2.1.2 Surfactant

Benzyl dimethyl hexadecyl ammonium chloride (16-BAC), was obtained from Sigma-Aldrich. It is an organic compound that has a molar mass of $396.09 \text{ g mole}^{-1}$. The structural formula of Benzyl dimethyl hexadecyl ammonium chloride (16-BAC) is shown in Fig. 2.2.

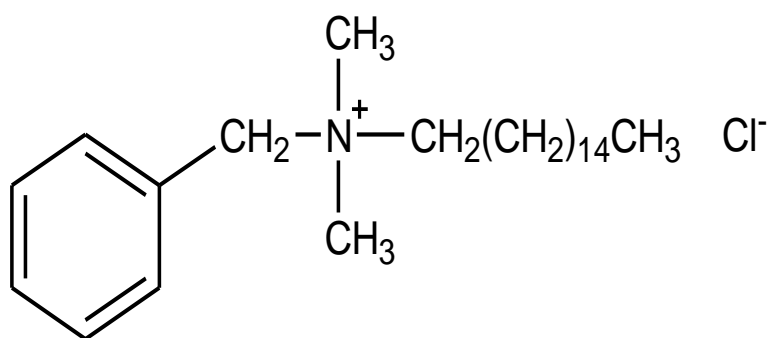


Fig.2.2. Structural formula of Benzyltrimethylhexadecylammonium chloride (16-BAC).

2.1.3 Salts

1. Sodium chloride (NaCl) from Sigma-Aldrich with purity of 99.99% by mass and molar mass of 58.44 g mole⁻¹.
2. Calcium chloride (CaCl₂) from Sigma-Aldrich with purity of 99.99% by mass and molar mass of 110.98 g mole⁻¹.
3. Sodium sulfite (or sodium sulphite) (Na₂SO₃)
4. Sodium sulfate (Na₂SO₄)

2.2 Equipment and Tools

2.2.1 Tensiometer

Surface tension was measured with the state – of – the – art K11 – MK3 tensiometer (Krüss, Germany) using the plate method which is shown in Fig. 2.3. The tensiometer is fully automatic, with high resolution (± 0.01 mN/m) and constant position force measurement with overload protection. It is equipped with high precision force sensor that does not have to be recalibrated and with thermostat jacket for temperature-controlled measurements between -10 and 130 °C.

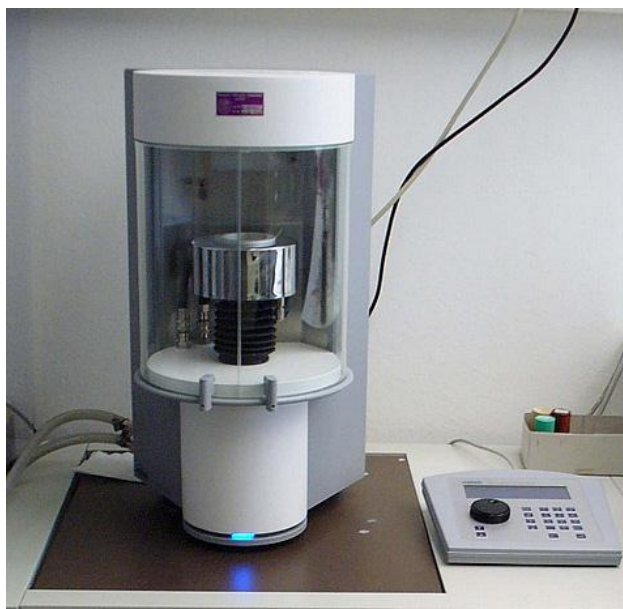


Fig. 2.3. Force Tensiometer – K11 (Krüss -Germany)

2.2.2 Temperature Control

A refrigerated circulating water bath connected to the tensiometer was used to control temperature. It has an accuracy of ± 0.1 °C. The temperature controller shown in Fig. 2.4. was connected to the tensiometer and has the ability to provide cooling or heating. An effective system to thermostat and control temperature was very important during this work as surface tension is temperature dependent.



Fig. 2.4. Refrigerated circulating water bath with temperature controller that has an accuracy of $\pm 0.1^{\circ}\text{C}$.

2.2.3 Furnace

A Lab furnace manufactured by CM Furnaces and has a maximum operating temperature up to 2000 K was used for drying salts. The furnace shown in Fig. 2.5. has sealed designs that support atmosphere control necessary for advanced processes including heat treating, sintering, annealing, glass or ceramic firing.



Fig. 2.5. A Lab furnace by CM Furnaces with heating temperature up to 2000 K

2.3 Methods

2.3.1 Preparation of Tools and Measuring Procedure

All glassware (beakers, volumetric flasks, pipets, burets, funnels) were carefully cleaned by filling them with hot distilled water for several hours and then rinsed thoroughly with distilled water. Freshly prepared distilled water that was used to prepare solutions throughout this work was tested repeatedly for the values of surface tension and conductivity to ensure its purity.

The procedure followed for all surface tension measurements was as follows: before the onset of each measurement, the tensiometer was switched on for two hours to get the magnet inside the measuring chamber to the right temperature. This was recommended by the manufacturer. The surface tension of the freshly prepared distilled water was measured repeatedly to ensure that:

- The quality of water purity is accepted to prepare surfactant solutions.
- The tensiometer is working properly.

The accepted values of surface tension of distilled water at room temperature was in the range between 71 – 72 mN/m. For each reading of surface tension measurement the plate was flame-annealed to redness for several seconds using propane torch to get rid of surface impurities according to manufacturer instructions. The temperature of the solution vessel was brought to the desired value and kept for about half an hour to reach thermal equilibrium. Before each measurement the beaker of the tensiometer was washed with distilled water followed by rinsing with the solution that was used. Measurement of surface tension of each sample was repeated three times and the average value was tabulated. The temperature of the sample was measured at the surface as it is known that bulk and surface temperatures are not the same. This surface temperature was measured with an accurate thermocouple that was supplied with the tensiometer.

A stock solution of NaPSS was prepared. Eleven solutions were prepared from the stock solution by successive dilution. The latter method was used to minimize errors and proven to be an effective one. Using serial dilution from stock solution was the preferred

procedure. A 7.5 g of NaPSS in 500 ml of the highest concentration was prepared and 100ml of this stock solution was used for surface tension measurements and the other was diluted by added distilled water in the 500 mL volumetric flask to the mark and thoroughly mixed. The process was repeated until 7 solutions were prepared, another 100 ml was withdrawn in 200 mL volumetric flask was then diluted by using distilled water. This process was repeated until the other 4 solutions were prepared and the lowest desired concentration was achieved. The surface tension of NaPSS alone or in the presence of added salts, oppositely charge surfactant or oppositely polyelectrolyte at different temperatures were determined by plotting the needed data using the powerful plotting and fitting program Origin 8.

Chapter 3

Results and Discussion

3.1 Surface Tension of Water at Different Temperatures

The surface tension of pure distilled water was measured using the K11 – tensiometer in the temperature range of 273 – 343 K. The measurements were carried out using Wilhelmy plate (platinum). These measurements were performed as preliminary training and testing the precision of method and checking the reproducibility and validity of the data obtained from the tensiometer with the heating system integrated to it. As shown in table 3.1, the measured surface tension values are in good agreement with the reported values according to Vargaftik et. Al [56]. The linear decrease of surface tension of water with temperature is shown in Fig. 3.1. This decrease is expected because increasing temperature means molecules are moving faster and the intermolecular forces (hydrogen bonds in case of water) between molecules become weaker and less effective. The measured and reported values of surface tension at different temperatures are very close with no significant difference between them. This is a solid indication that the tensiometer and the heating system were functioning properly.

Table 3.1 Measured and reported values surface tension of pure water at different temperatures in the range 273 – 343 K

T (K)	273	283	293	303	313	323	333	343
$\gamma_{\text{meas.}}$ (mN/m)	75.12	73.95	72.78	71.13	69.61	67.63	66.18	64.98
$\gamma_{\text{rep.}}$ (mN/m)	75.64	74.23	72.75	71.20	69.60	67.94	66.24	64.47

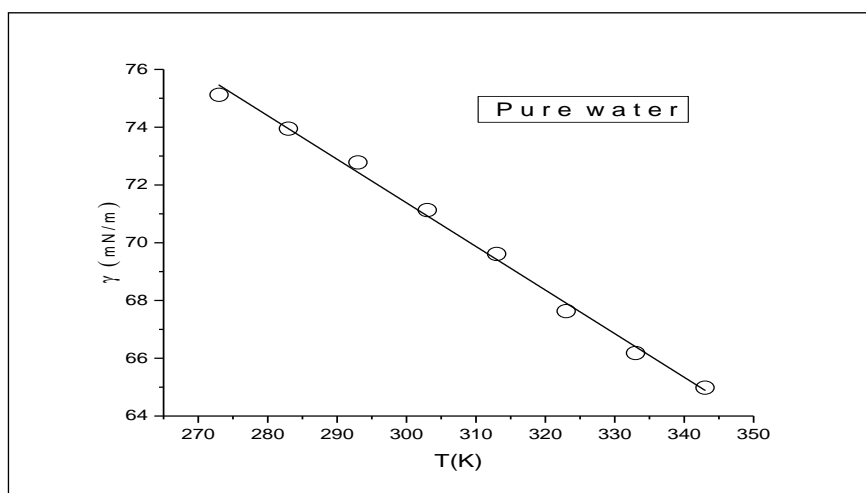


Fig. 3.1. Surface tension of pure water as a function of temperatures. The solid line is to guide the eye.

3.2 Surface Tension of Dialyzed Sodium Poly(styrene sulfonate) and UN-Dialyzed Sodium Poly(styrene sulfonate) at Different Temperatures

Fig. 3.2 shows the surface tensions of two samples of aqueous solutions of NaPSS. The first type (dark square) has white crystalline solid, and second type (open square) has light brown powder) as a function of NaPSS concentration at 30°C.

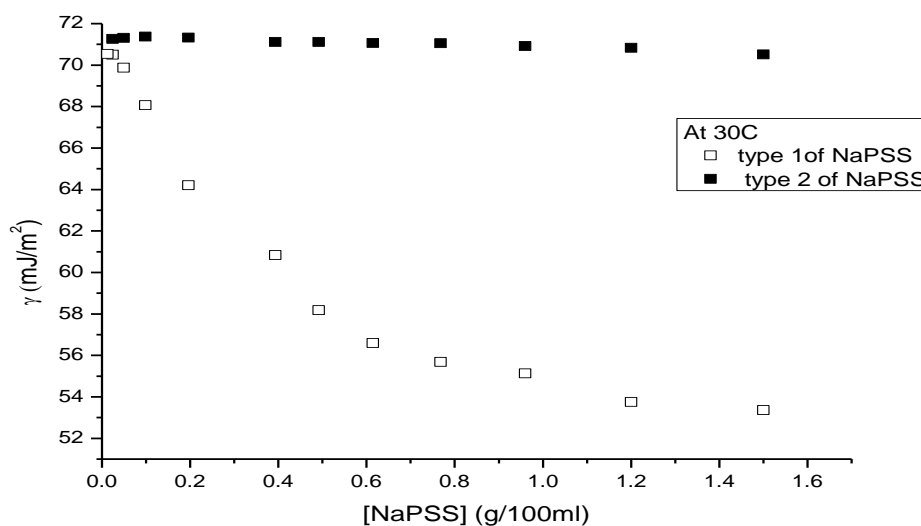


Fig.3.2: Surface tensions of aqueous solutions of dialyzed NaPSS, (dark squares), and undilyzed NaPSS (open squares), both at temperature of 30°C.

From Fig. 3.2, NaPSS type1 sample shows less surface activity than the type 2 NaPSS sample. As can be seen, the surface tension exhibited by our type1 NaPSS sample is almost similar to the UN- dialysis NaPSS sample of [53]. The surface activity of type 2 is nearly similar to that of the dialysed sample of NaPSS. In addition, and as can be seen in Fig.3.2, the surface tension UN-dialyzed of polyelectrolyte solutions begins to decrease only at relatively high concentrations when the ionic strength is high enough and the lateral repulsion of charged groups is screened to a great extent. At this high concentration, the polyelectrolyte molecule is aggregated and any further addition of the polyelectrolyte leads to little decrease of the surface tension. This concentration is called critical aggregation concentration (cac) which Okubo, [57], called the critical polymer concentration c^* when the surface pressure starts to increase.

In Figs. 3.3 and 3.4, the temperature dependence of the surface tension of UN-dialyzed NaPSS and pure NaPSS (dialyzed) are shown.

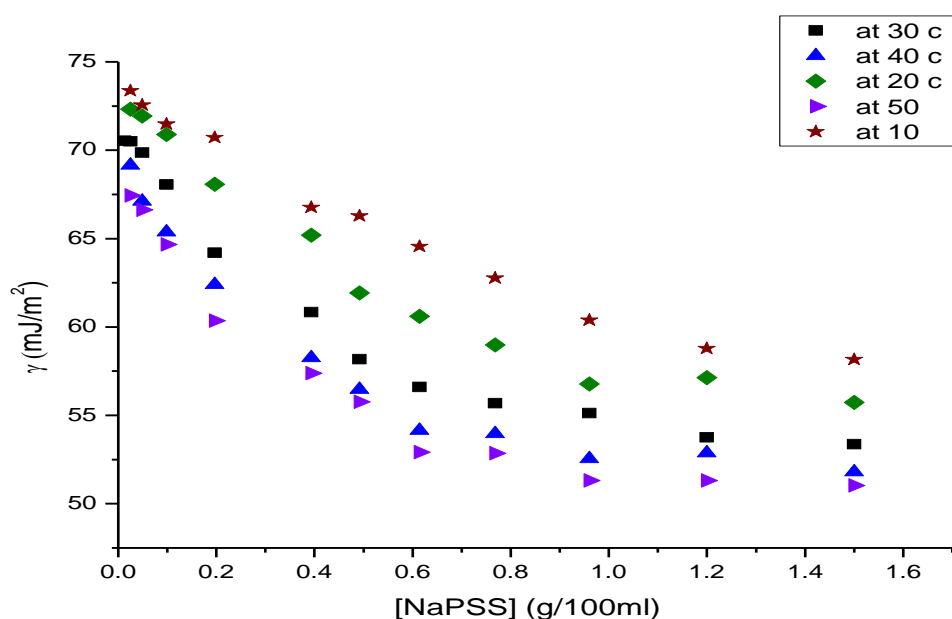


Fig 3.3 Surface tensions of UN-dialyzed NaPSS, (solid squares), at temperatures of 10, 20, 30, 40, and 50°C.

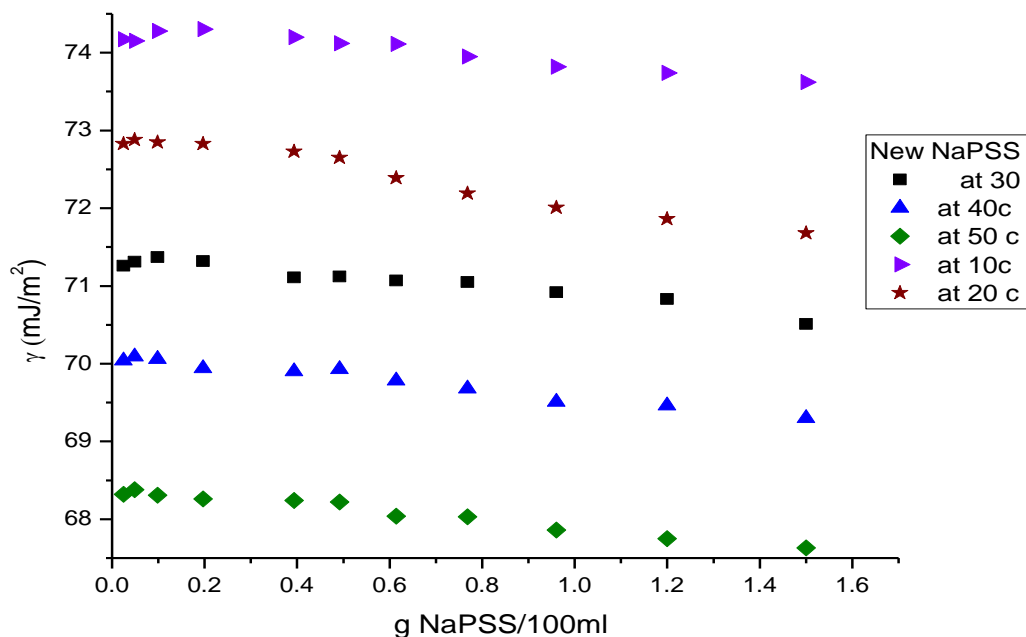


Fig.3.4 Surface tensions of pure NaPSS(dialysis), (solid squares), at temperatures of 10, 20, 30, 40, and 50°C.

It is clear that the un-dialyzed samples indeed show surface activity due to the presence of impurities.

3.3 The Dialyzed Sodium Poly(styrene sulfonate) with Different Salt and Some Acid

Fig. 3.5 shows the surface tensions of aqueous solutions of pure NaPSS, (solid squares), and of NaPSS with added salt NaCl, CaCl₂, Na₂SO₃ and Na₂SO₄, respectively. Also shown in the same figure is the behaviour of surface tension of pure NaPSS with added acids, namely, H₂SO₄ and HCl, as a function of NaPSS concentration at 30°C.

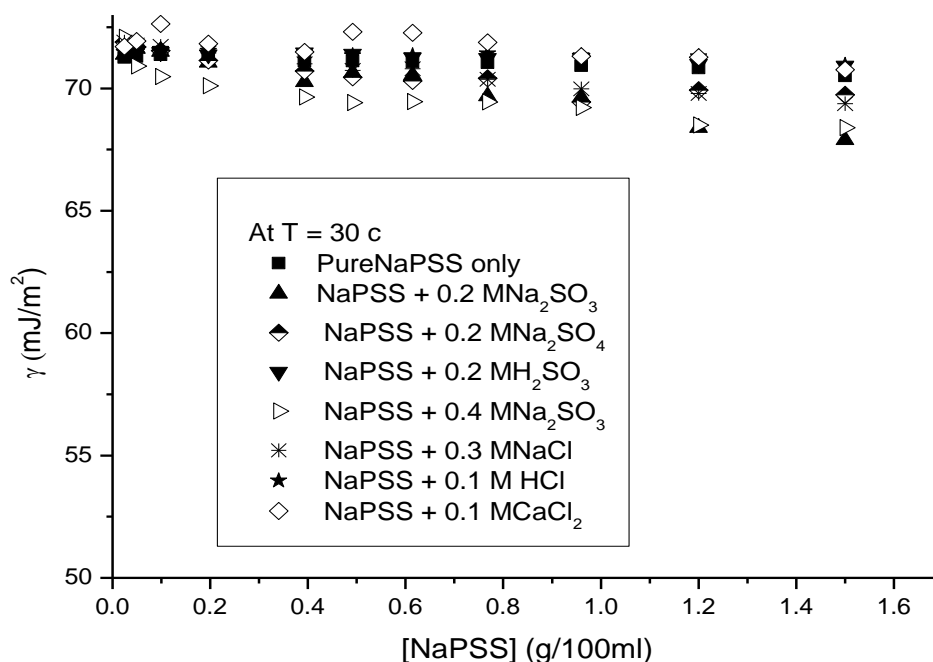


Fig.3.5 Surface tensions of pure NaPSS (dialyzed) and that of added selected salts and acids, as is indicated in the figure, at a temperature of 30°C.

The salts and acids were added to try to change the surface inactivity of pure NaPSS but those did not have any significant effect on the behavior of the surface tension.

The 0.2M Na₂SO₃, 0.4 M Na₂SO₃ displays a very little change in the surface tension due to the repulsion between the same ions in the bulk of the solution of NaPSS.

3.4 The System of Sodium Poly (styrene sulfonate)/ Benzyltrimethylhexadecylammonium Chloride

Fig.3.6 shows the surface tensions of aqueous solutions of pure NaPSS, (solid squares), and of NaPSS with added 0.001g BAC, (open squares), as a function of NaPSS concentration at 30°C. It is clear that pure NaPSS displays no surface activity due to the fact that the NaPSS is a polyanion with negative charges at the segments where charge repulsion is taking place. The charges at the polymer chain prefer to stay in the bulk solution with the water molecules surrounding them and not at the surface near the air side.

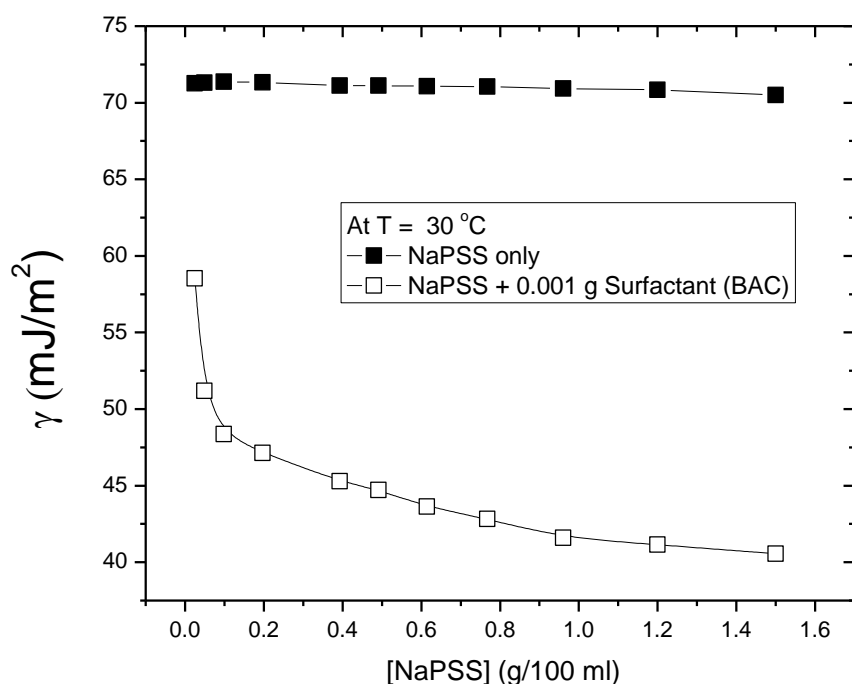


Fig. 3.6. Surface tensions of aqueous solutions of pure NaPSS, (solid squares), and that of NaPSS + 0.001 g of the cationic surfactant BAC, (open squares), both at temperature of 30 °C. The solid line is drawn to guide the eye.

Upon addition of 0.001 g of the BAC surfactant the surface tension starts decreasing with an increase of NaPSS concentration. The concentration of the surfactant is below its critical micelle concentration. The surfactant head groups having a positive charge is expected to associate with the negative charges on the sulfonate groups of the NaPSS while using counter ions. This association is the origin of the displayed surface activity. The surface tension saturates at a value of 40 mN/m. The NaPSS /BAC association process decrease the charge-charge repulsion on the NaPSS and allow its structure to become more surface active relative to that of pure NaPSS. This in turn leads to reduction in the surface tension.

For the sake of comparison, we have made measurements as a function of BAC concentration keeping the NaPSS concentration constant. Figure 3.7 below displays the results of these measurements. The surface tension of pure BAC surfactant as a function of its concentration is shown by the open squares, while open circles and open stars represents those with added 0.5 g and 0.1 g of NaPSS, respectively. The CMC of the BAC surfactant was determined to be 6.12 mmol/L. This value is very

close to the reported value of 6.28 mmol/L by El-Dossoki *et al* [58] using conductivity measurements. As can be seen in Figure 3.7, the value of the surface tensions of the NaPSS/BAC complex is lower than that of pure BAC, at the same conditions. To make things more clear, the value of the surface tension at 0.001 g BAC and 0.1 g NaPSS (obtained from Figure 3.6) is 46.6 mJ/m², while that at 0.001 g pure BAC (obtained from Figure 3.7) is 59.24 mJ/m². This corresponds to about 21% decrease, which is a significant change.

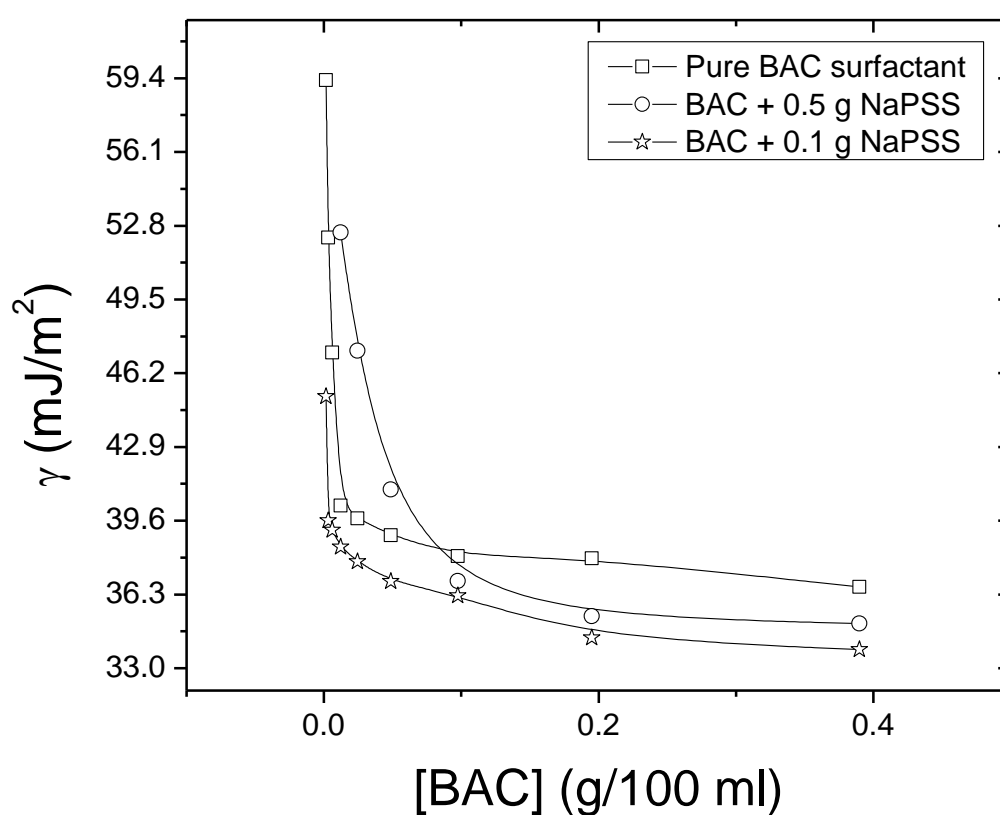


Fig.3.7. Surface tension as a function of BAC concentration, for pure BAC (open squares), with added 0.1 g NaPSS (open stars) and 0.5 g NaPSS (open circles) as indicated in the figure. The solid lines are drawn to guide the eye.

The value of the surface tension of 0.001 g BAC and 0.1 g NaPSS extracted from Fig.3.7 is 46.2 mJ/m² which is again very close to the value extracted from Fig.3.6. The surface tension values, when 0.5 g NaPSS is added, are higher than those obtained when 0.1 g NaPSS is added. This may indicate that the complexation process

is more effective in lowering the surface tension at low NaPSS concentrations than at higher ones. Based on our results, it seems reasonable to assume that the complexation process occurs at the surface rather than in the bulk. The surfactant molecules will migrate to the surface upon addition and these will attract the polyelectrolyte chains for the sake of charge neutrality.

Figure 3.8 shows the surface tensions of NaPSS solutions at a constant added amount of 0.001 g of BAC at temperatures from 10°C to 50°C. As was mentioned before, temperature dependent measurements are lacking in the literature and thus it is important to carry out such measurements as they yield information about the surface excess entropy (S^σ) of the system. As can be seen, the surface tension decreases both as the concentration of NaPSS and temperature increase. As more NaPSS is added, the association probability with the cationic surfactant head groups increases, thus the surface activity of the NaPSS/BAC complex increases. On the other hand, by comparing the change in the surface tension at different temperatures it is clear that the surface activity is increasing with increasing temperatures, which indicates more association between the polyelectrolyte and the surfactant.

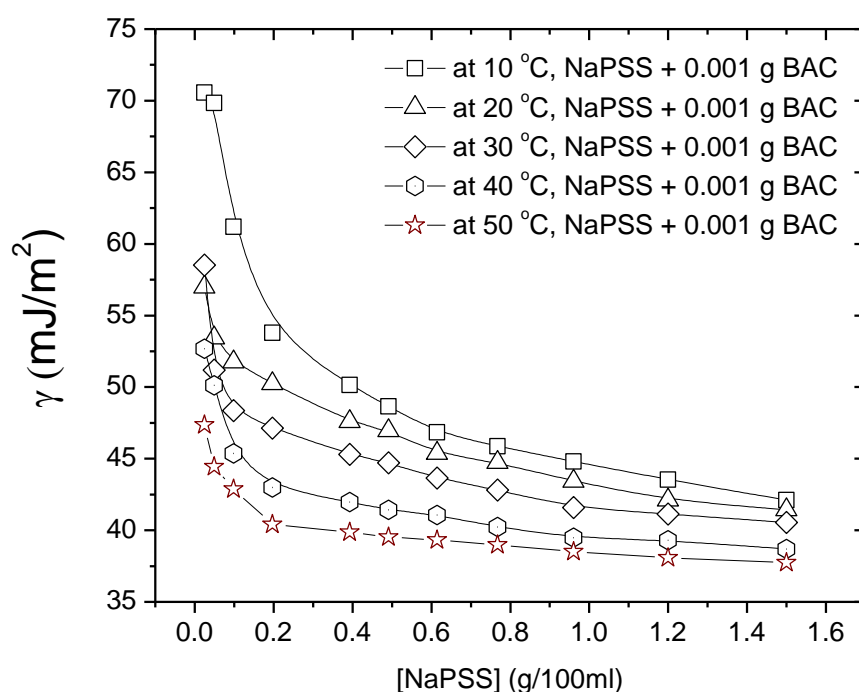


Fig. 3.8 The surface tensions of the NaPSS solutions at a fixed added amount of BAC of 0.001 g at temperatures from 10°C to 50°C. The solid lines are drawn to guide the

The change in surface tension as a function of temperature at three different NaPSS concentrations is extracted from Fig. 3.8 and the results are plotted in Fig. 3.8.a. The surface tension shows a linear decrease with increasing temperature. Fig. 3.8.b is even more informative as it shows the surface excess entropy as a function of NaPSS concentration. The surface excess entropy is related to the temperature gradient of the surface tension by the following relation:

$$S^\sigma = -\frac{d\gamma}{dT}$$

All terms in the equation have already been defined.

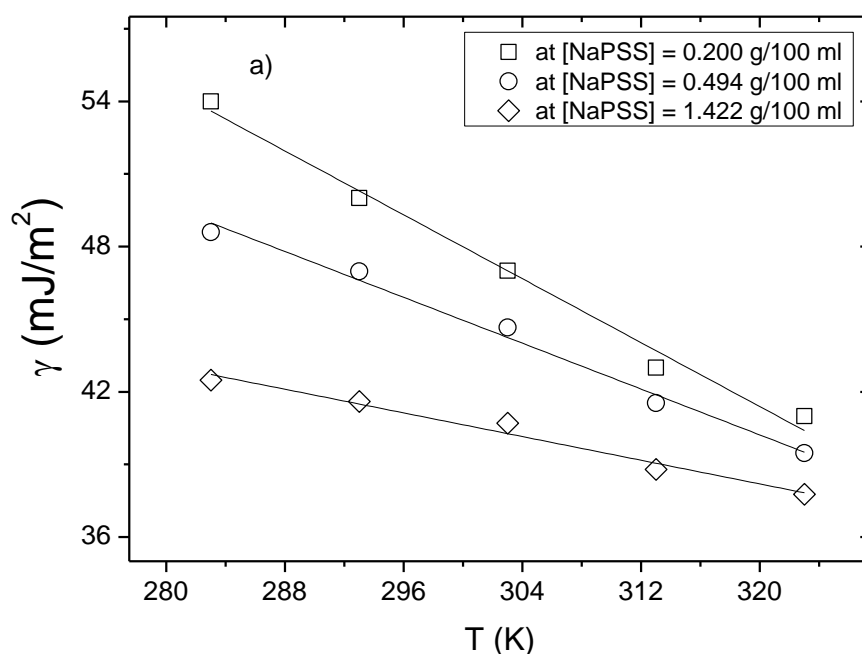


Fig. 3.8.a Surface tension as a function of temperature at three different NaPSS concentrations. The solid lines are least square linear fits to the

From Fig. 3.8.b the surface excess entropy of the polyelectrolyte/surfactant mixture as a function of NaPSS concentration is calculated. The S^σ value shows a decrease to about 30% of its initial value upon increasing the concentration of NaPSS concentration from 0.2 to 1.4 g/100 mL. Such change in entropy gives information about surface ordering. The decrease in S^σ values with increasing the NaPSS concentrations implies that the surface becomes more ordered as more NaPSS is added. This could be explained by the fact that when more of NaPSS is added while

keeping the concentration of the oppositely charged surfactant constant the association process is more effective and thus more of NaPSS will be present on the surface rather than in bulk. However, and referring to Fig.3.8, it is clear that at relatively low NaPSS concentrations (less than about 0.2 g/100 mL), the decrease in surface tension values is rapid, signalling a more effective association process between the surfactant and the polyelectrolyte. This effective association can be attributed to the presence of almost equal numbers of charges of the surfactant head groups and the negative charges at the styrene groups attached to the backbone of the NaPSS.

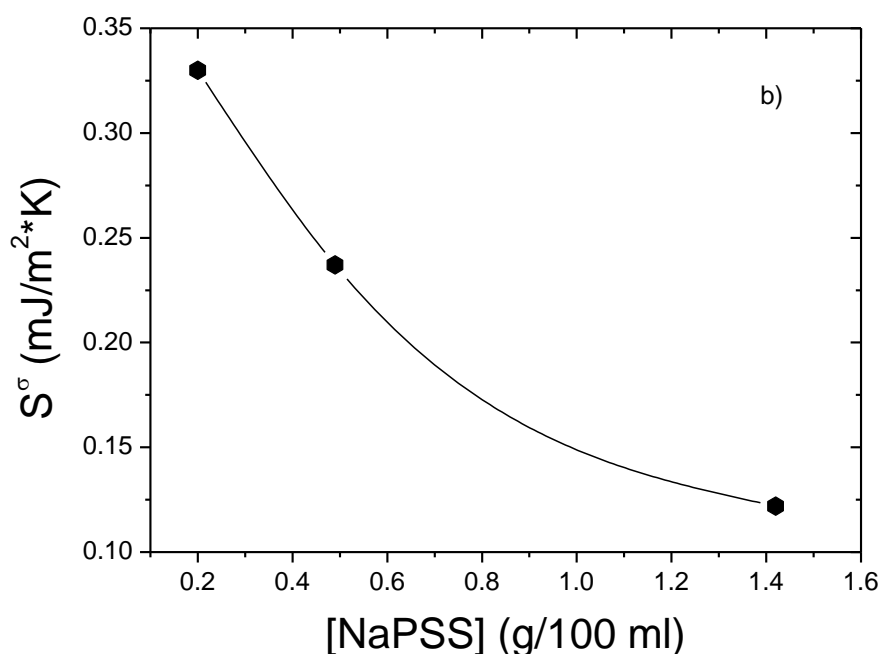


Fig. 3.8.b Surface excess entropy as a function of NaPSS concentration. The solid line is drawn to guide the eye.

Fig. 3.9 shows the surface tensions of aqueous solutions of a mixture of NaPSS and 0.001 g of BAC without (open squares) and with (open circles) 0.1 M of added NaCl solution at 30°C. The surface tension behaviour is completely different in the presence of the monovalent NaCl salt than in its absence. At low NaPSS concentration and without the salt the surface tension starts at about 58 mJ/m² and reaches saturation at

about 40 mJ/m^2 . In the presence of NaCl salt the initial value of the surface tension is about 40 mJ/m^2 and it stays almost constant in the whole concentration range studied. This indicates that the presence of NaCl enhances the association of NaPSS with the oppositely charged BAC surfactant and makes it more surface active. The presence of salt decreases the repulsion between similar charges at the polyelectrolyte backbone, and that between the surfactant head groups. At the same time the presence of the salt results in a decrease of thickness of solvation layer around ionic heads of both the surfactant and the polyelectrolyte, and so the electrostatic repulsion between similar ions is also reduced. This leads to a decrease in hydrophilic property of both surfactant and polyelectrolyte, and hence decreases in surface tension and increase in surface activity of their solutions.

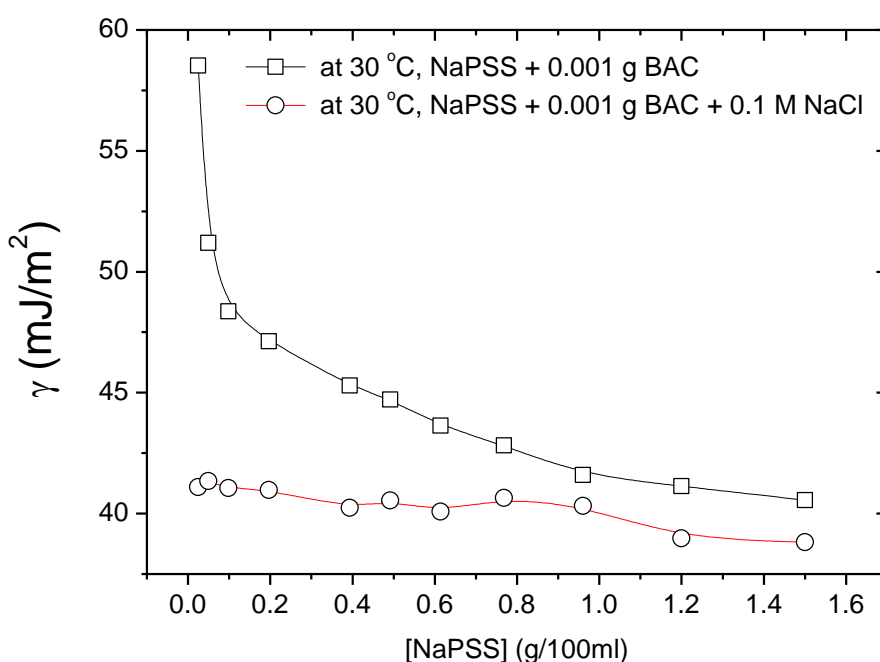


Fig.3.9. Surface tensions of aqueous solutions of NaPSS plus 0.001 g of BAC without (open squares) and with (open circles) added 0.1 NaCl and both at 30 °C. The solid lines are drawn to guide the eye.

Fig. 3.10 shows the surface tensions of aqueous mixtures of NaPSS and 0.001 g of BAC without (open squares) and with (open circles) added 0.1 M CaCl_2 and both at 30 °C. The effect of this divalent salt is slightly larger than that of the monovalent salt NaCl. In this case, at low NaPSS concentration and without salt the surface tension

starts at about 58 mJ/m^2 and saturates at about 40 mJ/m^2 , whereas in the presence of CaCl_2 the initial value is about 38 mJ/m^2 and stays almost constant in the whole concentration range studied. This indicates that the presence of CaCl_2 enhances the association of NaPSS with the oppositely charged surfactant BAC and makes it more surface active as in the case of NaCl. The valency of the cation seems to play a negligible effect because the decrease in the surface tension is only 2 mJ/m^2 in comparison to the value of the surface tension in the case of NaCl. However, the presence of salt itself has a significant effect of the association process and the surface activity of the associated complex.

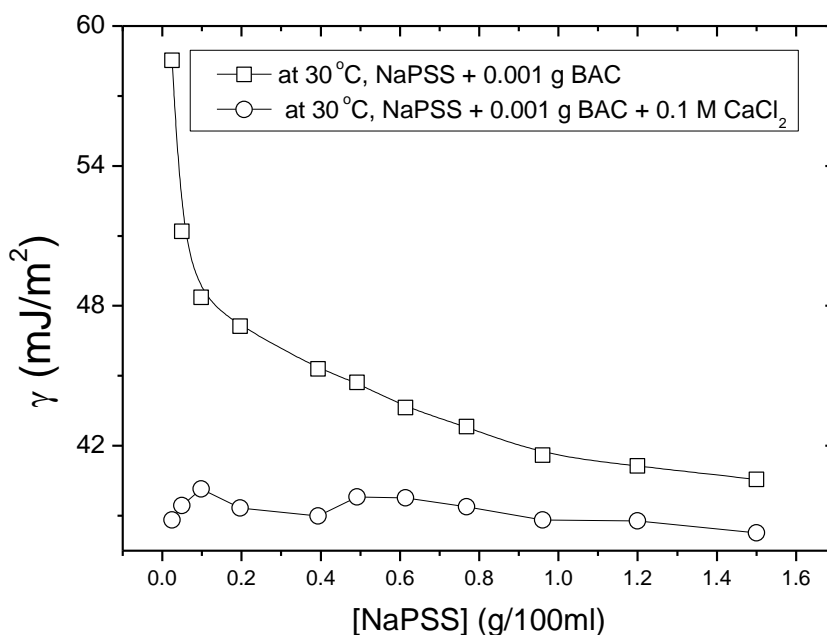


Fig. 3.10. Surface tensions of aqueous solutions of NaPSS plus 0.001 g of BAC without (open squares) and with (open circles) added 0.1 CaCl_2 both at 30°C . The solid lines are drawn to guide the eye.

Fig. 3.11 shows the surface tensions of aqueous solutions of mixtures NaPSS with different amounts of added BAC and all at 30°C . Above NaPSS concentration of 0.4 g/100 ml, the surface tension is slightly influenced by increasing the BAC concentration. However, below this concentration of NaPSS the effect of BAC concentration is only seen at 0.009 g/100 ml where the surface tension value at the lowest NaPSS concentration studies is about 41 mJ/m^2 whereas at lower BAC

concentration it is about 60 mJ/m^2 . The association process between the oppositely charged surfactant/polyelectrolyte in this case is accomplished at low concentration where the opposite charges neutralises each other and the resultant complex exhibits its surface activity and any addition of the BAC surfactant is dissolved in the bulk. The latter behaviour resembles the behaviour of pure charged surfactant in pure water, in which there will be no change in surface tension accompanying the increase in the surfactant concentration when the concentration exceeds the critical micelle concentration of the surfactant.

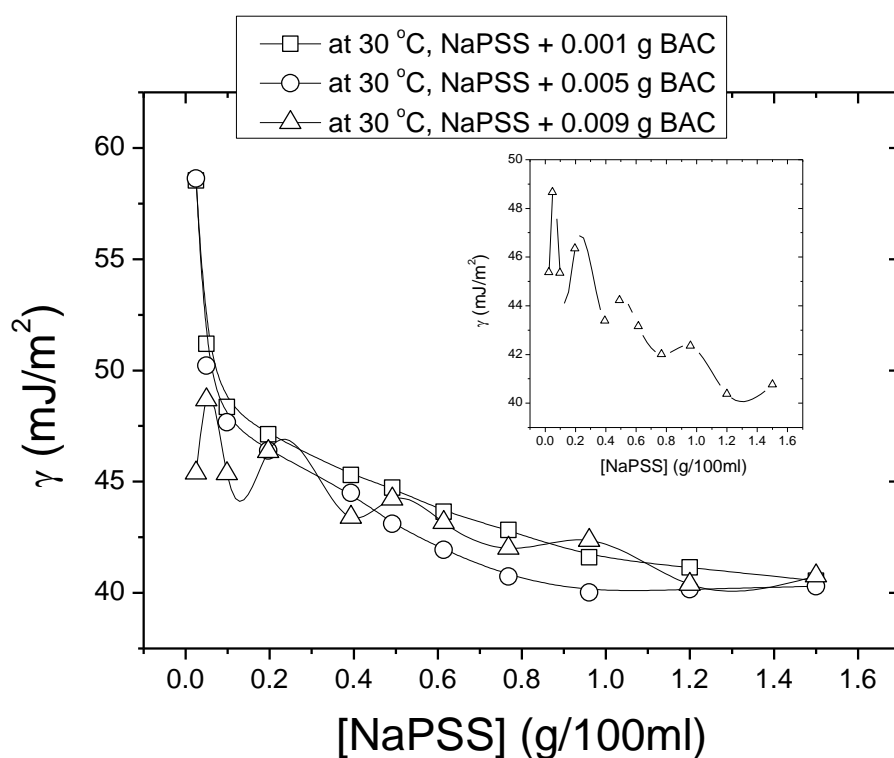


Fig. 3.11. Surface tensions of aqueous solutions of NaPSS plus 0.001 g (open squares), 0.005 g (open circles) and 0.009 g (open triangles) g of BAC and all at 30°C . The solid lines are drawn to guide the eye. The inset is the surface tension of NaPSS solutions at 0.009 g/100ml BAC.

3.5 The System of Sodium Poly(Styrene Sulfonate)/Poly(Allylamine Hydrochloride).

The surface tension of mixtures of two oppositely charged polyelectrolytes system is shown in Fig.3.12. The effect of changing the concentration of NaPSS solutions added to two different concentrations of polyallylamine hydrochloride (PAACl) is examined. The open squares represent the values when 0.005 g of PAACl is added while the open circles represent those of addition of 0.01 g. It is clear that at low concentrations of the polycation PAACl there is almost no effect on the surface tension of the NaPSS. At these low concentrations, the charges on the PAACl are not enough to equalize the charges on the polyanion NaPSS.

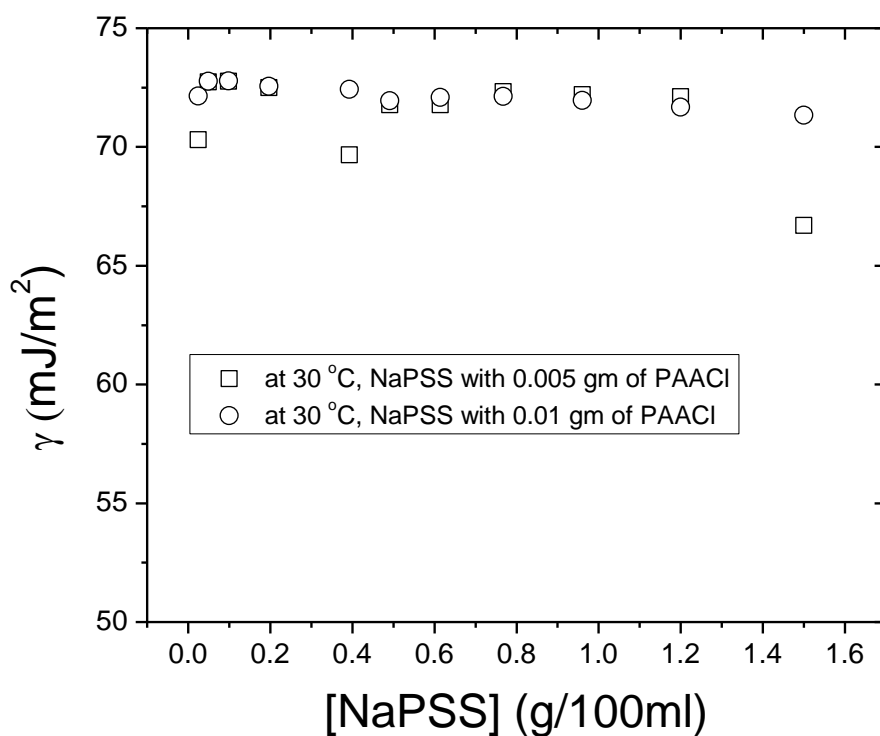


Fig.3.12. Surface tension of NaPSS solutions at two different concentrations of polyallylamine hydrochloride (PAACl), open squares at 0.005 g of PAACl and

As the concentration of PAACl is increased to 0.1 g/100ml, the effect on the value of surface tension becomes obvious as shown in Fig. 3.12. This is the lowest concentration of PAACl studied where such effect is found. The surface tension value goes from that of water (72 mJ/m^2) at low NaPSS concentration to a value of 63 mJ/m^2 . This is about 14% decrease in the surface tension value and cannot be attributed to experimental errors taking into consideration the high accuracy of the tensiometer. Measurements were repeated several times and the same behaviour was observed. The appearance of the peak in Fig. 3.13 can be explained as follows: at low concentrations of NaPSS (lower than 0.1 g/100 mL) the surface tension is almost that of water indicating that the association process of polyanion/polycation is not complete and the observed effect is that of PAACl alone which in fact does not display significant surface activity. At equal concentrations of the two polyelectrolytes of 0.1 g/100 ml, the surface tension decreases to about 63 mJ/m^2 indicating that at equal concentrations of the two polyelectrolytes the conservation process is at maximum play. As the concentration of NaPSS is increased to 0.2 g/100 ml, signalling an association process in which the coacervate displays surface activity. However, as the concentration of the NaPSS is increased to 0.4 g/100ml, the surface tension goes back to values of NaPSS solution when it is alone. So below one to one concentration of 0.1 g/100 mL the effect is that of the PAACl which does not show much surface activity. At 0.1 g/100 mL concentration, the effect is that of the coacervate, and above 0.4 g/100 mL concentration the effect is almost that of pure NaPSS. Clearly there is charge inversion around the one to one concentration; positive below 0.1 g/100 mL and negative at a concentration of 0.4 g/100 mL. It has to be mentioned that this behaviour is only observed at this particular concentration and at higher concentration values of PAACl.

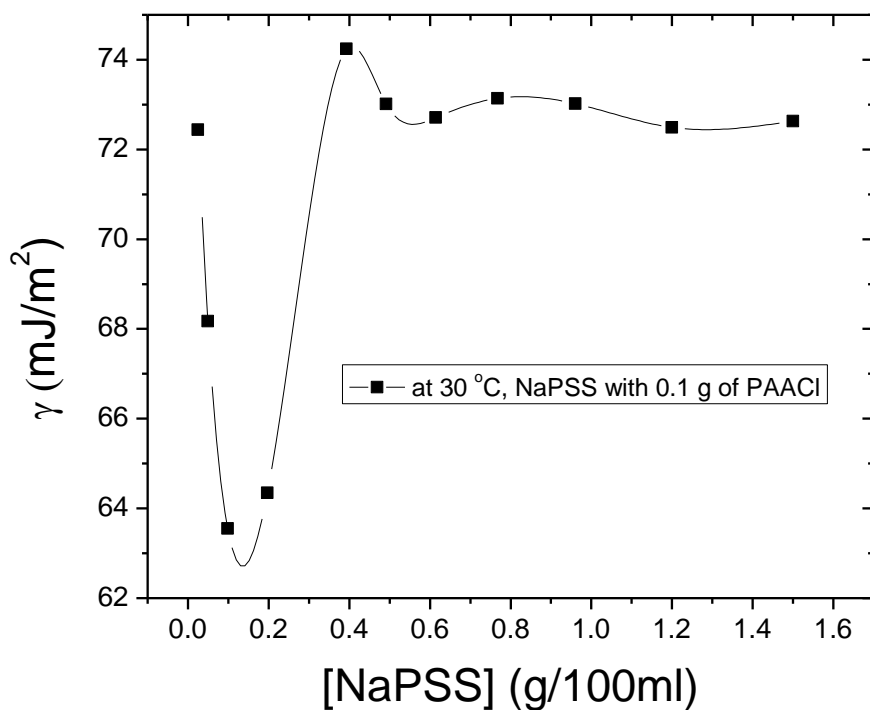


Fig.3.13. Surface tension of NaPSS solutions with added fixed amount of 0.1 g of PAACl at a temperature of 30°C. The solid line is drawn to guide the eye.

When monovalent and divalent cation salts were added to the previous coacervate, no change in surface tension behaviour was observed. This is probably due to the presence of large quantities of the counter ions of the polyelectrolytes. Addition of NaCl salt means that more sodium and chloride ions will be added to the already existing Na^+ (from NaPSS) and the Cl^- (from PAACl). The addition of the CaCl_2 salt also displayed no effect whatsoever.

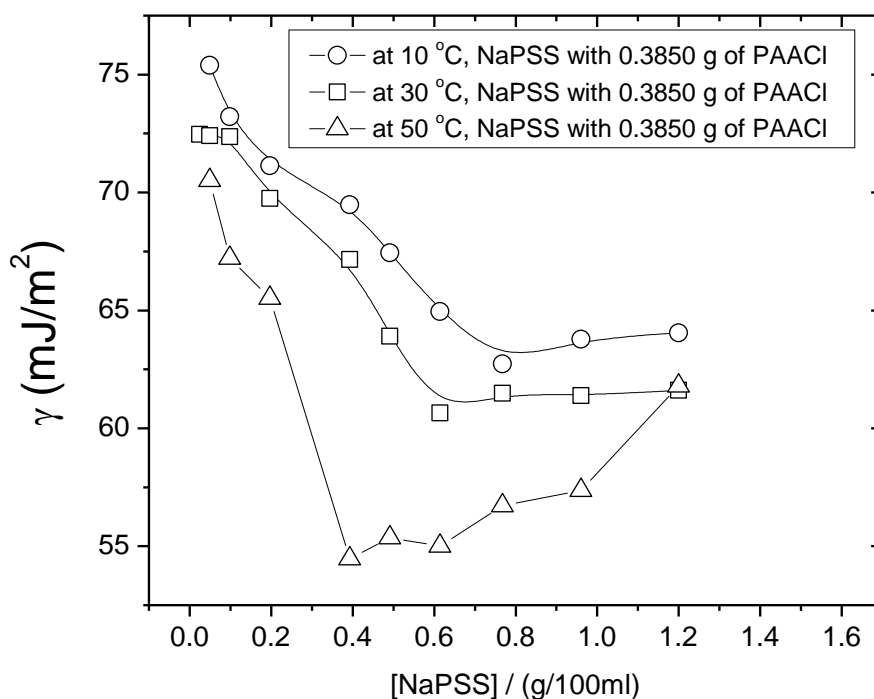


Fig.3.14. Surface tensions of NaPSS with added 0.3850 g/100ml PAACl at three different temperatures as indicated in the figure. The solid lines are drawn to guide

The effect of changing temperature on the surface tension of the coacervate NaPSS/PAACl is shown in Fig. 3.14. The concentration of PAACl is 0.3850 g/100ml and measurements were carried out at 10°C, 30°C and 50°C. As can be seen, increasing the temperature decreases the surface tension of the coacervate, specially in the concentration range of 0.1 g to 1.0 g/100ml of NaPSS. The largest decrease occurs around 0.4 g/100ml concentration where the surface tension decreases by 23% as the temperature is raised from 10°C to 50°C.

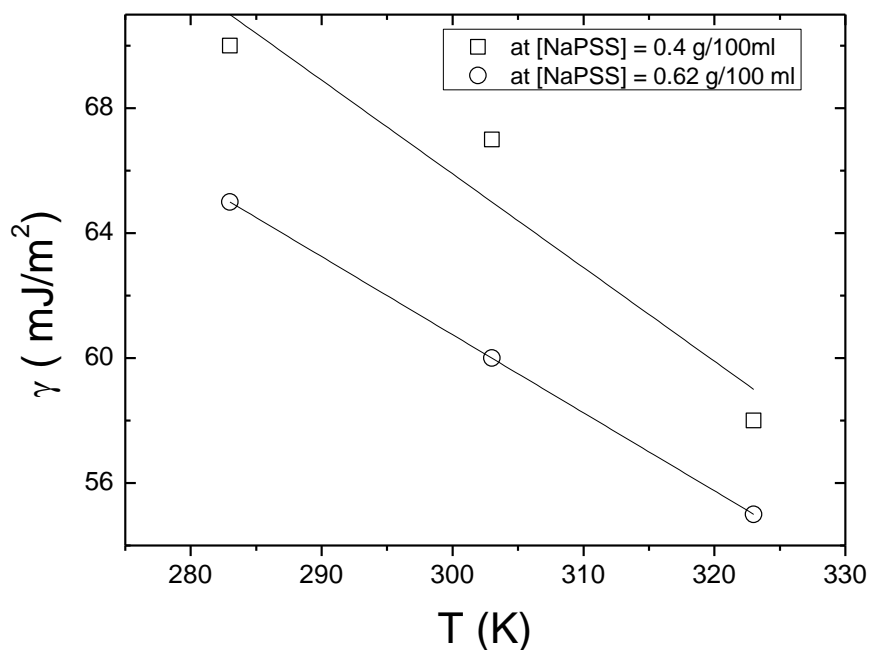


Fig. 3.15. Temperature behavior of the surface tension of the coacervate NaPSS/PAACl at two different NaPSS concentrations. The solid lines are the least square linear fits to the experimental points

Fig. 3.15 shows the temperature behaviour of the surface tension at two different NaPSS concentrations. From this figure the surface excess entropy is determined to be $0.3 \text{ mJ/m}^2\text{K}$ at NaPSS concentration of 0.4 g/100 ml and $0.22 \text{ mJ/m}^2\text{K}$ at NaPSS concentration of 0.62 g/100ml . This is about 25% decrease in the surface excess entropy which indicates a significant decrease in entropy with increasing NaPSS concentration. The surface goes from a less ordered one at low concentration (0.4 g/100ml) of NaPSS to a more ordered one at higher concentration (0.6 g/100ml). This shows that the coacervation and the association process are influenced by temperature changes. Since the surface becomes more ordered as NaPSS amount is increased beyond the almost one to one concentration ($[\text{NaPSS}] = 0.4 \text{ g/100 mL}$ and $[\text{PAACl}] = 0.3850 \text{ g/100 mL}$), then the added NaPSS molecules has enhanced the well-established coacervation process as coacervates imparts ordering at the surface.

Conclusions

Contrary to previously published work on this subject, we have studied the surface tension of surfactant/polyelectrolyte mixtures by varying the concentration of the polyelectrolyte while keeping the surfactant concentration constant at a value lower than its critical micelle concentration. The surfactant/polyelectrolyte mixtures showed increase in surface activity as the concentration of NaPSS was increased. The surface activity was also affected by changing the temperature, and from the obtained data the surface excess entropy was estimated. The decrease in surface excess entropy as more NaPSS presented indicates that the surface became more ordered. Addition of NaCl or CaCl₂ salts showed significant impact on the association process of the surfactant with the polyelectrolyte. In the case of two polyelectrolytes coacervates, the surface tension behaviour displayed a peak at one to one concentration of the polycation/polyanion but only at low concentration of about 0.1g/100 ml. This result showed that the coacervation process was at its climax at relatively low polyelectrolyte concentrations. Future work will concentrate on studying the coacervation process in more details and will only include measurements at low concentrations of both polyelectrolytes.

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