

Equilibrium, dynamic surface tension properties of alkyl and alkyl ether sulfates and their relation to foaming behaviour.



A thesis submitted towards partial fulfilment of BS-MS Dual Degree Programme

by

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CERTIFICATE

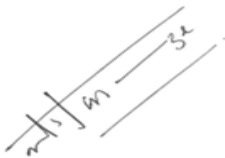
This is to certify that this thesis titled “**Equilibrium, dynamic surface tension properties of alkyl and alkyl ether sulfates and their relation to foaming behaviour**” submitted towards the partial fulfilment of the BS-MS dual degree programme at the Indian institute of Science Education and Research (IISER), Pune represents original research carried out by Farzeena C at Unilever R&D, Bangalore, under the supervision of Dr. Narayanan Subrahmaniam during the academic year 2014-2015.

Signature : 
Name of the supervisor: Narayanan Subrahmaniam

Date: 24/03/2015

DECLARATION

I hereby declare that the matter embodied in the report entitled “**Equilibrium, dynamic surface tension properties of alkyl and alkyl ether sulfates and their relation to foaming behaviour**” are the results of the investigations carried out by me at the Department of Laundry, Hindusthan Unilever Research Center, Bangalore under the supervision of Dr. Narayanan Subrahmaniam and the same has not been submitted elsewhere for any other degree.



Farzeena. C

Date: 25.03.2015

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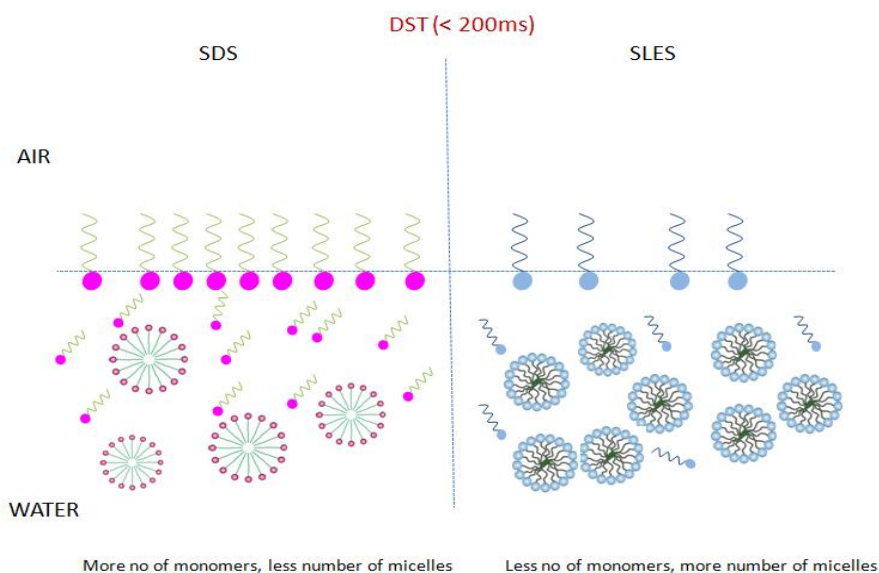
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ABSTRACT

Alkyl sulfates and alkyl ether sulfates are widely used anionic surfactants in cleaning products. There have been several studies showing the effect of ethoxylation on the equilibrium surface properties. However, an understanding of the dynamic behaviour at air water interface is required to explain foaming ability of the surfactants. This project is therefore undertaken to infer the effect of ethoxylation on equilibrium as well as dynamic surface tension (DST) and its relation to foaming behaviour of alkyl sulfates Sodium Dodecyl Sulfate (SDS), Primary Alkyl Sulfate (PAS) and alkyl ether sulphate, Sodium Lauryl Ether Sulfate (SLES). The submicellar solutions of SLES showed a low equilibrium and dynamic surface tension compared to both the alkyl sulfates, SDS and PAS. The study revealed an interesting fact that, the micellar solution of SLES is poor in reducing the dynamic surface tension compared to its nonethoxylated counterpart SDS, as a consequence of increased micellar stability. The foamability of submicellar and micellar solutions showed a good correlation with the observed dynamic surface behavior. Addition of NaCl resulted in a reduction in both equilibrium as well as dynamic surface tension. As expected SLES showed an excellent hardness tolerance, as the ethoxyl group binds the Ca^{2+} ions preventing its interaction with the sulfate head groups.



1. INTRODUCTION

Surfactants are of widespread importance in detergent industry, in emulsification, lubrication, catalysis, oil recovery, and in drug delivery. Surfactants constitute the major portion of detergents. Although water is used for cleaning; high surface tension makes it less efficient in wetting and removing dirt. In the cleaning process surface tension of water must be reduced so that water can spread and wet surfaces. Surface tension reduction in aqueous systems is achieved by the addition of surface active agents or surfactants. *“A surfactant (a contraction of the term surface-active agent) is a substance that, when present at low concentration in a system, has the property of adsorbing on to the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces)”*[1]. Surfactant can be considered as a versatile molecule, because they are responsible for the good wetting, cleaning and foaming properties of water. However, wetting is related to equilibrium surface tension, whereas foaming is a dynamic phenomenon. Surfactants having excellent equilibrium surface tension may show poor dynamic surface tension. For example, the nonionic surfactants such as alkylphenol or alcohol ethoxylates, shows good equilibrium surface tension performance but are not efficient in reducing dynamic surface tension [2]. Hence a reduction in both equilibrium and dynamic surface tension is required for a better performance of detergents. Micellization is another characteristic feature of surfactants which helps in solubilising dirt during cleaning process.

The surface activity of a surfactant molecule can be attributed to their characteristic structure. Surfactants are amphiphiles. They are composed of a hydrophobic tail, usually a long alkyl chain attached to a hydrophilic head group, which enables them to orient at surfaces/interfaces (Fig1.1a). They are classified as anionic, cationic, Zwitterionic and non-ionic based on the charge of their head groups. Surfactant molecules align at the surface (air-water) with its head group in the aqueous phase and tail pointed towards air/nonpolar phase. Such an alignment decreases the dissimilarity between two phases and causes a reduction in the surface tension of water. Because of their amphiphilic nature the concentration of surfactants at the air - water interface

exceeds than the bulk. As the concentration of a surfactant increases the surface tension keeps on reducing until the surface gets saturated with surfactant monomers. This point corresponds to the minimum value of surface tension (Fig1.2). Moreover, the additional surfactant molecules move into the bulk and form aggregates in such a way that their hydrophobic groups directed toward the interior of the cluster and hydrophilic head groups directed toward the aqueous phase. These aggregates are termed as micelles (Fig1.1b). The concentration at which this phenomenon occurs is termed as Critical Micelle Concentration (CMC). Micelles acquire different shapes depending on the packing parameter of a surfactant monomer, which in turn depends on the volume of the hydrophobic chain, cross-sectional area of the hydrophobic core, and the length of the hydrophobic chain. The hydrophobic core of micelles helps in solubilising dirt during cleaning process. Critical micelle concentration of a surfactant is influenced by several factors like the structure of surfactant, the presence of added electrolyte and the temperature of the solution [1].

Generally, CMC decreases as the hydrophobic character of the surfactant increases. Moreover, ionic surfactants show higher CMC than the equivalent non ionic surfactant. This is due to an increased repulsion among the charged head groups of ionic surfactants. CMC of ionic surfactants are affected by the addition of counter ions. Figure 1.3 shows a portion of anionic surfactant micelle with added sodium salt. As shown in the figure the counter ion binds to the head group of the surfactant, reducing the head to head coulombic repulsion. Increased binding of counter ion, causes a reduction in CMC. The degree of counter ion binding increases with increase in the charge of the counter ion and decreases with an increase in the hydrated radius. If we

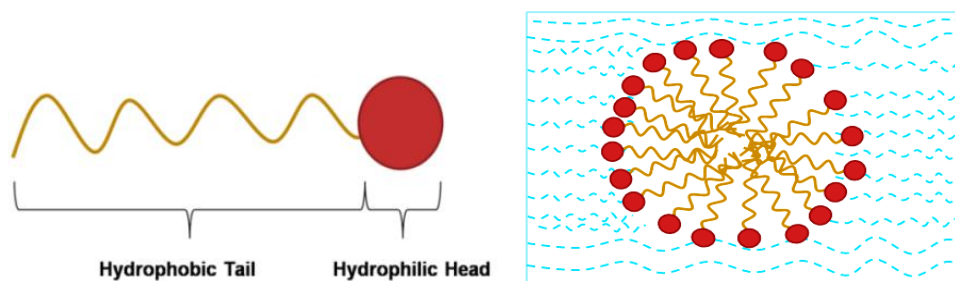


Figure 1.1: Schematic diagram of **a)** A surfactant molecule **b)** Micelle (in water)

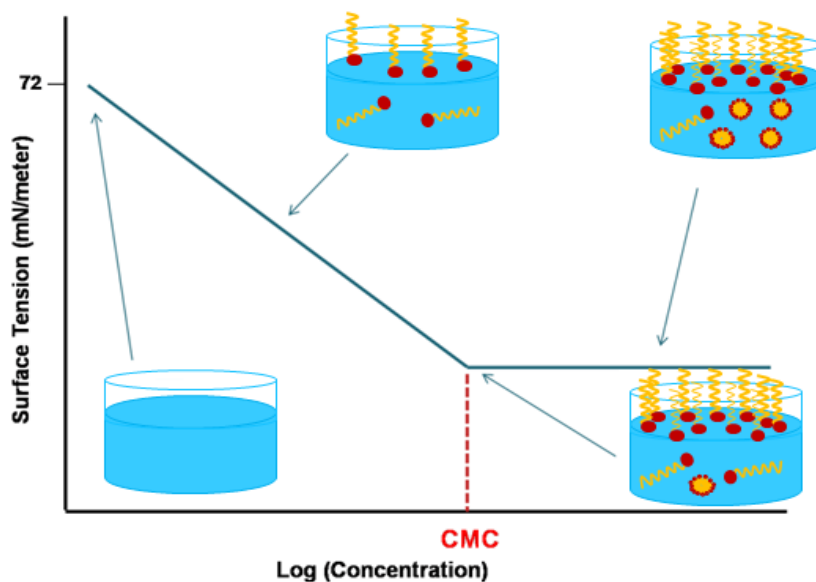


Figure 1.2: Surface Tension as a function of surfactant concentration

consider the alkali metals in aqueous surfactant solutions, CMC decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ due to an increase in its hydrated radius. Since an increase in hydrated radii causes a reduction in effective nuclear charge. Moreover, an increase in valency results in a decrease in CMC i.e.; monovalent > divalent > trivalent ions [1]. The effect of added electrolyte on surfactants is given by Corrin and Harkins [3],

$$\log CMC = a \log C_i + b \quad (1.1)$$

where a and b are constants for a given ionic head at a particular temperature and C_i is

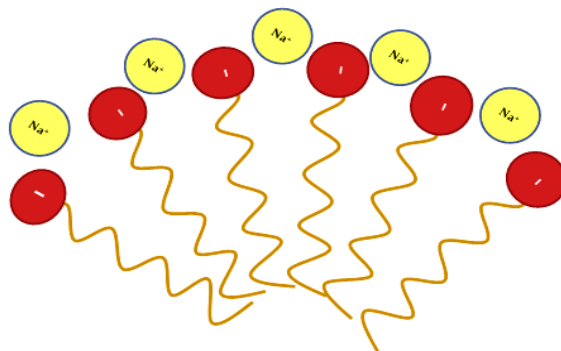


Figure 1.3: Showing a portion of anionic surfactant micelle with bounded sodium ions

the total counterion concentration in equivalents per liter [1].

The equilibrium surface properties of aqueous surfactant solutions are also affected in presence of counterions. Ionic surfactants in presence of excess electrolytes, shows a reduction in surface tension compared to the salt free system. This is a consequence of counterion binding to the head groups, resulting in a reduction in electrostatic repulsion among the head groups. However the dynamic surface properties are quite different from equilibrium micellar as well as surface properties. The time-dependent surface tension, where the time is measured starting from the formation of a new interface until equilibrium is reached, is referred to as the dynamic surface tension [4]. DST depends on the surfactant concentration, rate of diffusion of monomers from bulk to the surface, from the subsurface (an imaginary plane few molecular diameters below the surface) to the interface and the micellar stability [4, 5].

As mentioned earlier, foaming is a property related to dynamic surface tension. Foam is a colloidal dispersion of gas in a liquid or solid [6]. In general, foaming properties of surfactant solutions are defined in terms of foamability and foam stability, i.e. the 'ability to foam' and the 'stability of the foam'. Adsorption of surfactants at the air water interface results in a lowering of surface tension, resulting in an increase in interfacial area. The volume of foam generated when a sufficient amount of work is done on surfactant solution, depends on the surface tension of the solution, since the minimum amount of work required to produce the foam is, the product of the surface tension and the change in interfacial area upon foaming ($W = \gamma\Delta A$). Therefore, lower the surface tension of the aqueous solution, the greater is the foam volume [1]. Stability of the foam is described as the change in volume with time [7]. Foam stability is determined by several factors. Drainage of solution from the foam lamellae under the influence of gravity or pressure gradient along the lamellae is one of the important factors affecting the foam stability. As a result of drainage, the thickness of lamellae diminishes and eventually results in its rupture. However, the flow of liquid is opposed due to a surface tension gradient induced at the air water interface (Marangoni effect). As the film thins and stretches and the surface area in that region increases, its surface tension increases, establishing a surface gradient which cause a liquid flow against

gravity. Furthermore, foam stability depends on surface viscosity and the electrostatic repulsion between the films. As the film thins upon drainage, the ionic surfactants adsorbed at the surface come closer, which strengthens the repulsive force among them. This reduces further thinning of the foam lamellae. Consequently, the addition of electrolytes decreases the stability of foams, as it reduces the columbic repulsion between the films [1, 7].

In 1993 *Garret et.al* [8] showed the existence of a correlation between foaming and dynamic surface tension of Linear alkyl benzene sulfates (LAS). Later in 1995 *Tamura et.al* [9], obtained a relationship between the foamability and DST of a series of aqueous polyoxyethylene n - dodecyl ether solutions. At shorter time region (<1s), the increase in foamability with an increase in ethoxyl (EO) group number was directly related to the reduction in surface tension. However, at longer measuring time region (>1s), as the system approaches equilibrium, the surface tension decreases with an increase in EO group. This indicates that, the foamability depends on dynamic surface tension rather than the equilibrium surface tension. However, this relation strictly depends on the rate of foam generation. *Patist et.al (1998)* [10], have shown that the dependence of foamability on dynamic or equilibrium surface tension is solely determined by the foaming techniques. In high shear rate process (vigorous shaking), foam generation depends on DST. However, if enough time is allowed (single bubble foam generation), DST approaches the equilibrium surface tension, hence foamability in this case depends on the equilibrium surface tension. The dynamics of ethoxylated foams in presence of multivalent counterions was studied by *Dushkin et.al. (2003)* and *M. Buzzacchi.et.al (2006)* investigated the foam behaviour of an anionic sulfate and non-ionic ethoxylated surfactant using dynamic surface tension data [11, 4].

Anionic surfactants like Linear Alkyl Benzene Sulfonate (LAS), Sodium Dodecyl Sulfate (SDS), Sodium Lauryl Ether Sulfate (SLES), and Alkyl Olefin Sulfonate (AOS) are some of the commonly used surfactants in detergents. Anionic surfactants are proven to be an efficient candidate in cleaning process. Earlier, Alkyl sulfates were used in cleaning products, but then recently the use of ethoxylated surfactants has been promoted due to its high hardness tolerance [12]. Since anionic surfactants tend to precipitate in presence of divalent cations, their use in hard water is limited. Hence

ethoxylated surfactants are preferred over alkyl sulfates. Moreover, ethoxylated surfactants were verified to be milder than the corresponding alkyl sulfates. A knowledge of equilibrium, dynamic surface properties and micellar properties is required for its utilisation in detergents. Equilibrium surface tension gives an insight about the wetting ability of the surfactant and the dynamic surface tension gives awareness about the foamability. Stability of foam is often required for the emulsification of dirt and in maintaining such emulsions in suspension [13].

The present study is undertaken to predict the effect of structure on the equilibrium as well as dynamic surface properties of alkyl and alkyl ether sulfates. Though there have been several independent studies on the equilibrium surface properties of alkyl and alkyl ether sulfates, the structural effects on the dynamic phenomenon is not widely studied. In this study, a thorough investigation has been carried out to understand the effect of ethoxyl groups on the surface properties. Electrolytes are usually introduced into the surfactant system to enhance the equilibrium surface properties. The effect of electrolyte on dynamic and foaming behavior was therefore studied and a comparison was made with the equilibrium properties. Micellization parameters like CMC and binding coefficient was measured to explain the observed Dynamic surface properties. The dynamic surface tension data is used to predict the foaming behavior and an attempt was made to put forward a possible adsorption mechanism for the observed dynamic behavior.

2. MATERIALS AND METHODS

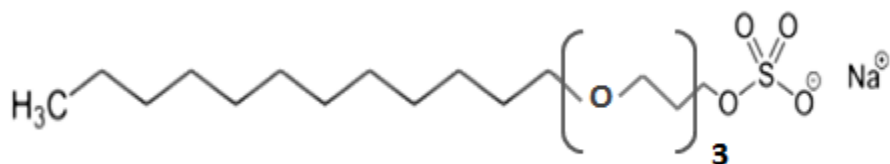
2.1. Materials used

Table 2.1: Chemicals used, purity and company

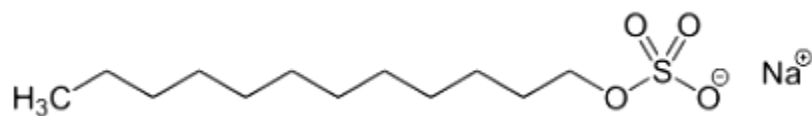
Chemicals	Company	Purity (%)
SLES (3EO) (Sodium salt of dodecyl ether sulfate)	Galaxy	~70
SDS (Sodium salt of Dodecyl Sulfate)	Sigma Aldrich	≥ 99
PAS (Sodium salt of Primary Alkyl Sulfate)	Galaxy	90 – 92
Sodium Chloride (NaCl)	Merck Specialties pvt Ltd	≥ 99
Dihydrate Calcium Chloride (CaCl ₂ · 2H ₂ O)	Merck Specialties pvt Ltd	≥ 98

➤ Chemical structure of the anionic surfactants used:

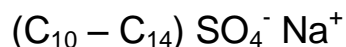
- SLES (3EO)



- SDS



- PAS



2.2 Experimental methods

The samples were prepared in ultra pure water and the concentration was estimated via hyamine titration. The equilibrium surface tension, Dynamic surface tension and foamability measurements were carried out at 25°C.

2.2.1. Determination of concentration

➤ **Estimation of surfactant concentration via Two phase Hyamine Titration**

The anionic surfactants were titrated against Hyamine, (Fig2.1b) a cationic surfactant in water/chloroform two phase medium, in presence of a mixed indicator of a cationic (diimidium bromide) and anionic (disulfine blue) dye. As shown in Fig2.1a the anionic surfactant forms a pink nonpolar complex with the cationic dye, which is then extracted into the organic phase. Hyamine when added to the surfactant displaces the cationic dye, forming a stable colourless complex with the anionic surfactant, which results in a gradual fading of the pink colour. At the end point Hyamine forms a blue nonpolar complex (Fig2.1a) with the anionic dye [14]

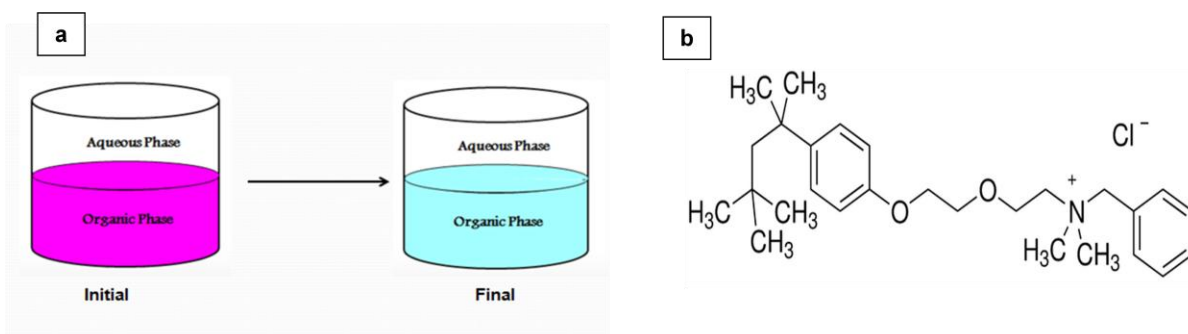


Figure 2.1: a) Showing the initial and final stage of titration b) Chemical structure of Hyamine

➤ Estimation of Calcium concentration via Complexometric Titration

Calcium is titrated against EDTA (Ethylene Diamine Tetraacetic Acid) a complexing agent in presence of Erichrome black T. Indicator forms a red coloured complex with calcium. However, calcium ions are always titrated in presence of a known amount of magnesium cation. Because calcium forms a weak complex with the indicator. As soon as both the ions are titrated, the EDTA displaces the indicator forming a blue coloured complex. Ammonium buffer is used to maintain a pH of 10 [15].

2.2.2. Determination of Equilibrium Surface and micellar properties

➤ Equilibrium surface tension and CMC determination

The equilibrium surface tension of varying concentrations of the surfactant was acquired by means of Wilhmely plate method and plotted against Logarithm of surfactant concentration. CMC was then obtained from the sharp break in the plot (As shown in the Fig1.2). However, some CMC plots show a minimum in the presence of hydrophobic impurities. Since these impurities adsorb at the surface and reduces the surface tension to a minimum value. But as the concentration of surfactant increases, micelle begins to form in the bulk of the solution and solubilises the impurities. Hence, the surface gets devoid of these impurities, which results in an increase in the surface tension. Therefore, the point which indicates an onset of surface tension increase can be considered as the CMC. Moreover, as the impurities get solubilised by the micelles, the surfactant molecules begin to adsorb at the surface and eventually saturates the surface, giving rise to a plateau in the plot. The measurement was performed in Kruss tensiometer (K12). Before starting the experiment, the instrument has been calibrated with ultra pure water. The temperature was maintained at 25°C with the help of a thermostat.

Wilhelmy plate method: A thin platinum plate is used as a probe. The plate is oriented perpendicular to the air water interface. To ensure perfect wetting, the plate was cleaned and flamed before the experiment. As shown in Fig2.2, when immersed, the surfactant solution adheres on to the platinum plate as a result of surface tension

acting along the perimeter of the plate, increasing the surface area and leading to a force tending to pull the probe toward the plane of the surface [16]. The force applied to the plate is equal to the weight of the liquid meniscus uplifted over the horizontal surface. This force measured using microbalance, is used to calculate the surface tension calculated using the equation,

$$\gamma = \frac{F}{P \cos \theta} \quad (2.1)$$

γ - Surface Tension.

θ - Contact angle measured for the liquid meniscus.

P - Perimeter of the platinum plate, $P = 2(L+t)$.

F - Force applied for uplifting the plate.

Contact angle here is assumed as zero owing to the high surface energy of platinum.

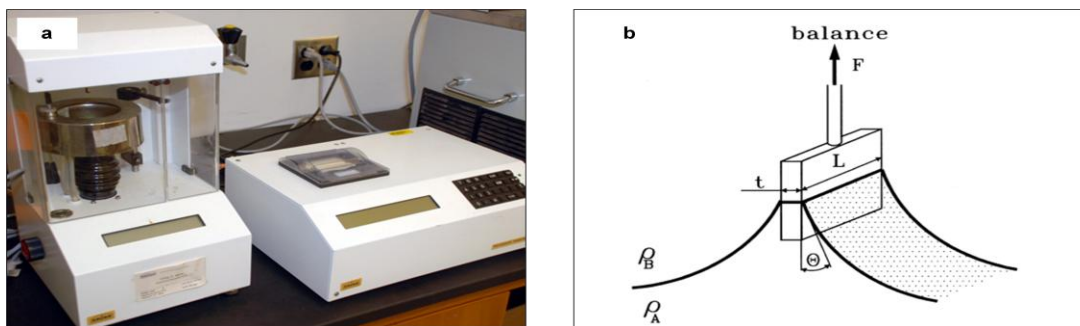


Figure 2.2: a) Kruss Tensiometer – K12 b) Schematic of the wilhelmy plate method.

➤ Binding Coefficient via Corrin Harkins model

Binding coefficient or degree of counter ion binding of sodium ions were obtained from Corrin - Harkins plot [16]. It is a characteristic micellar property. Corrin and Harkins have shown that the critical Concentration is affected only by the concentration of that ion opposite in charge to that on the colloidal aggregate. In order to compare the effect of salts on CMC of different surfactants, they have proposed a convenient model, in which they have shown that the logarithm of the critical micelle concentration of a colloidal electrolyte is a linear function of the logarithm of the total concentration of the ion opposite in charge to that on the aggregate. The total ion concentration is the sum of counter ions provided by the surfactant and the added electrolyte. The slope of this plot

is considered as the binding coefficient of the counter ion. Binding coefficient when represented in percentage shows the number of sodium ions attached to the micelles out of hundred.

➤ **Determination of Area per molecule**

Area per surfactant molecule was calculated using Gibbs adsorption isotherm equation (2.2).

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (2.2)$$

$d\gamma$ – change in Surface tension.

Γ_i – Surface excess concentration of ith component in the system.

$d\mu_i$ – change in chemical potential of the ith component.

Equation 2.2 is the most general form of Gibbs isotherm equation. For surface-active solutes the surface excess concentration (Γ_i), can be considered to be equal to the actual surface concentration without significant error. As shown in equation 2.3 and 2.4, surface concentration can be calculated using the surface tension data [1]. The slope of submicellar region of surface tension versus log C plot is used calculate the surface concentration.

Surface concentration in presence of swamping amount of electrolyte,

$$\Gamma = -\frac{1}{2.303 RT} \left(\frac{\partial \gamma}{\partial \log C} \right) \quad (2.3)$$

For solutions in the absence of any other solutes,

$$\Gamma = -\frac{1}{4.606 RT} \left(\frac{\partial \gamma}{\partial \log C} \right) \quad (2.4)$$

R – Universal gas constant.

T – Absolute temperature.

C – Concentration of the surfactant.

N – Avagadro's number.

Area per surfactant molecule is;

$$a = \frac{10^{23}}{\Gamma N} \quad (\text{in Sq. Angstroms}) \quad (2.5)$$

The area per molecule at the surface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule [1].

➤ Thermodynamics of Micellization

Thermodynamic feasibility of micellization process is expressed through Gibbs free energy change on micellization(2.6). A negative ΔG_m^o value indicates the spontaneity of the process [17].

$$\Delta G_m^o = (1 + \beta)RT \ln X_{CMC} \quad (2.6)$$

ΔG_m^o – Gibbs free energy change on micellization.

β – Binding coefficient of the counter ion.

X_{CMC} – Critical micelle concentration in mole fraction units

$$(X_{CMC} = CMC / (CMC + 55.5))$$

2.2.3. Determination of Dynamic Surface properties

➤ Dynamic Surface Tension (DST)

Dynamic surface tension data has been determined by Maximum Bubble pressure method. Maximum bubble pressure method allows measurements in short time scale down to milliseconds. It uses a capillary tube to generate bubbles continuously at the tip and determine the internal pressure of the bubble. The formation of bubble through the capillary is schematically shown in the figure 2.3, along with the original picture of bubbles formed during the experiment. The pressure inside the bubble reaches a maximum when the bubble attains a hemispherical shape, where the radius of curvature is exactly equal to the radius of the capillary. This maximum pressure is related to the surface tension via Young - Laplace equation (2.7).

$$\gamma = \frac{(P_{max} - P_o)}{2} \cdot R \quad (2.7)$$

- P_o – Hydrostatic pressure resulting from the immersion depth
- P_{max} – Maximum pressure inside the bubble
- R – Maximum bubble radius/radius of the capillary
- γ – Surface Tension

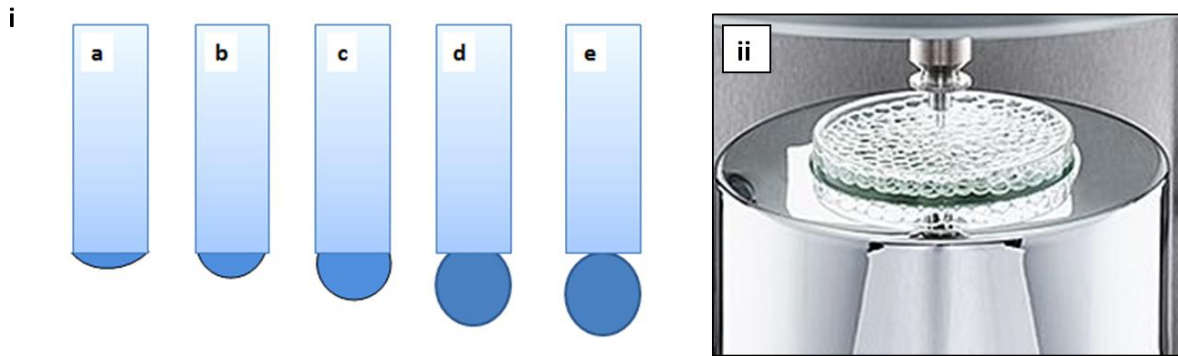


Figure 2.3: i) Radius of curvature initially from a to c forming a minimum, then increases again from d to e, ii) Bubble formation during DST measurement.

Surface tension can be determined if P_o , P_{max} and R are known. The time interval from bubble generation to the hemisphere stage (maximum pressure stage), is termed as bubble life time (or surface age). By suitably tuning the frequency of bubble formation, the bubble life time can be changed, thus allowing the surface tension measurement at different time [18].

The experiment was carried out in Kruss Bubble pressure Tensiometer (BP100) at 25 °C. The capillary diameter was determined initially using ultra pure water.

- *Diffusion coefficient from Joos and Rillaerts:* At lower concentrations and shorter measuring time regions, the diffusion from bulk to the subsurface is the rate determining step.

Under these conditions the DST is described using Joos – Rillaerts equation, which can be used to calculate the diffusion coefficient of submicellar concentrations [24].

$$\gamma_t = \gamma_o - 2RTc \left(\frac{D_s t}{\pi} \right)^{0.5} \quad (2.8)$$

γ_t – Interfacial tension at surface age 't'

- γ_o – Interfacial tension of the pure solvent
- R – Universal gas constant
- T – Absolute Temperature
- C – Concentration of the additive
- D_s – Diffusion coefficient for short or small time scale

➤ **Foam measurements**

Foamability measurements are carried out via cylindrical shaking method. In this method foam is produced by rapid shaking of a constant volume (40mL) of surfactant solution for 10 times in a 250mL cylinder causing a sudden expansion of interfacial area. The measurement is repeated at least 3 times. Foam stability was determined by monitoring the change in foam volume with time.

The relation between dynamic surface tension and foam generation is,

$$W = \gamma \Delta A \tag{2.9}$$

W – Work done

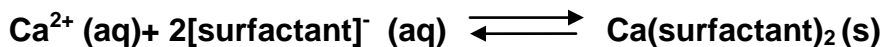
γ – Surface tension

ΔA – Change in surface area

When the amount of work applied remains the same, a lower surface tension results in more surface area.

2.2.4. Determination of Solubility product

Turbidity measurement was carried out to find out the precipitation boundary (minimum concentration of calcium ions required to precipitate the surfactant from the solution) of each surfactant in presence of calcium ions. Surfactant solution may remain super saturated for days; therefore the samples were kept at 4°C to force precipitation, followed by 24 hours in room temperature. Solubility product was then calculated using these data [19].



$$\text{Solubility product, } K_{sp} = [Ca^{2+}]_{unb} ([S^{-}]_{mon})^2 \tag{2.10}$$

- K_{sp}** – Activity based solubility product
[Ca²⁺]_{unb} – Concentration of unbound calcium
[S]_{mon} – Monomer concentration of anionic surfactant

Turbidity measurement was performed in Benchtop turbidimeter. Benchtop turbidimeter allows the measurement of highly turbid samples. Turbidity is recorded in Nephelometric turbidity units (NTU). Initially, the instrument is calibrated using ultra pure water, for which the turbidity lies in 0.02NTU - 0.04NTU range.

2. RESULT & DISCUSSION

3.1. Critical Micelle Coccentration (CMC).

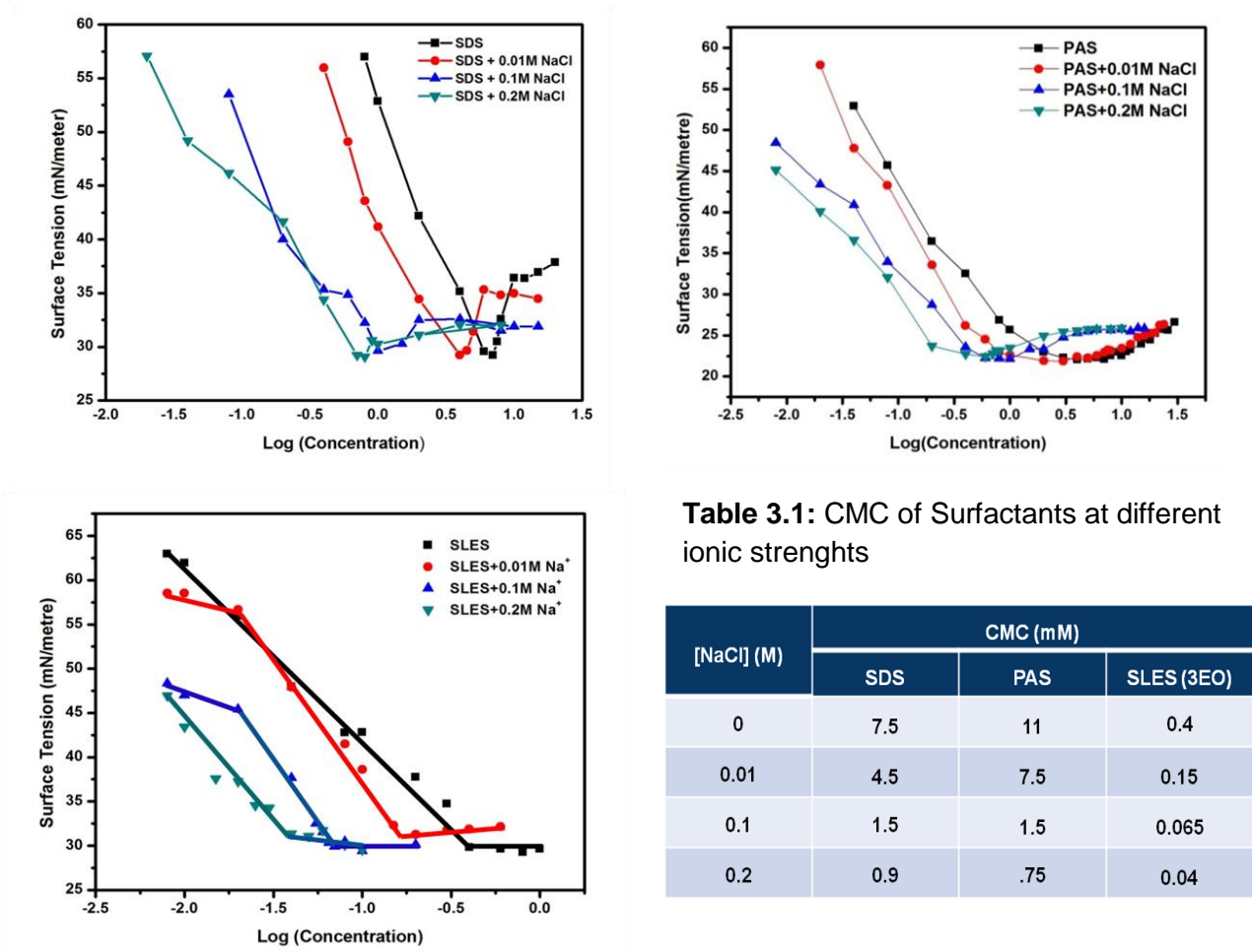


Figure3.1: Surface tension versus Log (concentration), **a) SDS b) PAS c) SLES.**

Figure3.1 shows the Surface tension versus Log (concentration) plots of aqueous solutions of SDS, PAS and SLES solutions. The results are tabulated in Table3.1.

➤ Salt free system

In the absence of sodium chloride, SLES showed a very low CMC compared to its nonethoxylated counterpart SDS and PAS. In general, CMC decreases as the overall

hydrophobic character of the surfactant increases [1]. The presence of ethoxyl groups makes SLES more hydrophilic. Therefore, SLES is expected to show higher CMC compared to SDS and PAS. But in this case, SLES is showing lower CMC compared to SDS and PAS. Such an unusual reduction was earlier attributed to the reduced ionic character of sulfate group in presence of adjacent ethoxyl group. Later this hypothesis was discarded by *M.Aoudia et.al.* 2009 [20] and proposed a new theory for this anomalous behavior. *M. Aoudia et.al* have shown that this drastic decrease in CMC is a consequence of intramolecular and intermolecular ion (SO_4^-) dipole ($\text{O} \rightarrow \text{CH}_2$) interaction in the micelles. These interactions results in a reduction in the self repulsive force between the head groups at the micelle water interface. The same is schematically shown in Figure3.2 [20].

The higher CMC value shown by SDS and PAS is a result of the strong electrostatic repulsion experienced by the sulfate groups. However, PAS which has a mixture of $\text{C}_{10} - \text{C}_{14}$ alkyl chains is showing a higher CMC compared to SDS. If we assume that the repulsion experienced by both SDS and PAS is the same, then the higher CMC in case of PAS must be arising from the difference in the alkyl chain

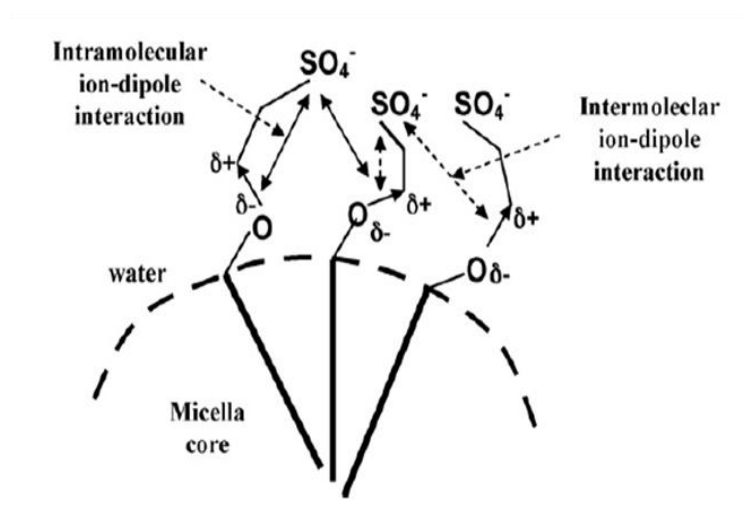


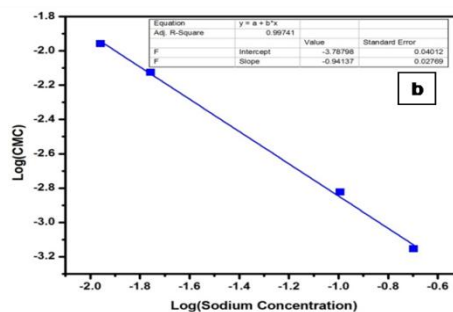
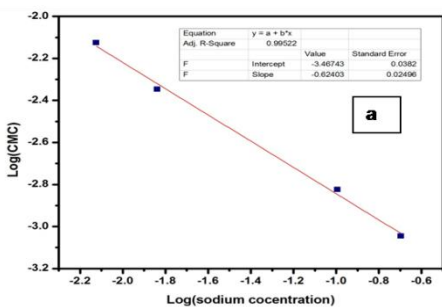
Figure3.2: Schematic diagram of the intramolecular and intermolecular ion (SO_4^-) dipole ($\text{O} \rightarrow \text{CH}_2$) interactions in micelles

structure. A strong hydrophobic interaction among the alkyl chains is necessary for micellization. PAS being a mixture of C₁₀ – C₁₄ alkyl chains will show less interaction compared to SDS, which possesses only a C₁₂ chain. This is a possible reason for the observed increase in the CMC of PAS.

➤ **Effect of added NaCl on micellization**

Addition of sodium chloride resulted in a reduction in CMC. This can be attributed to the reduction in columbic repulsion in presence of added sodium ions. Binding coefficient of sodium ions was obtained from Corrin – Harkins plot, which is shown in Figure3.3. As shown in Table 3.2 binding coefficient of sodium is very low for SLES. Only 35% of sodium ions are bounded to the micelles. Both SDS and PAS show higher binding coefficient compared to SLES. PAS shows 94% binding coefficient, while SDS possess only 62% sodium ions bound to it.

The effect of added salt on micellization was inferred from Gibbs free energy change. The Gibbs free energy change on micellization with and without added salt is shown in figure3.4 and Table3.3. According to equation 2.6, ΔG_m^0 depends on both binding coefficient and CMC. As shown in Table 3.3, in all three cases, the absolute negative value of ΔG_m^0 increased with an increase in salt concentration. This indicates that micellization is more favoured in the presence of added salt i.e, an increase in ionic strength helps in reducing the columbic repulsion between the sulfate groups. According to the data, the micellization is slower in SDS compared to SLES and PAS. The absolute negative value of free energy change during micellization is higher for SLES compared to its non ethoxylated counterpart SDS. Micellisation process is more favoured in case of PAS, which is evident from its binding coefficient.



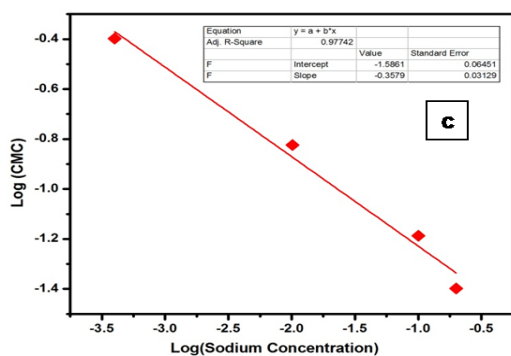


Figure 3.3: Corrin Harkins plot of a) SDS b) PAS c) SLES

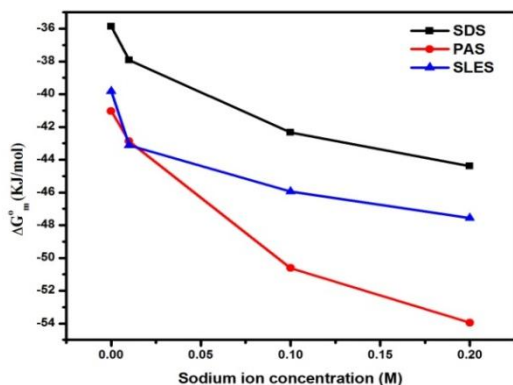


Figure 3.4: Effect of sodium chloride on Gibbs

Table 3.2: Binding coefficient for SLES, SDS and PAS

Surfactant	Degree of Na ⁺ binding (%)
SDS	62.4
PAS	94.14
SLES	35.7

Table 3.3: Gibbs free energy on micellization of SLES, SDS and PAS

[NaCl] (M)	ΔG _m ⁰ (KJ/mol)		
	SDS	PAS	SLES
0	-35.8656	-41.0325	-39.8284
0.01	-37.9217	-42.8753	-43.1276
0.1	-42.3441	-50.62	-45.9405
0.2	-44.4004	-53.9556	-47.5737

3.2. Equilibrium Surface tension and area per molecule

Though SLES is only 70% pure, it doesn't show any minimum (Fig.3.1), indicating the absence of surface active impurities at the surface. The minima in case of SDS and PAS are due to the presence of hydrophobic impurity, which in most cases arises from the hydrolysis of the surfactant, forming the analogous alcohol. As mentioned in section 2.3.2, the plateau region in these plots corresponds to the equilibrium surface tension data of the surfactants above CMC. The equilibrium surface tension data of SDS, PAS and SLES are given in Table 3.5. Figure 3.5 represents the effect of sodium salt on the area per molecule. The same is given in Table 3.4. Area per molecule gives an insight into the orientation of surfactants at the air water interface.

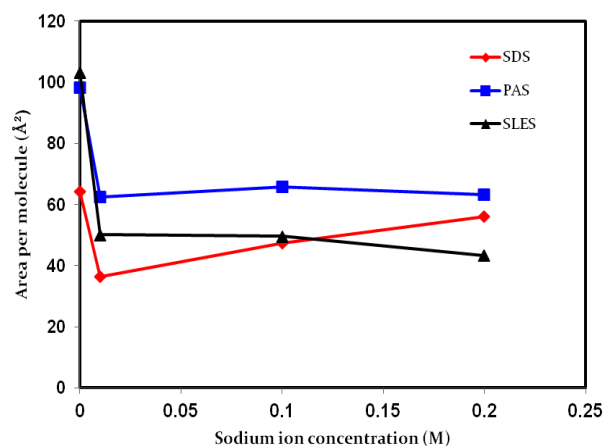


Figure 3.5: Effect of sodium chloride on area per surfactant molecule.

All the surfactants showed an abrupt change in area per molecule with the addition of 0.01M sodium salt. This is a consequence of effective screening of the oriented head groups in the presence of sodium ions. As a consequence, the molecules pack more efficiently, increasing the number of surfactant molecules at the surface. An increase in surface concentration results in a reduction in surface tension. However, the equilibrium surface tension above CMC shown in Table 3.5 doesn't show any relation with the observed area per molecule. Though the surface tension of SLES is less than that of SDS, its area per molecule is higher than that of SDS. This might be due to a great extent of reduction in the slope in presence of dodecanol.

The surface activity follows the order PAS > SLES > SDS. However, the high surface activity of PAS has to be a result of alcoholic impurities, since alkyl sulfates alone cannot make such a huge reduction in surface tension.

Table 3.5: Showing the effect of sodium chloride on equilibrium surface tension

[NaCl] (M)	Surface Tension (mN/meter)		
	SDS	PAS	SLES
0	36.9	25.81	29.59
0.01	34.9	25.63	31.88
0.1	31.75	25.62	30.04
0.2	31.35	25.7	30.75

3.3. Dynamic behavior of Surfaces

3.3.1. Dynamic surface tension versus Foamability

➤ Salt free system

Dynamic surface tension and foamability were measured above and below CMC at 25 °C. In cylindrical method, the generation of foam occurs at a very short time scale. Figure 3.6 a, b and c shows the dynamic surface tension plot of the surfactants at 0.02mM, 0.05mM and 0.2mM. To investigate the correlation between DST and foamability, DST was plotted at shorter time scale (10ms to 250ms) which is shown in Figure 3.6 d to f. From Figure 3.6 d, e and f, it can be observed that 0.02mM and 0.05mM surfactant solutions are not showing any significant difference in surface tension, and the value at 120ms is close to the value of pure water at 25 °C. This can be directly related to the low foam volume observed at these concentrations (Table3.6). However at 120ms, 0.2mM SLES shows approximately 1.1mN/meter difference with SDS. 120ms is as an arbitrary time chosen to examine the difference in surface tension among the surfactants. The difference in surface tension can be correlated with the higher foam volume of SLES at 0.2mM. SDS and PAS showed similar foam volume at 0.2mM, which can be ascribed to the very similar surface tension values at 120ms. SDS is not foaming at 0.02mM and 0.05mM, while PAS exhibited a very small foam volume. SLES is consistently showing higher foam volumes at all the concentrations. Joos – Rillaerts diffusion coefficient plot and the calculated diffusion coefficient is shown in Figure 3.7 and Table 3.7 respectively. SLES showed a higher diffusion coefficient, whereas PAS and SDS is showing similar diffusion coefficient values.

In Figure3.6a, b and c at older surface ages (>100s), as the system approaches equilibrium, there is a marked difference in the surface tension, decreasing in the order SLES > PAS > SDS. However, there is no significant difference in the foam volume of the three surfactants. This proves the existence of a correlation between foamability and dynamic surface tension.

From the above observations, we can conclude that ethoxylation favors foam generation in submicellar solutions. DST of submicellar solutions only depends on the rate of diffusion. Therefore, the slightly higher foam volume of SLES can be attributed to

an increased rate of diffusion of monomers. At dilute conditions the diffusion from bulk to the subsurface is the rate determining step as the surface concentration is very low, resulting in faster adsorption from subsurface to the interface [6, 24]. Hence, the higher DST value of SLES has to be due to the rapid adsorption of monomers from the bulk to the subsurface. This is evident from the calculated diffusion coefficient from Joos – Rillaerts plot. We can assume that the cause of increased rate of adsorption in case of SLES is a result of reduced electrostatic repulsion due to inter and intra ion dipole interaction between the sulfate head groups, which facilitates the adsorption process. This is the reason for higher foamability of SLES than SDS and PAS. PAS and SDS contains highly surface active alcohol (dodecanol in case of SDS) as impurity, which can interact with the surfactant molecules and can reduce the surface tension to a great extent. However, in submicellar solutions, the adsorption of alcohol and surfactant occurs at different time domains. The adsorption of impurity takes place only if diffusion equilibrium between the bulk and subsurface is established [22], therefore the alcohol monomers will not be able to adsorb at the surface in the given time range. More the number of monomers at the surface, lower will be the surface tension. Hence the foam volume of SLES increases in the order $0.02\text{mM} < 0.05\text{mM} < 0.2\text{mM}$. The head to head repulsion in case of PAS and SDS slow down their adsorption at the interface, resulting in a lower foam volume.

Figure 3.8 shows the DST plot of micellar solutions of SLES, SDS and PAS at shorter and longer time scale. DST was measured at 15mM , which lies above the CMC of all the surfactants. At shorter time scale, (Fig3.8b) SLES is showing higher surface tension than its nonethoxylated counterpart SDS. This trend is unexpected since the equilibrium surface tension of SLES is well below that of SDS (Table3.5). SDS started off with lower surface tension but later at 120ms PAS crossed SDS and thereafter showed a surface tension less than SDS. As shown in figure3.8a, this is a trend followed by SDS and PAS as it approaches equilibrium. The foamability data of these solutions are given in Table3.8. The foamability of micellar solutions is very high compared to submicellar solutions, which can be attributed to the lesser monomer concentration below CMC. As shown in table3.8, the foamability of micellar solution is

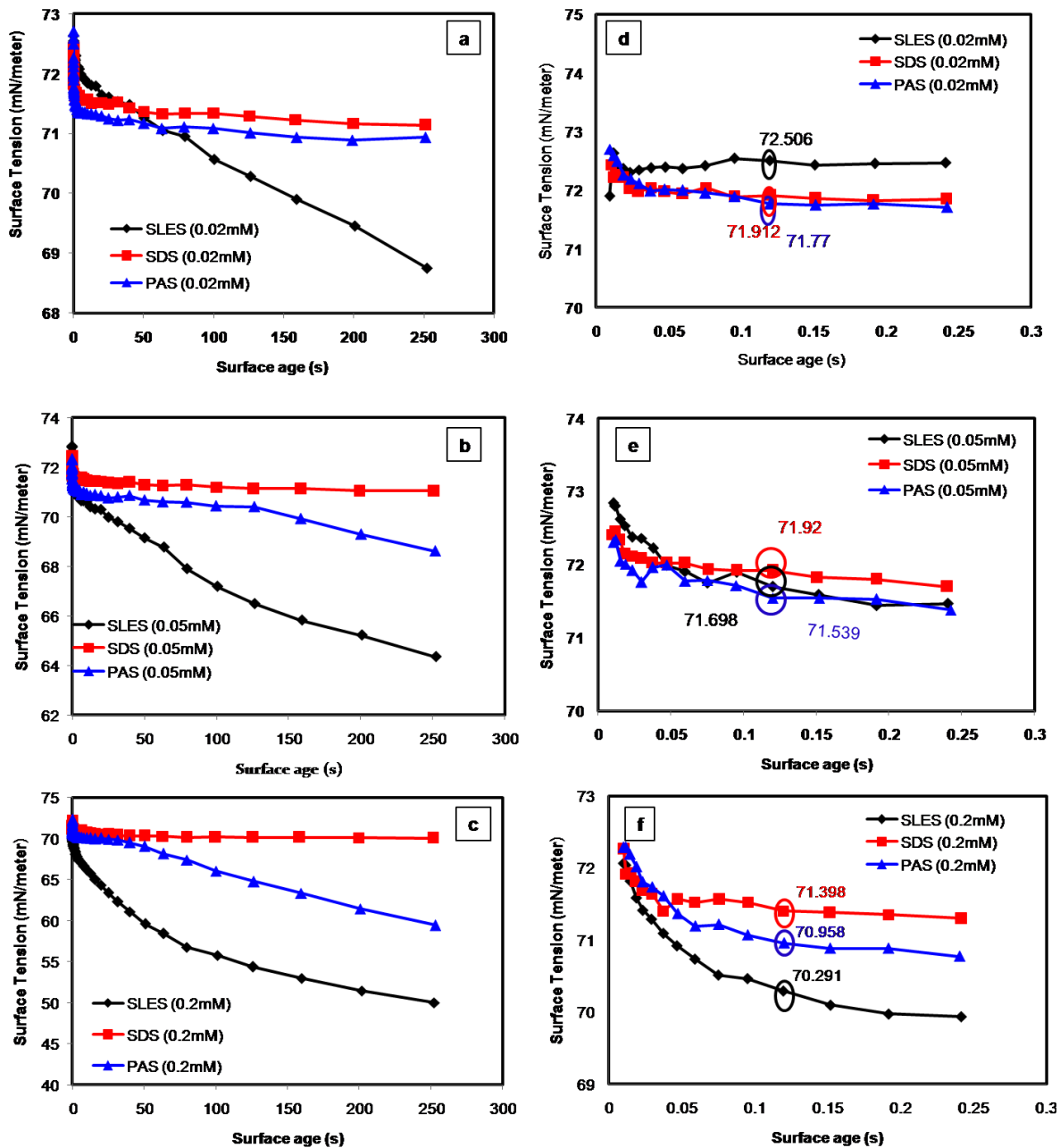


Figure 3.6: DST curve of 0.02mM, 0.05mM and 0.2mM of SLES, SDS and PAS a, b & c - 0.1s to 250s , d, e & f – 0.1s to 0.25s

Table 3.6: Foamability data below CMC

Surfactant concentration (mM)	Anionic surfactant	Foam ability (mL)
0.02	SDS	0
	PAS	2
	SLES	10
0.05	SDS	0
	PAS	4
	SLES	16
0.2	SDS	10
	PAS	9
	SLES	22

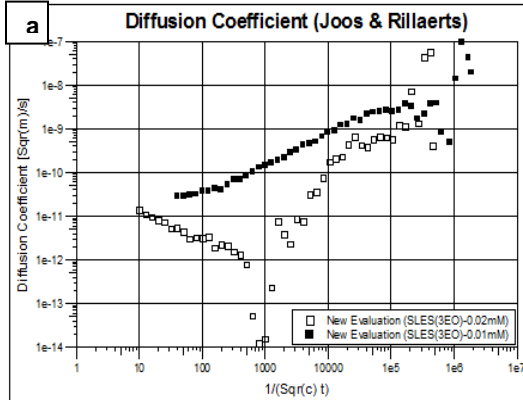
Table 3.7: Diffusion coefficient of SLES, SDS and PAS.

Surfactants	Diffusion coefficient (cm ² /s)
SLES	1.391 * 10 ⁻⁵
SDS	1.058 * 10 ⁻⁶
PAS	1.022 * 10 ⁻⁶

Evaluation Range:
1.808E+04 to 1.603E+05 [(m²/mol)²/s]

Results:
Diffusion Constant: 1.391E-09 m²/s

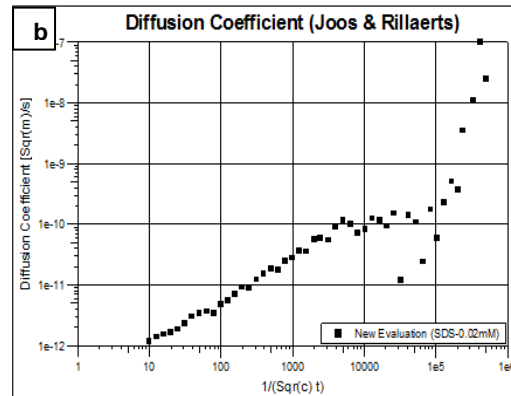
Diagram 1



Evaluation Range:
5.146E+03 to 1.409E+05 [(m²/mol)²/s]

Results:
Diffusion Constant: 1.058E-10 m²/s

Diagram 1



Evaluation Range:
1.019E+03 to 7.922E+03 [(m²/mol)²/s]

Results:
Diffusion Constant: 1.022E-10 m²/s

Diagram 1

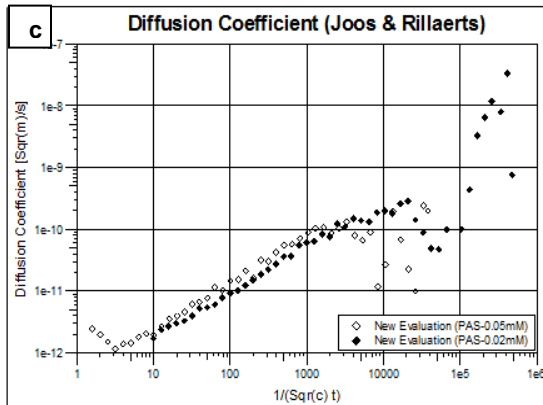


Figure 3.7: Joos & Rillaerts plot; a) SLES, b) SDS, c) PAS.

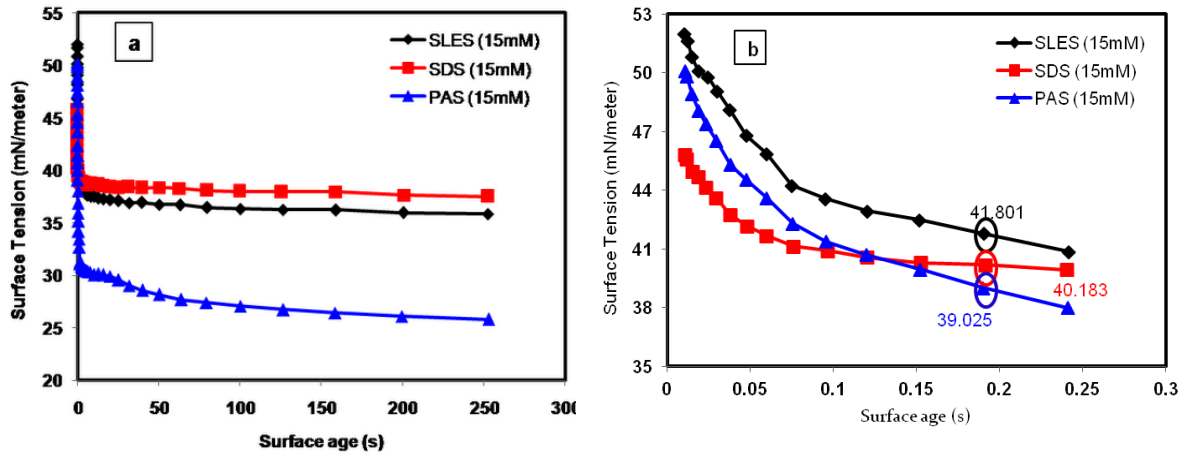


Figure 3.8: DST plot of 15mM SLES, SDS and PAS **a)** 0.1s – 250s **b)** 0.1s - .25s

increasing in order SLES < SDS < PAS. PAS showed a very high foamability. This indicates that the foam generation occurs above the cross over point, since below this point, SDS show lower surface tension than PAS. Hence, 0.2s is chosen as an arbitrary reference time. The DST values of SDS, SLES and PAS at 0.2ms is given in Figure3.8b. The difference in surface tension between SDS – SLES, SDS – PAS and SLES – PAS is ~1.2mN/m, ~ 1.6mN/m and ~ 2.8mN/m respectively. If we analyze the foamability data, we can see that a 1.2mN/m difference in surface tension causes a 31mL reduction in foam volume. However, the 1.1mN/m reduction shown by 0.2mM SLES compared to SDS (Fig3.6f) solution resulted in only 12mL (Table 3.6) increase in foam volume. This can again attribute to an increase in the bulk concentration of the surfactants.

Table 3.8: Foamability data above CMC

Surfactant Concentration (mM)	Surfactant	Foamability (mL)
15	SLES	158
	SDS	189
	PAS	242

The DST and foam behaviour of micellar solution is entirely different from that of submicellar solution. Unlike submicellar solutions, the micellar solutions are effected by the rate of micelle break down. Though the bulk concentration remains the same, the number of monomers decreases with a decline in CMC. The rate of micelle breakdown depends on the structure of the surfactant; the more stable the micelle more will be the micelle relaxation time (τ_2). If the required time for the micellar breakdown (micelle relaxation time) is greater than the foam generation time, then the surfactant will show a high DST and low foamability value. This also indicates that, if sufficient time is given, the micelle will break down to augment more monomers and reducing the surface tension to a great extent, generating more foam (Fig3.8a). This is the case with SLES. At high concentrations, the bulk diffusion is faster compared to the diffusion from subsurface to the interface [6]. Then the factors going to affect the DST are micelle stability and rate of diffusion from subsurface to the air water interface. The time scale of these two processes determines the overall rate. If the time scale for diffusion (τ_1') is greater than the micellization relaxation time (τ_2), then micelle break down is the rate limiting step and vice versa. The higher surface tension and lower foamability of SLES can be attributed to the slow micellar relaxation time, due to increased micellar stability. The stability of the micelles is arising from the reduced repulsion among the oriented head groups, which help them to pack efficiently. Since SLES possess an intrinsic way of reducing the surface tension, its rate of diffusion from the subsurface will be faster. Both SDS and PAS show lower surface tension than SLES. The micelles of SDS and PAS are less stable due to the increased repulsion between the sulfate groups, resulting in its faster break down, providing more number of monomers. However, the micelles of PAS and SDS can solubilise the alcohol, which can increase the micellar stability via ion dipole interaction. But, the exchange of dodecanol is rapid compared to the time scale of dynamic surface tension measurement [23]. Therefore, the adsorption process in this case is purely diffusion controlled. If the enhanced rate of adsorption of PAS molecules was a consequence of faster micelle break down, then SDS would have shown similar foam volume.

Therefore, based on these observations, the following assumptions are made to predict the deviation in case of PAS and SDS. To begin with, the difference in the

surface tension and foam volume has to be a result of slower rate of diffusion (τ_1'). The enhanced diffusion rate of PAS can be attributed to the reduced electrostatic repulsion in presence of long chain alcohol present as impurity. Similar to SLES, there exists an ion – dipole interaction between the sulfate group and hydroxyl group of alcohol. This efficiently screens the charge density of sulfate group and enhances adsorption. However, as evident from the CMC plot, SDS contains dodecanol as an impurity. Therefore, a scenario similar to PAS can occur in SDS solution, which would have resulted in a similar foam volume in PAS and SDS. But, the concentration of dodecanol is low compared to the alcohol content present in PAS, since SDS is ~99% pure, while PAS is only 90% pure. Therefore, similar to submicellar solutions the low concentration of dodecanol makes it unavailable at surface at short time scale. However, the diffusion time required for the SDS monomers to get adsorbed at the surface is always less than that of micellar relaxation time of SLES, resulting in a lower surface tension.

➤ **Effect of added NaCl on DST and foamability**

The DST plot of submicellar solutions 0.02mM and 0.05mM in presence of 0.1M sodium chloride is shown in Figure 3.9a to, d. As shown in Figure 3.9c and d, at shorter timescale (10ms – 250ms), the DST curve of all the surfactants lies on the same line, indicating no significant reduction in surface tension. A comparison of the surface tension values of 0.05mM solutions in presence and absence of Sodium chloride at 120ms and the corresponding foam volume is shown in Figure 3.10. 0.02mM is not chosen since, SDS and PAS doesn't foam at this concentration. The DST values at 120ms show slight difference in presence of salt. SLES and PAS showed a decline in presence of salt, while SDS showed a marginal increase. However, the surface tension and the foamability of PAS doesn't show much difference hence, can be approximated to be the same. Though, SDS showed an increase in surface tension, the foam volume decreased, however there is only a 4mL difference in the foam height, which comes inside the error limit of cylindrical shaking method (5mL). Therefore for SDS and PAS we can assume a similar foam height in presence and absence of salt. SLES is showing an increase of 8mL in foam height in presence of salt which can be relate with the slight

decline in the surface tension. But on the whole, the addition of a swamping amount of sodium chloride is not significantly affecting the DST or foambility.

Since NaCl is present in excess, the observed ineffectiveness is not caused as a result of concentration difference between the surfactants and salt. Therefore, this can be ascribed to the slow rate of diffusion of sodium ions. So, given adequate time it will get adsorbed at the surface, resulting in a reduction in the surface tension at older surface ages. This is evident from figure 3.9a and b, where at older surface age sodium ion causing a considerable reduction in surface tension. So we can conclude that the submicellar solutions of SLES, SDS and PAS is not much effected in presence of added salt.

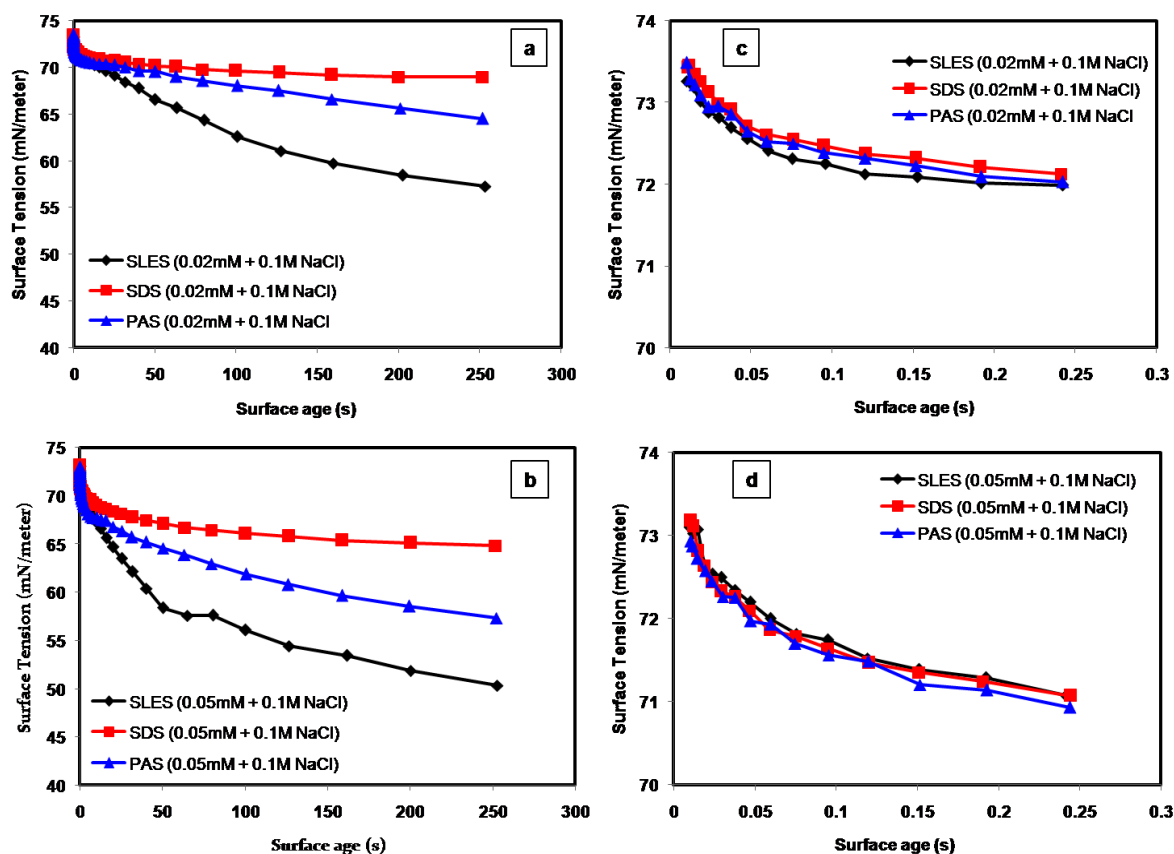


Figure 3.9: DST curve of submicellar SDS, PAS and SLES in presence of 0.1M NaCl, **a)** 0.02mM (0.1s to 250s) **b)** 0.05mM (0.1s to 250s) **c)** 0.02mM (0.1s to 0.25ms) **d)** 0.05mM (0.1s to 0.25ms).

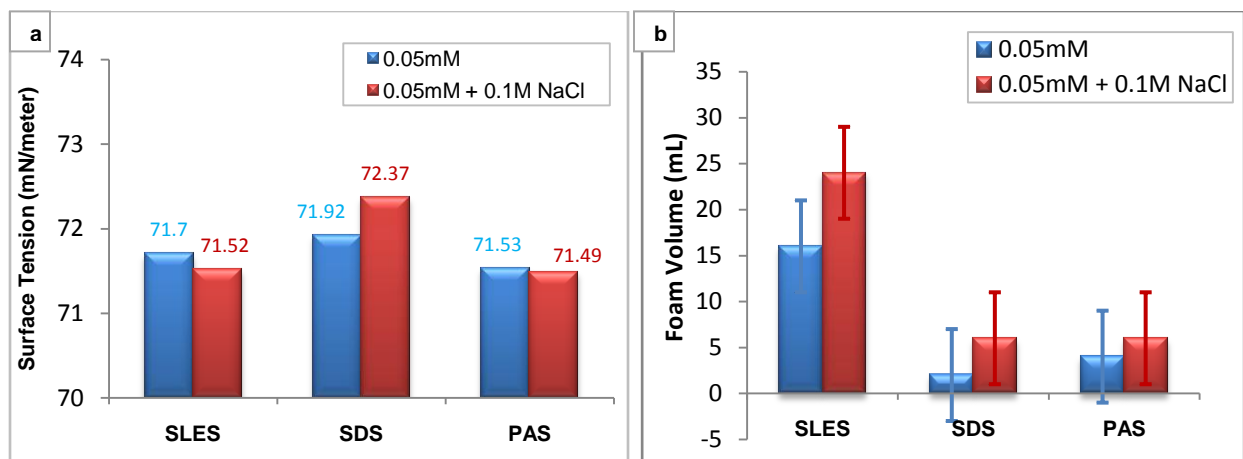


Figure 3.10: A comparison of **a)** Surface tension at 120ms and **b)** Foam volume of 0.05mM SLES, SDS and PAS in presence and absence of salt.

DST curve of 15mM micellar solutions in presence of 0.1M NaCl are shown in Figure 3.11a,b. A crossover point similar to that of salt free system can be observed between SDS and PAS. Unlike submicellar solutions, micellar solutions are showing reasonable difference in the surface tension value in presence of sodium ions. A comparison of surface tension (at 200ms) and foamability is given in Figure 3.12. All the surfactants showed about 5mN/m reduction in surface tension with 0.1M NaCl. This can be attributed to the reduction in columbic repulsion among the oriented head groups in the presence of sodium ions. Both SDS and SLES are showing an increase in foam volume complementing the DST data. However, PAS is not showing any change in foam volume. The trend followed is similar to that of salt free system, i.e. PAS > SDS > SLES.

Based on the DST and foamability data, we can conclude that sodium ions can enhance the foaming properties by reducing the surface tension at smaller surface ages. This has to be a result of the ability of sodium ions to shield the electronic cloud of sulfate groups aligned at the surface. The added sodium ions can adsorb at the surface and can bind to the micelles, resulting in an increased micellar stability. However, the reduction in surface tension indicates an increased adsorption at the surface. This happens only if the micelles break down to augment monomers to the surface, which indicates that the exchange of sodium ions between the micelles and free

ions is faster compared to the time scale of the experiment, a situation similar to that of alcohol solubilised in micelles. Hence, the free sodium ions facilitate the adsorption of surfactant. So the characteristic time required for diffusion from the subsurface to the air water interface (τ_1') is smaller than micellar relaxation time (τ_2). So the scenario here is parallel to that of salt free system. The difference is that, the presence of excess amount of sodium ions in the system, is causing more reduction in the surface tension. However the pattern of reduction in surface tension or increase in foamability is the same, indicating a similar kind of interaction with all the surfactants at the surface. This can also relate with the similar change observed in the surface tension ($\sim 5\text{mN/meter}$) of SLES, SDS, PAS.

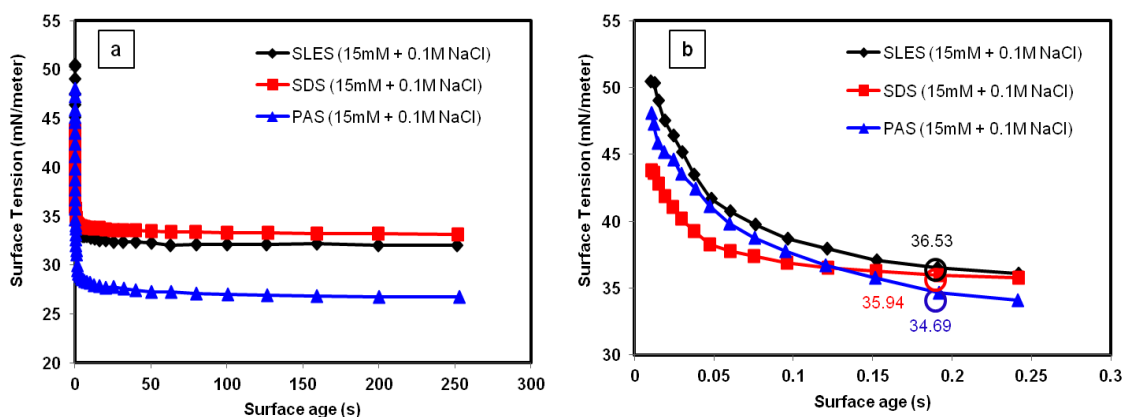


Figure 3.11: DST curve of 15mM SDS, PAS and SLES in presence of 0.1M NaCl, **a)** 0.1s to 250s **b)** 0.1s to 0.25ms.

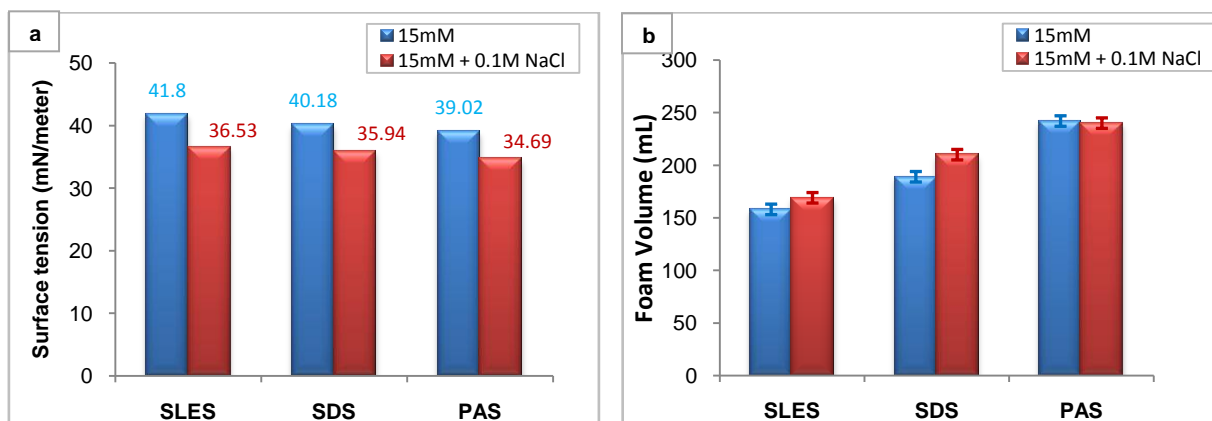


Figure 3.12: A comparison of **a)** Surface tension **b)** Foam volume of 15mM SLES, SDS and PAS in presence and absence of salt.

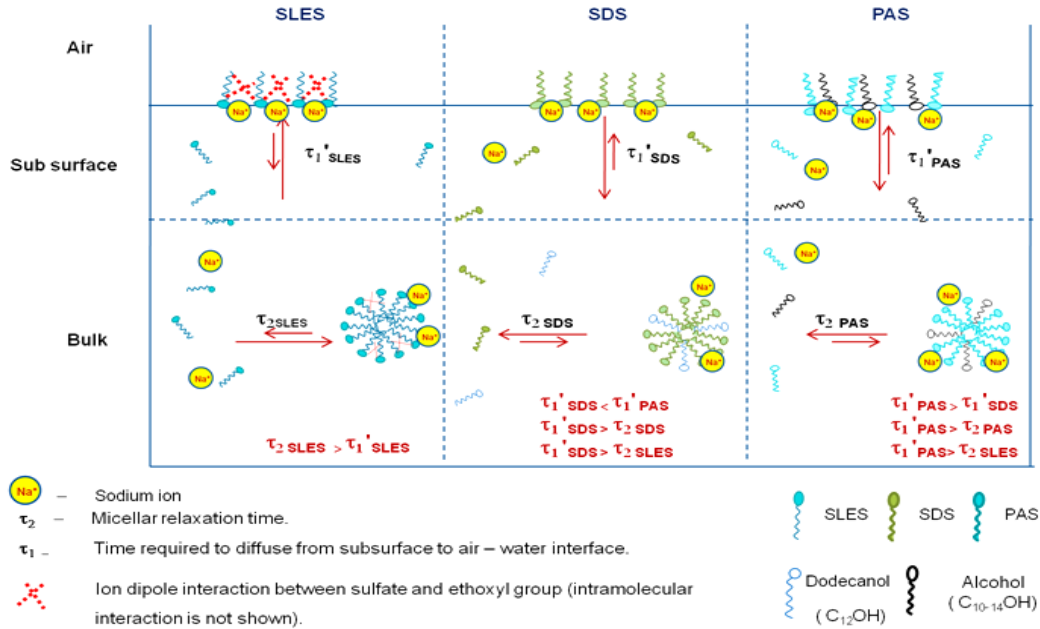
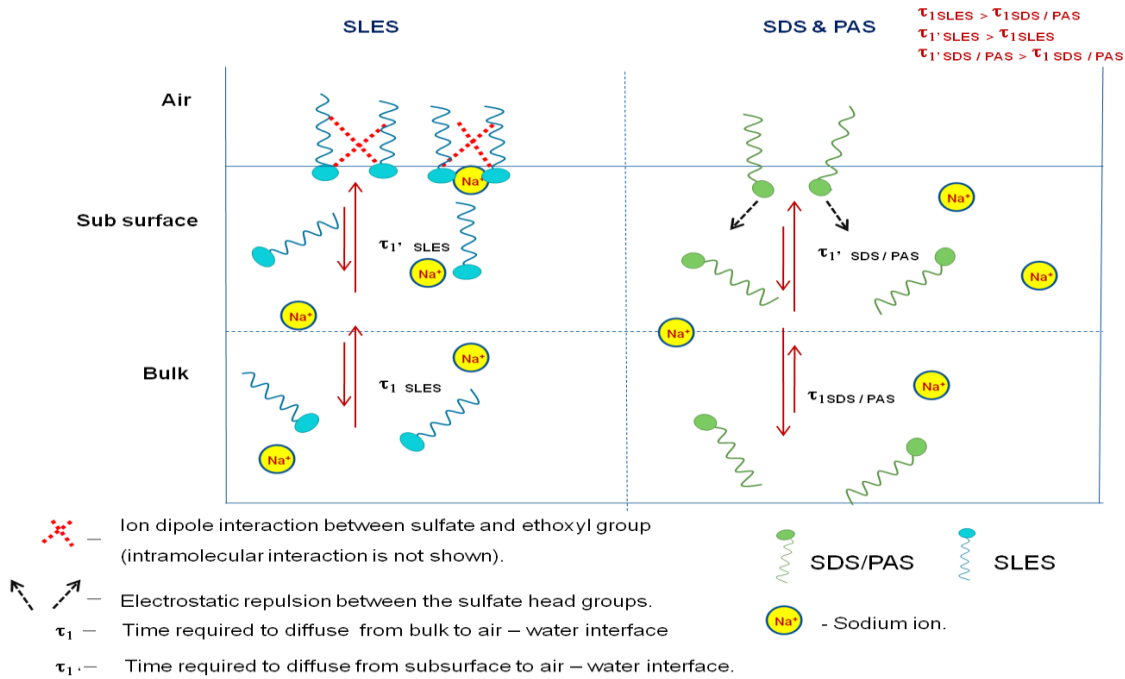


Figure 3.13: A schematic diagram showing the adsorption processes that occurs in submicellar solutions of SLES, SDS and PAS at shorter time scale in presence of sodium ions.

The schematic is only shown for surfactants in presence of added sodium chloride, as the situation is similar in the salt free system also.

3.4. Foam Stability

Foam stability of the surfactants was monitored by keeping the solution for one hour after foam generation. Stability ratio, a dimensionless parameter was introduced in order to normalize with respect to the initial and final foam height.

$$\text{Stability ratio} = \frac{\text{Foam volume at } t=0}{\text{Foam volume at } t=t'}$$

Figure 3.14 represents the stability ratio of micellar solutions. The stability of submicellar solutions was not monitored, due to its very low foam volume. As shown in Figure 3.14, all the surfactants showed a reduction in stability ratio in the presence of added electrolyte. But the amount of reduction is more in case of SDS, while SLES and PAS showed only 2 – 3% reduction. The reduction in foam stability with added salt is a result of reduced coulombic repulsion between the foam films, which facilitate the thinning of foam lamellae. Foam stability depends on several factors; the difference in the amount of reduction cannot be explained based on the equilibrium or the dynamic surface tension data. Hence at this point we can only conclude that the addition of NaCl helps in reducing the stability of foam.

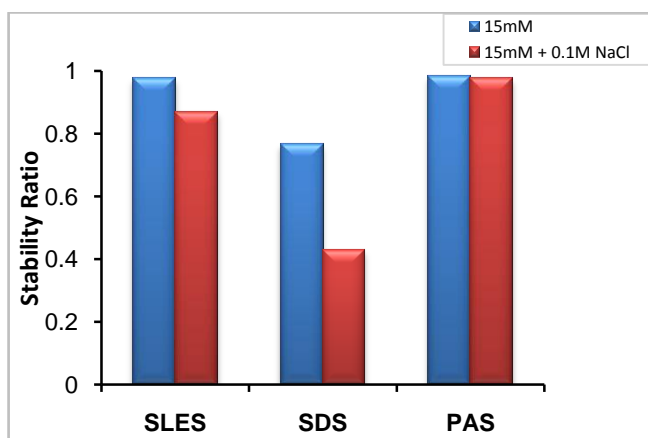


Figure 3.14: Stability ratio in presence and absence of salt, SLES, SDS and PAS above CMC.

3.5. Hardness tolerance

Anionic surfactants often precipitate in presence of divalent cations, which limits its performance in hard water. The solubility product of SLES, SDS and PAS in presence of calcium ions is given in Table 3.9. SLES showed a high solubility product compared to SDS and PAS. This indicates that, ethoxylation suppresses the precipitation of the surfactant. The ethoxyl group can bind the Ca^{2+} ions preventing its interaction with the sulfate head groups, and thereby hinders precipitation [11].

Table 3.9: Solubility product of SLES, SDS and PAS

Surfactant	Ksp (M ³)
SLES	$4.4 * 10^{-9}$
SDS	$4.8 * 10^{-10}$
PAS	$1.7 * 10^{-12}$

The work so far revealed the equilibrium and dynamic surface properties of SDS, PAS and ethoxylated alkyl sulfate SLES and the correlation between Dynamic surface tension and the foamability of the surfactants. However the foam stability of these surfactants cannot be explained with the help of the Dynamic or equilibrium surface tension. Foam stability is affected by several other factors like drainage, surface viscosity, and electrostatic repulsion between the sides of the foam lamellae. Hence, further experiments are required to explain this phenomenon.

3. CONCLUSIONS

- SLES achieved CMC well below that of SDS and PAS, due to intramolecular and intermolecular ion dipole interaction.
- The submicellar solutions of SLES showed a low equilibrium and dynamic surface tension compared to both the alkyl sulfates, SDS and PAS.
- The micellar solutions of SLES showed higher dynamic surface tension compared to its nonethoxylated counterpart SDS, as a consequence of increased micellar stability.
- The micellar solutions of PAS showed a greater reduction in both equilibrium and dynamic surface tension, which can be attributed to the presence of long chain alcohols at the surface.
- The foamability of submicellar and micellar solutions showed a good correlation with the observed dynamic surface behavior.
- Addition of NaCl resulted in a reduction in both equilibrium and dynamic surface tension of SLES, SDS and PAS.
- Micellar solutions of SLES showed higher foam stability compared to SDS.
- Addition of NaCl resulted in a reduction in the stability, as sodium ions facilitate the thinning of foam lamellae by reducing the repulsion among the foam films.
- SLES showed an excellent hardness tolerance, as the ethoxyl group binds the Ca^{2+} ions preventing its interaction with the sulfate head groups.

5. REFERENCES

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