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Studies on Surfactant Adsorption at the Cellulose-Water Interface

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Contents Page No.

3. Kinetics of Adsorption of Surfactants from its Solution at the Cellulose-Water Interface 46

4. Adsorption from Solutions Containing one Surfactant in Presence of Electrolyte at the Cellulose-Water Interface 77

5. Adsorption from Solutions Containing a Mixture of Anionic-Cationic Surfactants at the Cellulose-Water Interface 111

6. Role of Surfactant Adsorption in Detergency 129

7. Conclusions and Suggestions for Future Work 142

List of Figures

Figure No. Title Page No.

List of Table

Nomenclature

a_{air} = Mean area occupied per molecule at the air-water interface, $nm^2.molecule^{-1}$.

a_{sm} = Mean area occupied at the solid-liquid interface, $nm^2.molecule^{-1}$.

a_{smh} = Mean area occupied on hydrophobic site at the solid-liquid interface, $nm^2.molecule^{-1}$.

C_b = Bulk concentration of adsorbate in solution, k mole. m^{-3}.

C_{Crit} = Critical concentration of CTAB, k mole.m^{-3}.

C_{CTAB} = Concentration of CTAB, k mole.m^{-3}.

C_{eq} = Equilibrium concentration, k mole.m^{-3}.

C_M = Molar concentration of micelle, k mole.m^{-3}.

Cb_0 = Initial concentration, k mole. m^{-3}.

C_Q = Monomer concentration of counter ion, k mole.m^{-3}.

C_S = Concentration of adsorbate at the solid surface, k mole.m^{-2}.

C_{SM} = Maximum adsorption capacity at the solid surface, k mole.m^{-2}.

C_{sub} = Concentration of adsorbent at the sub layer, k mole.m^{-3}.

C_t = Concentration at time t, k mole.m^{-3}.

C_T = Total concentration, k mole.m^{-3}.

C_L, C_S, C_x = Monomer concentration of surfactant, k mole.m^{-3}.

D = Diffusivity, $m^2.s^{-1}$.

e = Electronic charge, C.

E = Adsorption enhancement, %.

E_A = Potential energy of the van der Waals attraction, J.

E_{ads} = Electric field strength, J.

E_B = Height of the energy barrier, J.

E_{cal} = Calculated adsorption enhancement, %.

E_R = Electrical double layer repulsion, J.

E_S = Resultant of attraction and repulsion energy in electrical double layer, J.

F = Faraday constant, C.mole^{-1}.

f_L, f_S = Activity coefficient.

ΔG^0_{ads} = Free energy of adsorption, J.

ΔG^0_{c-c} = Free energy for chain-chain interaction, J.

ΔG^0_{chem} = Free energy for covalent bonding, J.

ΔG^0_{coul} = Free energy for columbic interaction, J.

ΔG^0_{dip} = Free energy for dipole interaction, J.

ΔG^0_{elec} = Free energy for electrical interaction, J.

ΔG^0_{H} = Free energy for hydrogen bonding, J.

$\Delta G^0_{H_2O}$ = Free energy for solvation, J.

ΔG^0_{hm} = Standard free energy change for hemimicellazation, J.

ΔG^0_{spec} = Free energy for non electrical term, J.

K = Equilibrium constant.

k = Langmuir constant, k mole. m^{-3}.

k_{ae} = Adsorption rate constant on hydrophilic site, m^3.kg^{-1}.s^{-1}.

k_{ah} = Adsorption rate constant on hydrophobic site, m^3.kg^{-1}.s^{-1}.

k_{de} = Desorption rate constant on hydrophilic site, s^{-1}.

k_{dh} = Desorption rate constant on hydrophobic site, s^{-1}.

k_B = Boltzmann constant, J.K^{-1}.

K_{hm} = Equilibrium constant for hemimicellization.

K_S = Average soil removal coefficient, s^{-1}.

M = Molecular weight.

m = Mass of adsorbent, kg.

m_Q = Number of counter ion per micelle.

N_A = Avagadro’s number, mole^{-1}.

n = Micellar aggregation number.

n_{hm} = Hemimicellar aggregation number.

n_s = Order of the soil removal process.
r = Radius of the surfactant molecule, m.
R = Gas constant, J. K^{-1}. $mole^{-1}$.
S = Concentration of soil on substrate, $kg.kg^{-1}$.
t = Time, s.
T = Absolute temperature, K.
V = Solution volume, m^3.
x = Distance, m.
X_S = Total solid phase concentration of surfactant (amount adsorbed), $kg.kg^{-1}$.
X_{Se} = Solid phase concentration of surfactant on hydrophilic site, $kg.kg^{-1}$.
X_{Sh} = Solid phase concentration of surfactant on hydrophobic site, $kg.kg^{-1}$.
X_{Sm} = Maximum amount of surfactant adsorbed on hydrophobic and hydrophilic site, $kg.kg^{-1}$.
X_{Sme} = Maximum amount of surfactant adsorbed on hydrophilic site, $kg.kg^{-1}$.
X_{Smh} = Maximum amount of surfactant adsorbed on hydrophobic site, $kg.kg^{-1}$.
y_L = Micellar mole fraction.
z = Valency of ion.

Greek letters
α, α_L, α_S = Mole fraction of surfactants.
δ = Stern layer thickness, nm.
ε = Dielectric permittivity, $C^2.J^{-1}.m^{-1}$.
ε_0 = Dielectric permittivity in vacuum, $C^2.J^{-1}.m^{-1}$.
Γ = Amount adsorbed at the interface, k. $mole.m^{-2}$.
Γ_{cal} = Calculated amount adsorbed at the interface, $kg.kg^{-1}$.
Γ_{hm} = Amount adsorbed at HMC, $kg.Kg^{-1}$.
Γ_{NaDBS} = Amount NaDBS adsorbed at the interface, kg. kg^{-1}
Γ_{∞} = Amount adsorbed at saturation, $kg.kg^{-1}$.
γ = Surface tension, $N.m^{-1}$.
$\tilde{o}_P$ = Splitting pressure of the surfactant layer on the particle, $N.m^{-2}$.
$\tilde{o}_S$ = Splitting pressure of the surfactant layer on the surface, $N.m^{-2}$.

κ = (Debye length)$^{-1}$, nm^{-1}.

μ = Dipole moment, C. m.

ψ = Electric potential, mV.

ψ_δ = Electric potential at the stern plane, mV.

ψ_0 = Electric potential at the solid surface, mV.

σ_δ = Charge density at δ, C. m^{-2}.

σ_0 = Charge density at the surface, C. m^{-2}.

τ = Diffusion time scale.

ξ = Zeta potential, mV.

Abbreviations

CMC = Critical Micellar Concentration.

CMC$_{Mix}$ = Mixed CMC.

CPC = Cetylpyridinium chloride.

CTAB, C$_{16}$TAB = Cetyl trimethyl ammonium bromide.

DDAB = Dimethyldioctadecylammonium bromide.

DLVO = Derjaguin-Landau-Verwey-Overbeek.

DPB = Dodecyl pyridinium bromide.

DPC = Dodecyl pyridinium chloride.

EO = Ethylene oxide.

HLB = Hydrophilic lipophilic balance.

HMC = Hemimicellar concentration.

NaDBS = Sodium dodecylbenzenesulfonate.

SDS = Sodium dodecyl sulfate.

TPB = Tetradecyl pyridinium bromide.

TPC = Tetradecyl pyridinium chloride.

Abstract

The adsorption of anionic - sodium dodecylbenzenesulfonate (NaDBS), cationic – cetyl trimethyl ammonium bromide (CTAB) and nonionic - Triton X-100 (TX-100) surfactants under different conditions on cellulose-water interface are investigated and the adsorption results are compared with detergency of particulate and composite soil.

The kinetics of adsorption of different surfactants on cellulose-water interface show that a cationic surfactant adsorbs rapidly and nonionic and anionic surfactants adsorb relatively slowly. The equilibrium time for cationic surfactant is less (~ 10 min) but higher for the anionic and nonionic surfactants (~ 1 hr). The cellulosic surface is shown to have dual sites of hydrophobic and hydrophilic in nature. It is shown that anionic and nonionic surfactant molecules mostly adsorb on the hydrophobic site, while cationic surfactant molecules mostly adsorb on the hydrophilic site. Anionic surfactant molecules in presence of salt adsorb onto both hydrophobic and hydrophilic sites. A simple model based on two-site adsorption is developed to describe the kinetics of adsorption. The values of rate constants are determined by using the experimental data and are compared with those reported in literature.

The adsorption isotherms with four different regimes for anionic, cationic and nonionic surfactant are identified. Two important phenomena reflected in the adsorption isotherms are the steep enhancement in adsorption due to hemimicellization below the critical micellar concentration (CMC) and the reduction in the adsorption above the CMC. Adsorption of NaDBS shows a maximum in adsorption but does not show hemimicellization. However, for TX-100 and CTAB, hemimicellization occurs but maximum is not observed. Adsorption of anionic surfactant, NaDBS gets enhanced in presence of monovalent (K^+) or bivalent (Ca^{++}) cation while for nonionic surfactant, TX-100 there is no such enhancement in adsorption in presence of salt. Detailed analysis of adsorption data indicates 25% of the sites are hydrophobic in nature and the rest 75% of sites are negatively charged sites on cellulose surface.

It is observed that anionic surfactant adsorption gets enhanced significantly in presence of small amount of cationic surfactant at the cellulose-water interface. The enhancement in adsorption of NaDBS from the NaDBS-CTAB binary surfactant mixture depends on the mixing ratio of the two surfactants present in the solution. The enhancements in adsorption with two different regimes are identified for the mixed surfactant system. A mechanism for this two-regime adsorption is proposed. In anionic-cationic surfactant mixture anionic-cationic ion pairs are likely to be present, which are adsorbed on the solid-liquid interface and may form a two-dimensional hexagonal honeycomb or graphite like arrangement. With increase in the concentration of cationic surfactant at a particular anionic-cationic ratio, more compact hexagonal network may form and thus giving a two-regime adsorption.

Finally, the detergency experiments conducted to correlate the adsorption of surfactant on cellulose water interface to the removal of particulate and composite soil (particulate and oily) from cotton. Two different soiled cotton, terrace and WFK-10D show the maximum in detergency similar to maximum in adsorption isotherm. Adsorption of NaDBS on cellulose surface is enhanced with increasing ionic strength, but the effect of ionic strength in particulate soil detergency is reverse. Presence of bivalent cation (Ca^{++}) does not show any change in detergency.

Key words: Adsorption isotherm, Adsorption kinetics, Sodium dodecylbenzenesulfonate (NaDBS), CTAB, TX-100, Adsorption maximum, Cellulose-water interface, Mixed surfactant, Detergency.

Chapter-1

Introduction

1.1 Surfactant Adsorption and Detergency

The term surface-active agent or “surfactant” represents a heterogeneous and long-chain molecule containing both hydrophilic and hydrophobic moieties. Adsorption of surfactant is a process where surfactant molecules are accumulated at the surface/interface from the bulk solution. One of the characteristic features of the surfactant is their tendency to adsorb at the surface/interfaces mostly in an oriented fashion. The phenomenon of surfactant adsorption has been studied to determine: (1) A measure of coverage of surface/interface by the surfactant, which in turn determines the performance of surfactant in many industrial processes. Such as foaming/defoaming detergency and emulsification. (2) The orientation of the surfactant molecules at the surface/interfaces, which in turn determines how the surface/interface will be affected by the adsorption, that is whether it will become more hydrophilic or hydrophobic. These properties provide information on the type and the mechanism of any interactions involving the surfactant molecules at the surface/interface and its efficiency as a surface-active agent.

The term ‘detergency’ is used to describe the process of cleaning by surface-active agent. Detergency can be defined as removal of unwanted substance (soil) from a solid surface brought into contact with a liquid (Kissa, 1987). The word ‘soil’ in connection with textile surfaces most frequently denotes the unwanted accumulation of oily and/or particulate materials on the surfaces or interior of fibrous structure. A detergent contains one or more surfactants formulated with other components to enhance detergency, where removal of soils is difficult due to the strong attraction of soil to the fabric, poor penetration and adsorption of surfactant molecules onto the soil and fabric interface. Adsorption is an important step for removal of particulates and oily soils in detergency.

1.2 General Structural Features and Behaviour of Surfactants

Aqueous dilute solution of an ionic surfactant acts as a normal electrolyte at low concentration, but beyond a specific concentration it forms organized aggregates of a large number of molecules called ‘micelles,’ and this specific concentration is called critical micelle concentration (CMC). Above the CMC, sudden changes in many physico-chemical properties have been observed in aqueous solution of surfactants. These changes are illustrated schematically in Figure-1.1 (Preston, 1948). The physical properties like surface tension, interfacial tension and detergency changes below the CMC with concentration but there is no change in these properties above CMC. Some other physical properties like density, equivalent conductivity show a change in slope below and above the CMC.

The hydrophobic group of surfactant is usually a long chain hydrocarbon residue, less often a halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group is an ionic or highly polar group. Surfactants are classified and listed in Table-1.1 depending on the nature of the hydrophilic group. The surfactants are called anionic, if the head groups are negatively charged. The surfactants are called cationic if the head groups are positively charged. The cationic surfactants are usually quaternary ammonium, imidazolinium or alkyl pyridinium compounds. The head groups in zwitterionic surfactants contain both positive and negative charges and these

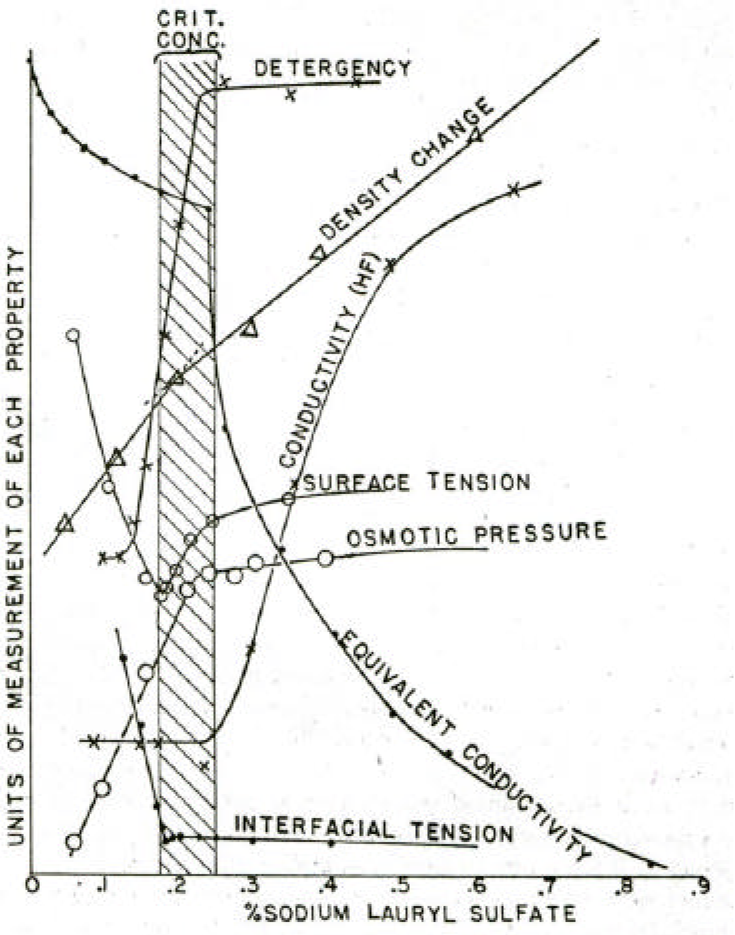
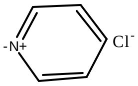


Figure-1.1 Physical properties changes for sodium dodecyl sulfate at 25-28 °C (Preston, 1948).

Table-1.1: Different types of hydrophilic groups of surfactant molecules and their main application (Clint, 1992).

Class	Head group	Main application
Anionic	$-CO_2^- Na$	Soaps
	$-SO_3^- Na$	Synthetic detergent
	$-O-SO_3^- Na$	Detergents, personal care products
	$-O-PO_3^- Na$	Corrosion inhibitors, emulsifiers
	$-(OCH_2CH_2)_n-O-SO_3^- Na$	Liquid detergents, toiletries, emulsifiers
Cationic	$-N(CH_3)_3^+Cl^-$	Bitumen emulsions
		Bactericides, antistatic agents
	$>N(CH_3)_2^+Cl^-$	Fabric and hair conditioners
Zwitterionic	$-N^+-(CH_3)_2-CH_2-CO_2^-$	Shampoos, cosmetics
	$-N^+-(CH_3)_2-CH_2-SO_3^-$	
Nonionic	$-(OCH_2CH_2)_nOH$	Detergents, emulsifiers

are used in the form of betaines ($-N^+-(CH_3)_2-CH_2-CO_2^-$) or sulphobetaines ($-N^+-(CH_3)_2-CH_2-SO_3^-$). Nonionic surfactants contain nonionic polar head groups like ethoxylates.

1.3 Adsorption of Surfactant at the Solid/Liquid Interface

The adsorption of surfactants at the solid/liquid interface is strongly influenced by the number of factors: (1) the nature of structural groups on the solid surface, i.e. highly charged sites or non-polar sites, (2) the nature of surfactant molecule i.e. the nature of hydrophilic (ionic or nonionic) or hydrophobic groups, (3) the environment of the aqueous phase i.e. presence of electrolyte, pH, and presence of other additives.

1.3.1 Mechanisms of adsorption

There are several mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution (Rosen, 1978). In general, adsorption of surfactants involves single ions rather than micelles (Griffith and Alexander, 1967).

(i) Ion exchange: Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

(ii) Ion pairing: Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions.

(iii) Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between the hydrophobic group of an adsorbed molecule and a molecule present in the solution.

(iv) Adsorption by polarization of π electrons: When the surfactant contains electron-rich aromatic nuclei and the solid adsorbent has strongly positive sites, attraction between electron rich aromatic nuclei of the adsorbate and positive sites on the adsorbent results adsorption.

(v) Adsorption by dispersion forces: Adsorption by London-van der Waals force between adsorbate and adsorbent increases with increasing the molecular weight of the adsorbate.

1.3.2 Adsorption isotherm

The relationship between the amount of surfactant adsorbed per unit mass or unit area of the solid and the bulk solution concentration of the adsorbate is called an adsorption isotherm. From the adsorption isotherm one can get idea how much of the surface of the adsorbent has been covered at a given equilibrium concentration of the surfactant in the liquid phase. A common adsorption isotherm is the Langmuir type, expressed by an equation (Langmuir, 1918),

$$C_S = \frac{C_{SM} C_b}{k + C_b} \tag{1.1}$$

where, C_S concentration of adsorbate at the solid surface, C_b is the bulk concentration of adsorbate in solution, C_{SM} is the maximum adsorption capacity at the solid surface and k is the Langmuir constant. A rather detailed review of surfactant adsorption onto solid-liquid interface is presented in chapter-2.

1.4 Applications of Surfactant Adsorption at Solid-Liquid Interface

1.4.1 Particulate soil detergency

Particulate soil and fabric (cotton) normally acquire a negative charge in neutral or alkaline aqueous medium. Cellulosic material (cotton) is a natural polymer, a long chain made by linking of β-D-glucose monomer molecules as shown in Figure-1.2 (Dorée, 1950). The chain length in cellulose varies greatly, from a few hundred sugar unit to 6000 for cotton. The cellulose chain contains polar hydroxyl groups, which develop negative charge in water.

The negative charge of soil and fabric is further increased by adsorption of anionic surfactants. The corresponding increase in mutual repulsion is responsible for an increase in the washing effect of detergency. Figure-1.3 is a schematic presentation of adsorption layer on substrate and soil particles (Jakobi and Löhr, 1987). One can see from the diagram that both the surfactant layers advance to the point of soil surface contact.

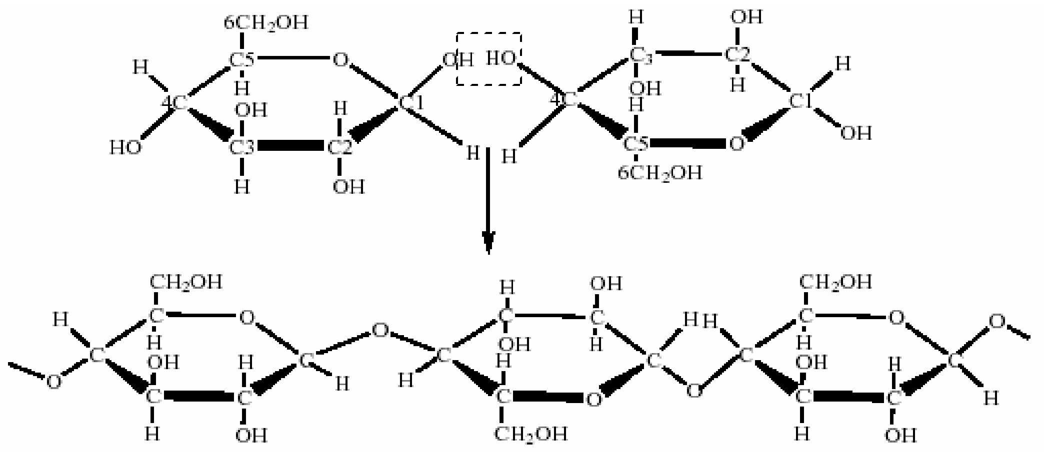


Figure 1.2 Structure of cellulose (Dorée, 1950).

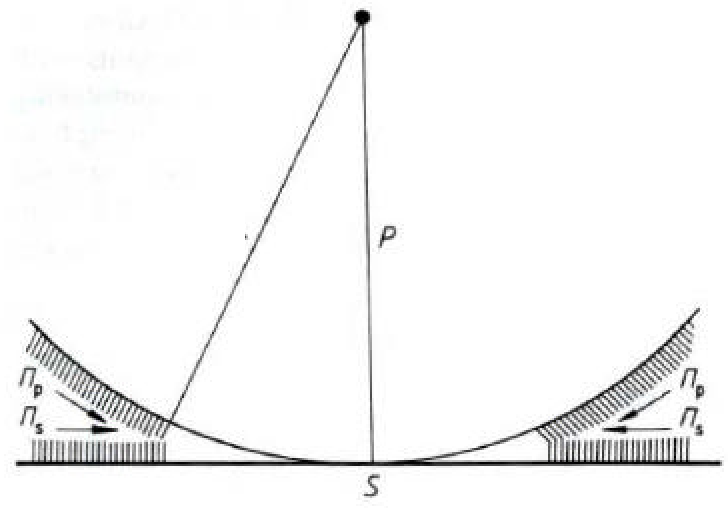


Figure-1.3 Schematic presentation of adsorption-induced separation of a spherical particle from a hard surface, S surface; P particle; $\tilde{o}_S$ splitting pressure of the surfactant layer on the surface; $\tilde{o}_P$ splitting pressure of the surfactant layer on the particle (Jakobi and Löhr, 1987).

One consequence of this is the development of a splitting pressure, which leads to separation of soil particle from the surface. This effect is obviously present in anionic surfactant, which will be absent in non-ionic surfactant due to absence of any repulsive components of electrostatic origin but hydration of hydrophilic group is extremely important.

Surfactants play a dual role in soil removal. They reduce the attraction between soil and fabric by attaching themselves to both. This way they not only loosen the soil from the fabric but also deflocculates the particles at the same time, i.e., they break up into colloidal particles and stabilize their aqueous dispersion. The soil, which forms a fine and stable dispersion in the wash liquor, is much less prone to attach itself to the fabric during remaining wash cycle than the soil present as a coarse and unstable dispersion.

1.4.2 Mineral/particulate flotation

Ore or mineral flotation is currently the most industrially important example of a particulate flotation process and may be considered as a model for the other particulate process. Particulates, which have been successfully removed from suspension by flotation, include bacterial spores, algae, clays and colloidal precipitates (Scamehorn and Harwell, 1988). Like ore flotation, each of these processes requires the addition of a suitably charged surfactant and either adjustment of pH or addition of an ion that promotes the adsorption of surfactant on the surface of the particulate.

1.4.3 Surfactant-enhanced carbon regeneration

Adsorption beds containing activated carbon are widely used to remove organic pollutants from wastewater streams. The adsorber will not be effective when break-through occurs and the carbon must be regenerated, this involves the removal of adsorbed organics from the carbon surface. In this method, a concentrated surfactant solution is passed through the adsorber containing the spent carbon, and the adsorbate desorbs and gets solubilized in the micelles (Scamehorn and Harwell, 1988).

1.4.4 Herbicide dispersions

In the present-day success of weed control technology in agriculture is attributable to the development and effective use of organic herbicides, then, to the use of herbicide adjuvants, particularly, surfactants. Surfactants perform a number of different functions in herbicide dispersions. Surfactants are primarily used in aqueous dispersions, where they reduce the surface tension and consequently increase spreading and wetting of the weed surface. This results in an uniform coverage of weed surface, greater absorption, reduced rate of evaporation, and other desirable effects (Sonntag, 1988). Surfactants help herbicides molecules to penetrate through the waxy surface of leaf. In nitrogen containing fertilizer (ammonium sulfate) - surfactant blends help the nitrogen compound to penetrate through the leaf surface. Generally, mixture of nonionic surfactants is used in these applications.

1.4.5 Deinking from paper and plastic film

Flotation deinking is the most important method for recycling of the paper. The surfactants are necessary in this process for the removal of ink from the fiber during pulping step and to cause the pigment particles to be separated from the paper fibers by flotation. It is also important for the plastic recycling. The cationic surfactants are the most effective while anionic surfactants are the least effective in removing printing ink from plastic film, probably because the binder is an acidic acrylate with a negative charge (Gecol et al., 2001).

1.4.6 Filtration of ultra fine particles

The removal of particulate contaminants is very important in many industries, such as water reclamation facilities, portable water treatment, microelectronics and pharmaceutical industries. As the size of the particles decreases particle removal becomes very difficult. Adsorption of proper surfactant on the filter surface can lower the energy barrier between the particles and the filter surface, and thus increase the deposition of small particles on the surface of the filter. One example of such phenomenon is micro porous polypropylene membrane filters which are modified with a cationic surfactant, dimethyldioctadecylammonium bromide (DDAB), to create a charged surface. Negatively charged nanoparticles can then be filtered by utilizing the electrostatic interaction between the charged particles and the polar head of the surfactants adsorbed on the filters (Kang and Shah, 1997).

1.4.7 Stability of particulate suspension

The stability of particle and colloidal slurries is an important phenomenon in many industries such as paint, printing ink, pharmaceutical etc. Particle settling, which destabilize the suspension, is often caused by the shielding of surface charges on the particles which would result in coagulation and subsequent settling. It has been found that the effects of addition of conventional stabilizing agents (e.g. ionic surfactants, polymers) increase the stability of the particle. However, sometimes the synergistic effects of mixed ionic-nonionic surfactant systems are used to improve the stability of particle suspension (Ma and Xia, 1992a, 1992b), especially when the system has high ionic strength (Palla and Shah, 2000).

1.5 Motivation

The motivation of this study comes from the facts that the study will find numerous practical applications, and the surfactant adsorption, particularly the mixed surfactant adsorption on solid-liquid interface is perhaps the most complex adsorption process that requires investigation.

Adsorption of surfactant from solution to the solid surface is of technological, environmental and biological importance. The phenomenon finds applications in many areas such as controlling various interfacial processes in food science and packaging, detergency, personal care products formulation, the extraction of petroleum resources and other areas that involves the stability of colloid dispersions. An understanding of the mechanisms of adsorption is essential for improving the efficiency of such process.

However, in many cases adsorption of a surfactant is significantly enhanced in presence of another surfactant as compared to adsorption of a single surfactant. Mixture of surfactants can show synergistic interactions, which can be manifested as enhanced surface activity, spreading, wetting, foaming, detergency and many other phenomena. Some of these synergistic actions have practical applications. The synergistic behaviour of mixed surfactant systems can be exploited to reduce the total amount of surfactant used in a particular application, resulting in the reduction in cost and environmental pollution.

Therefore, the study of adsorption of surfactant at the cellulose water interface is of significant interest in many practical application areas, especially in 'detergency'.

1.6 Objectives

The overall objective of the project is to understand the adsorption of surfactants onto the cellulose-water interface under a wide range of conditions such as the type of surfactant, presence of different electrolyte, pH, solid-liquid ratio, and mixed surfactant systems. The specific objectives of this study are:

- To study the kinetics of adsorption of anionic, non-ionic and cationic surfactant to determine the equilibrium time measurements. The effect of salt on the kinetics of adsorption. To develop a kinetic model to determine different parameters, which are important in the adsorption and can explain the process.
- To study the equilibrium of adsorption on cellulose-water interface and the influences of different parameters such as concentrations of mono-valent and di-valent salt, mixture of mono and di-valent salt, pH, solid-liquid ratio, type of surfactant.
- To study the adsorption of surfactants from a mixture of surfactant.
- To study the detergency of different soiled cotton to find more about the dependency of detergency and surfactant adsorption.

1.7 Scope of the Study

This study is of general interest to applications relating to solid/liquid interface and particle removal from the surface. This study shall give an idea about the mechanism of adsorption of different surfactants on the cellulose-water interface, which also has the scope of enhancing the basic understanding of the detergency process under different conditions.

1.8 Organization of Thesis

The thesis has been organized in seven chapters. The present chapter, chapter-1 is an introductory chapter. Chapter-2 contains pertinent literature review on the surfactant adsorption and detergency. Chapter-3 presents the experimental studies of adsorption kinetics of different surfactants and the effect of addition of salt on the adsorption kinetics. A kinetic model is included to explain the kinetic data on the cellulose water interface. Chapter–4 presents the equilibrium studies of NaDBS, TX-100 and CTAB. In this chapter the nature of adsorption isotherms of three different surfactants are compared. Importance is given on the effects of different parameters such as electrolyte, pH, solid-liquid ratio on the adsorption isotherm of NaDBS. Chapter-5 contains adsorption enhancement of NaDBS in presence of cationic surfactant. Chapter-6 presents on correlation between adsorption isotherm and the detergency under a range of conditions. Finally, chapter-7 presents the summary of the work and some suggestion for further study.

Chapter-2

Background Literature

2.1 Adsorption of Surfactant and Detergency

Surfactant adsorption is a process of transfer of surfactant molecules from bulk solution phase to a surface/interface, which plays an important role in many industrial applications of surfactants. Studies have been conducted to investigate the adsorption behavior on the solid-liquid interface. The surfactant adsorption studies at solid-liquid interfaces are conducted mostly using mineral-water interfaces. In particular, surfactant adsorption at cellulose-water interface is a major interest in detergency. Arising out of the continuing commercial importance, detergency has been the subject of research for a long time. The term ‘detergency’ is used to describe the process of cleaning by surface-active agent. Detergency can be defined as removal of unwanted substance (soil) from a solid surface brought into contact with a liquid (Kissa, 1987). The topic of detergency is many-faceted and the literature concerned with it is vast. Here, the review is mainly focused on the adsorption of surfactants and the pertinent aspects of detergency. In this chapter, literature review has been divided into four main sections, (1) surfactant adsorption kinetics on solid-liquid interface, (2) equilibrium adsorption studies of single surfactant on the solid-liquid interface, (3) equilibrium adsorption of mixed surfactant system, and

(4) detergency of particulate and oily soil. Before proceeding to review adsorption related studies, we present a brief review of techniques used to measure the concentration of surfactants in adsorption systems.

2.2 Techniques of Surfactant Analysis in Adsorption Process

Analysis of surfactant is the most important consideration in the study of adsorption process to determine the concentration of surfactant at the adsorbed phase. Various techniques are available to analyze the surfactant in either liquid or solid phase. Table-2.1 shows the different techniques of surfactant analysis in the different adsorption process.

- Radiotracer: In this technique, a radioactive tracer is put into surfactant molecules. The amount of surfactant adsorbed is calculated from the radioactivity measurements of the adsorbent and the liquid solution after the adsorption.
- Dye Complexation/Extraction: In this method, an oppositely charged dye is used to form complex with the surfactant. The complex is then extracted into an organic solvent in which dye itself is insoluble. The intensity of the color in the solvent is then determined which is directly proportional to the concentration of the surfactant.
- UV-Spectrometry: All the surfactants containing benzene or other aromatic rings and the aliphatic surfactants containing double bonds have measurable absorbance in the ultraviolet region is suitable for quantitative analysis by this method.
- Titrametric method: In this method, a cationic dye (e.g. methylene blue) is used as an indicator and one organic solvent is used to solubilize the surfactant-dye complex. The standard solution of oppositely charged surfactant is used as the titrant to that of unknown concentration of surfactant.
- HPLC: In this method a number of surfactants can be analyzed, the surfactants generate HPLC spectrum according to the retention time in the HPLC column. This method is useful when there is a mixture of surfactants present in the solution.
- Ellipsometry: In this method, adsorbent used is having an optically smooth surface. A laser beam is used to reflect from the adsorbent surface. By measuring the intensity of the reflected and the incident beams thickness of the adsorbed layer as well as the amount of adsorbed molecules can be calculated.

Table-2.1: Different techniques of surfactant analysis in different adsorption processes.

Techniques	**Surfactant**	**System**	**References**
Radiotracer	SDS	Air -Water	Tajima (1971)
	NaDBS	Cotton -Water	Fava and Eyring (1956)
	ABS	Cotton -Water	Meader and Fries (1952)
	CTAB	Polystyrene - Water	Connor and Ottewill (1971)
Dye Complexation/Extraction	Sodium dodecylsulfonate	Alumina -Water	Somasundaran and Fuerstenau (1966)
	CTAB	PTFE – Water	Desai and Dixit (1996)
	CTAB	PTFE – Water	Vanjara and Dixit (1996)
	CTAB	Silica – Water	Harrison et al. (1995)
	C_{16}TAB, C_{14}TAB, C_{12}TAB	Cellulose – Water	Biswas and Chattoraj (1998)
UV-Spectrometry	NP-13, NP-20, NP-30	PTFE – Water	Desai and Dixit (1996)
	TX-100	Alumina -Water	Wang and Kwak (1999)
	SNBS, DPC, TPC	TiO_2 – Water	Koopal et al. (1995)
	DPB, TPB	Silica – Water	Gao et al. (1987)
	TX-100, TX-165, TX-305	Silica, Quartz, Kaolin – Water	Denoyel and Rouquerol (1991)
	TX-102, TX-305, TN-101, TN-111, TN-150	Carbon black – Water	Douillard et al. (1992)

Table 2.1 (cont.)

Techniques	**Surfactant**	**System**	**References**
Titrametric	SDS	Alumina -Water	Wang and Kwak (1999)
	SDS, DAC	Alumina, TiO_2 - Water	Tamamushi and Tamaki (1959)
	NaDBS	Cotton – Water	Ginn et al. (1961)
HPLC	$C_{10}E_6$, $C_{12}E_6$, $C_{14}E_6$, $C_{16}E_6$	Silica – Water	Portet et al. (1997)
	SDS, $NP(EO)_{10}$	Alumina -Water	Harwell et al. (1988)
	3-ϕ-C_9ABS, 3-ϕ-C_{10}ABS, 4-ϕ-C_{12}ABS	Alumina -Water	Scamehorn, et al. (1982a)
	$C_{12}E_6$, $C_{12}E_8$	Silica – Water	Kibbey and Hayes (1998)
Ellipsometry	CTAB	Silicon wafers – Water	Furst et al. (1996)
	CTAB, SDS	Chromium- Water	Arnebrant et al. (1989)
	$C_{10}E_6$, $C_{12}E_6$, $C_{12}E_5$, $C_{12}E_8$	Silica – Water	Brinck et al. (1998a; 1998b)
Surface Tension	Polyoxyethylated-1-dodecanol	Cotton – Water	Schott (1967)

NaDBS = Sodium dodecylbenzene sulfonate; ABS = Alkylbenzene sulfonate; NP = Nonyl phenyl ethoxylates; SNBS = Sodium p-3-nonyl benzene sulfonate; DPC = Dodecyl pyridinium chloride; TPC = Tetradecyl pyridinium chloride; DPB = Dodecyl pyridinium bromide; TPB = Tetradecyl pyridinium bromide; TN = Triton N; DAC = Dodecyl ammonium chloride; 3-ϕ-C_9ABS = Sodium 4-[(3′)nonyl]benzene sulfonate; 3-ϕ-C_{10}ABS = Sodium 4-[(3′)decyl]benzene sulfonate; 4-ϕ-C_{12}ABS = Sodium 4-[(4′)dodecyl]benzene sulfonate.

- Surface Tension: In this method surface tension is measured before and after adsorption, and from the difference of the surface tension measurements, amount adsorbed can be calculated, using Gibbs adsorption equation.

2.3. Kinetics of Adsorption of Surfactants

Although the surfactant adsorption kinetics at the air-liquid and liquid-liquid interface has been studied extensively (Ward and Tordai, 1946; Ferri and Stebe, 2000; MacLeod and Radke, 1994; Vlahovska et al., 1997; Danov et al., 1999; Kralchevsky et al., 1993; Borwankar and Wasan, 1986; Lin et al., 1996a, 1996b, 1996c, 1990; Liggieri et al., 1996; Hsu et al., 2000a, 2000b; Miller et al., 1994), comparatively less number of studies are focused on the solid-liquid interface (Tiberg et al., 1994; Tiberg, 1996; Pagac et al., 1998; Brinck et al., 1998a, 1998b; Biswas and Chattoraj, 1998; Partyka et al., 1984; Fava and Eyring; 1956; Meader and Fries, 1952).

2.3.1 Surfactant adsorption kinetics at the fluid-fluid interface in absence of electrolyte

The first quantitative model for adsorption kinetics was established by Ward and Tordai (1946) at the air-liquid interface. They considered adsorption kinetics to be controlled only by diffusion. It is based on the assumption that the time dependence of interfacial tension, which is directly correlated to the interfacial concentration (Γ) of the adsorbing molecules, is a reflection of the time dependence of the transport of molecules to the interface. In absence of any external influences this transport is controlled by diffusion. The result of the so-called diffusion controlled adsorption kinetics model has the following form:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[C_b\sqrt{t} - \int_0^{\sqrt{t}} C_{sub}(0, t-\tau)d\sqrt{\tau}\right] \qquad (2.1)$$

where D is the diffusion co-efficient, C_b is the bulk surfactant concentration, C_{sub} is the sub layer immediately adjacent to the interface and τ is the diffusion time scale. In the last two decades, a number of studies on adsorption kinetics at the air-liquid interface have been reported.

Lin et al. (1990) have studied the adsorption of TX-100 at the air-liquid interface and computed diffusion coefficient using a diffusion controlled adsorption model. Kralchevsky et al. (1993) have studied the adsorption kinetics of surfactant at the air-liquid interface and developed a diffusion controlled model which is applicable for interpretation of data for dynamic surface tension for both ionic and nonionic surfactant below the CMC. Diffusion controlled kinetic model at the air-liquid interface was also reported by others (Borwankar and Wasan, 1986; Hsu et al., 2000a, 2000b). Hsu et al. (2000a) have developed a model to study adsorption of surfactant onto a clean spherical air-water interface with different curvature. They found from the simulation data, that (a) for any interfacial curvature, stronger the surfactant interactions, greater is the deviations in apparent diffusivity or in sorption rate constants obtained from a Langmuir analysis, (b) a larger deviation on diffusivity results at more dilute concentration, (c) and at the same interactions between the adsorbed surfactant molecules, larger the interfacial curvature, smaller is the deviation in diffusivity (D) or in sorption rate constants.

Liggieri et al. (1996) and Lin et al. (1996) have studied the mixed kinetic-diffusion controlled adsorption kinetics of ionic surfactant. Lin et al. (1996) have found that the shift in controlling mechanism from diffusion control at dilute concentration to mixed diffusion-kinetic control at more elevated bulk concentration.

2.3.2 Surfactant adsorption kinetics at the fluid-fluid interface in presence of electrolyte

MacLeod and Radke (1994) and Danov et al. (1999) have studied the adsorption kinetics of ionic surfactant in presence of electrolyte at the fluid-fluid interface. The existence of an electric double layer essentially influences the equilibrium (Tajima et al., 1970; Tajima, 1970; Tajima, 1971; Cross and Jayson, 1994; Lucassen-Reynders, 1966; Hachisu, 1970; Borwankar and Wasan, 1988; Hall, 1994; Kalinin and Radke, 1996) and the dynamic interfacial properties of the ionic surfactant solutions (Fainerman, 1991; Fainerman et al., 1994; Joos et al., 1992; Bonfillon et al., 1994; Hua and Rosen, 1991).

In the case of ionic surfactant in presence of electrolyte, the transport of each charged species, j (where j = 1, is the surfactant, j = 2, is the counter ion and j = 3 is the co-ion) with valence z_j and diffusion coefficient D_j under the influence of an electrical potential ψ, is described by the Nerst-Plank diffusion-migration equation (MacLeod and Radke, 1994):

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial}{\partial x}\left(\frac{\partial C_j}{\partial x} + \frac{z_j C_j e}{k_B T}\frac{\partial \psi}{\partial x}\right) \qquad j = 1, 2, 3. \tag{2.2}$$

Here, C_j is the bulk concentrations of the j th ion which depends on time t and the distance x to the interface; k_B is the Boltzman constant, T is the absolute temperature. The second term in the parentheses in equation (2.2), the electro migration term, accounts for the effect of the electric field on diffusion. The electric potential ψ is related to the bulk charge density through the relationship known as Poisson equation:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi e}{\varepsilon}\sum z_j C_j \tag{2.3}$$

where ε is the dielectric permittivity. Equations (2.2) and (2.3) have been solved with appropriate initial and boundary conditions to obtain the concentration profile of the species, which is then used to find the flux. Important findings are mentioned as follows.

At low electrolyte concentrations, difference between counter ion and surfactant ion diffusion coefficients influences the rate of surfactant transport to the interface. For the typical case, where the counter ion diffusion coefficient is up to an order of magnitude larger than the surfactant ion diffusion coefficient, the surfactant transport rate is increased in presence of counter ion, but it remains slower than the nonionic transport rate. At high electrolyte concentration, the counter ion diffusion coefficient has no effect on the rate of surfactant transport (MacLeod and Radke, 1994).

2.3.3 Surfactant adsorption kinetics at the solid-liquid interface

Reported studies on the surfactant adsorption kinetics on the solid-liquid interface are limited as compared to that on the fluid-fluid interface. Studies of surfactant adsorption or desorption kinetics from water at the hydrophilic solid surface, have been conducted mostly by using silicon oxide (silica) (Brinck et al., 1998a, 1998b; Tiberg et al., 1994; Tiberg, 1996; Pagac et al., 1998; Partyka et al., 1984), as this model hydrophilic surface has been well characterized. There seems to be consequences in the literature that the time variations on extent of adsorption can be divided into three different regimes, (1) linear increase in adsorption with time, (2) transition regime where the rate of adsorption levels off and (3) a plateau regime. The range over which the regions extend varies with the bulk concentration, nature of surfactant, presence of salt and so on. The nature of solid surface, that is hydrophobic or hydrophilic, and the electrical interactions play an important role in the kinetics of adsorption of surfactant at the solid-liquid interface.

Meader and Fries (1952) and Fava and Eyring (1956) have studied the adsorption kinetics of anionic surfactant on cotton by radiotracer method. Meader and Fries (1952) have found that adsorption was rapid during the first few minutes and was at least 50 % complete within 10 minutes of 2-3 hours of total equilibrium time. The rate of adsorption increased markedly with increasing temperature. Fava and Eyring (1956) found that the first order kinetic law can not describe the adsorption of surfactant on cotton surface. They have used a simple nonlinear equation to fit the kinetic data.

Adsorption kinetics of non-ionic surfactant (Tiberg et al., 1994; Tiberg, 1996; Brinck et al., 1998a, 1998b) and cationic surfactant (Pagac et al., 1998) on silica has been studied by ellipsometry technique. Kinetics model of adsorption of non-ionic surfactant on hydrophilic silica have been developed (Tiberg et al., 1994; Brinck et al., 1998a, 1998b) considering that three processes occur in the solution: monomer diffusion, micellar diffusion and micellar dissociation. It was assumed that micelles do not adsorb on the hydrophobic surface. Figure-2.1 represents a schematic picture of the process out side the silica surface. The adsorption was described as a two-step process, where the first step was diffusion from the bulk solution to a subsurface, and second step was transport from the subsurface to the surface and the concomitant adsorption. The stagnant layer out side the surface assumed to be finite due to convection caused by stirring during measurements. The adsorption was observed to be diffusion controlled, and the concentration immediately outside the surface was determined by a local equilibrium in the sublayer region. The micelles were assumed to contribute to the adsorption only by releasing monomers during diffusive transport and not by direct adsorption. The initial increase in adsorption is approximately linear with time. The rate of adsorption in the linear region for the pre-micellar solutions, has been shown to be a linear function of bulk

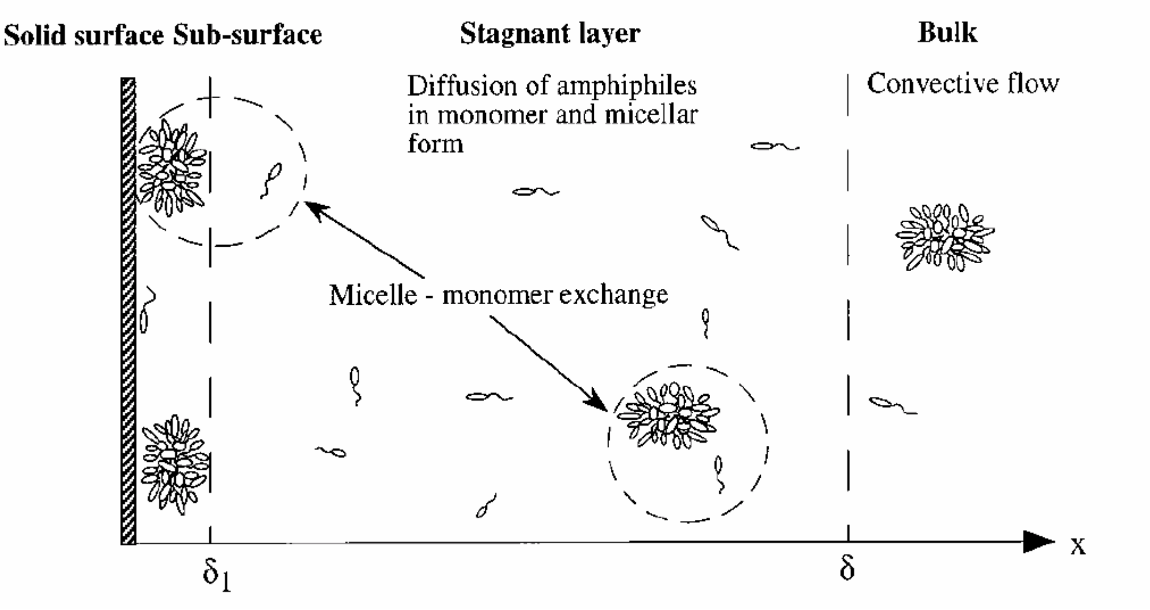


Figure-2.1 Schematic presentation of the solution profile outside the silica surface (Brinck et al., 1998a).

concentration, the csac (critical surface aggregation concentration), the thickness of the stagnant layer and diffusion coefficient of the monomer. Similar relation was found for the concentration above the CMC. As the amount adsorbed approaches the plateau value, the adsorption rate begins to decrease and finally becomes zero. Brinck et al., (1998b) have extended this model to the mixed surfactant system to predict the kinetic behavior of binary mixture of nonionic surfactants at silica-water interface.

Biswas and Chattoraj (1998) have studied the adsorption of cationic surfactant (C_{16}TAB, C_{14}TAB, C_{12}TAB) on silica-water interface at different bulk concentration, pH, ionic strength, temperature and electrolyte. It is shown that the adsorption follows a two-step first order rate process with two different process rate constants.

2.4 Equilibrium Adsorption of Surfactant (Adsorption Isotherm)

The study of equilibrium of surfactant adsorption is important to determine the maximum amount adsorbed per unit area or mass of the adsorbent and to determine the adsorption isotherm. This is a measure of extent of surface of the adsorbent that is covered by the adsorbent molecules at a given condition, and hence determines the interfacial properties in many applications. Most of the interfacial processes are related to the equilibrium adsorption of the surfactant.

2.4.1 Adsorption of ionic surfactant

The solid surfaces are either positively or negatively charged in the aqueous medium by ionization/dissociation of surface groups or by the adsorption of ions from solution onto a previously uncharged surface. So, electrical double layer at the solid-liquid interface is usually an important phenomenon for the adsorption of ionic surfactants.

2.4.1.1 Surface charge and the electrical double layer

At any interface there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of opposite sign, giving rise to a potential across the interface and so-called 'electrical double layer'. Since, overall electrical neutrality must be maintained, the net charge on one side of the interface must be balanced by an exactly equal net charge of opposite sign on the other side of the interface. Figure-2.2 shows the schematic presentation of electrical double layer. The mathematical analysis of electrical double layer gives the term κ, the length scale for the screening and 1/κ is associated with the thickness of the ionic atmosphere around each ion and is called Debye length (Adamson and Gast, 1997). This is the distance from the charged surface into the solution within which the major portion of the electrical interactions with the surface can be considered to occur. The Debye length is given by the expression (Adamson and Gast, 1997)

$$\frac{1}{\kappa} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{e^2 \sum C_i z_i} \right)^{\frac{1}{2}} \qquad (2.1)$$

where ε, ε_0 are dielectric constant or permittivity of the solution and in vacuum respectively ($J^{-1}m^{-1}$), k_B, T, e, C, z are the Boltzmann constant, absolute temperature, charge of electron, molar concentration of ion in solution and valency of ion in solution respectively. From the relationship it is noted that 1/κ is inversely proportional to valance z of the ions and to the square root of their concentrations. It is also noted that the solvent with high dielectric constant such as water show higher electrical effect than the solvent with low dielectric constant. In addition, it can be shown that in presence of electrolyte, electrical effects have shorter ranges or the electrical double layer is compressed.

2.4.1.2 Contributions to the adsorption energy

Much attention has been given to understand the various contributory mechanisms to the adsorption process for wide variety of surfactants and adsorbents. The free energy of adsorption ΔG^0_{ads} is the sum of number of additive contributions can be written as (Hough and Rendall, 1983)

$$\Delta G^0_{ads} = \Delta G^0_{elec} + \Delta G^0_{spec} \qquad (2.2)$$

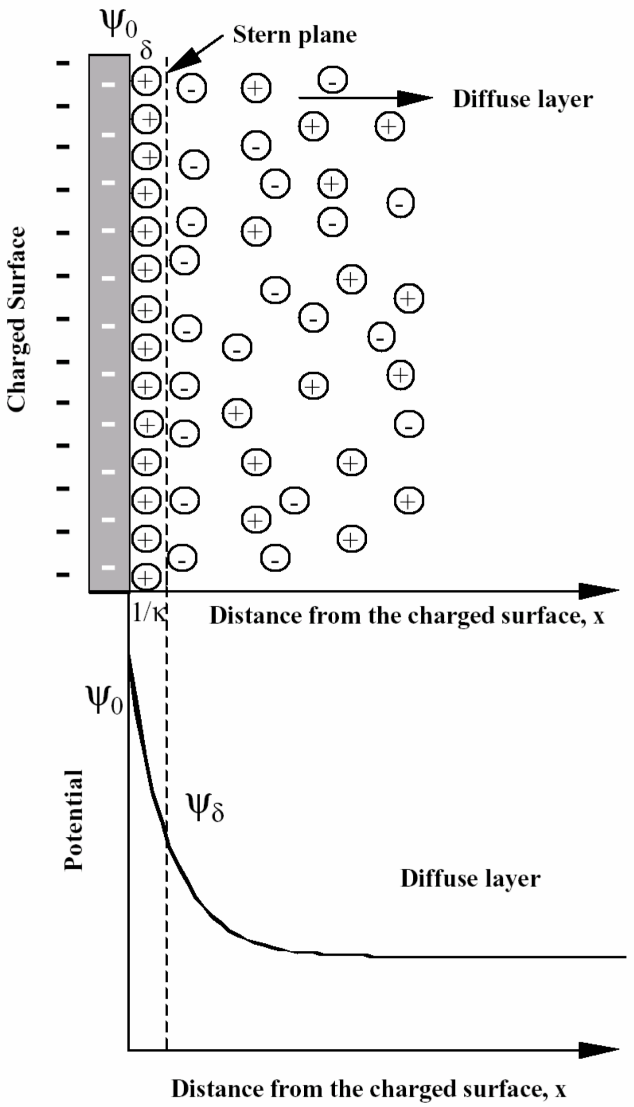


Figure-2.2: Schematic presentation of electrical double layer.

where ΔG^0_{elec} accounts for electrical interactions and ΔG^0_{spec} is a specific adsorption term, which contains all other contributions to the adsorption free energy that are dependent on the "specific" (non electrical) nature of the system. Using Stern-Grahame equation ΔG^0_{ads} can be calculated as to (Somasundaran and Huang, 2000)

$$\Gamma = rC_{eq} \exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \tag{2.3}$$

where r is the radius of the adsorbed ion, C_{eq} is the equilibrium concentration.

2.4.1.3 Electrical interactions

Usually, ΔG^0_{elec} is ascribed totally to columbic interactions. However, dipole term can be included in the electrical term such that (De Keizer and Lyklema, 1980):

$$\Delta G^0_{elec} = \Delta G^0_{coul} + \Delta G^0_{dip} \tag{2.4}$$

$$\Delta G^0_{coul} = z\,F\,\psi_\delta \tag{2.5}$$

$$\Delta G^0_{dip} = \sum_j \Delta n_j \mu_j E_{ads} \tag{2.6}$$

where ΔG^0_{coul} and ΔG^0_{dip} is the free energy term for columbic dipole respectively, ψ_δ is the potential at the stern plane (δ is the thickness of the compact part of the double layer), Δn_j is the number of adsorbed molecules j, μ_j is the dipole moment of j and E_{ads} is electric field strength across the plane of adsorbed species.

If we neglect ΔG^0_{dip}, the basic interpretation of ΔG^0_{elec} will be simplified and there will be three cases (Hough and Rendall, 1983);

(i) When the surfactant ions are counter ions, then z and ψ_δ are of opposite sign, so, $z\,F\,\psi_\delta < 0$ and the electrical interaction promotes the adsorption process. This situation will exist for cationic surfactant/negatively charged surface and anionic surfactant/positively charged surface.

(ii) If the net charge density ($\sigma_0 + \sigma_\delta$) is of same sign as the surfactant ions, then z and ψ_δ are of same sign and $z\,F\psi_\delta > 0$, i. e. electrical interaction oppose adsorption. In absence of specifically adsorbed ions this situation will exist for anionic surfactant/negatively charged surface and cationic surfactant/positively charged surface.

(iii) Under i.e.p. (isoelectric point) conditions referred to above, ΔG^0_{elec} will be zero (neglecting ΔG^0_{dip}) and adsorption is governed by ΔG^0_{spec} term.

2.4.1.4 Specific interactions

ΔG^0_{spec} can be subdivided into separate independent interactions. The contributing force can be written as (Somasundaran and Huang, 2000)

$$\Delta G^0_{spec} = \Delta G^0_{chem} + \Delta G^0_{c-c} + \Delta G^0_{c-s} + \Delta G^0_{H} + \Delta G^0_{H_2O} \ldots \qquad (2.7)$$

ΔG^0_{chem} is the chemical term due to covalent bonding. ΔG^0_{c-c} is the lateral interaction term owing to the cohesive chain-chain interaction among adsorbed long chain surfactant species, usually important for hemimicellization. ΔG^0_{c-s} is a similar interaction between the hydrocarbon chains and hydrophobic sites on the solid, ΔG^0_{H} is the hydrogen bonding term and $\Delta G^0_{H_2O}$ is the solvation or desolvation term, owing to the hydration of the adsorbate species or any species displaced from the interface due to adsorption.

2.4.1.5 Adsorption isotherm

At the solid-liquid interface, the plot of amount of surfactant adsorbed per unit mass or unit area of the solid vs. equilibrium concentration is called adsorption isotherm. A number of studies have been conducted on solid liquid interface (Fava and Eyring, 1956; Meader and Fries, 1952; Pagac et al., 1998; Ginn et al., 1961; Biswas and Chattoraj, 1997; Sexsmith and White, 1959a, 1959b; Vold and Sivaramakrishnan, 1958; Furst et al., 1996; Trogus et al., 1978; Arnebrant et al., 1989; Keesom et al., 1988; Rendall et al., 1979; Connor and Ottewill, 1971; Evans, 1958; Scamehorn et al., 1982a, 1982b; Somasundaran and Fuerstenau, 1966; Somasundaran et al., 1964; Tamamushi and Tamaki, 1959; Hoeft and Zollars, 1996; Vanjara and Dixit, 1996; Dixit et al., 2002; Wang and Kwak, 1999; Koopal et al., 1995; Chandar et al., 1987). Figure-2.3 depicts the

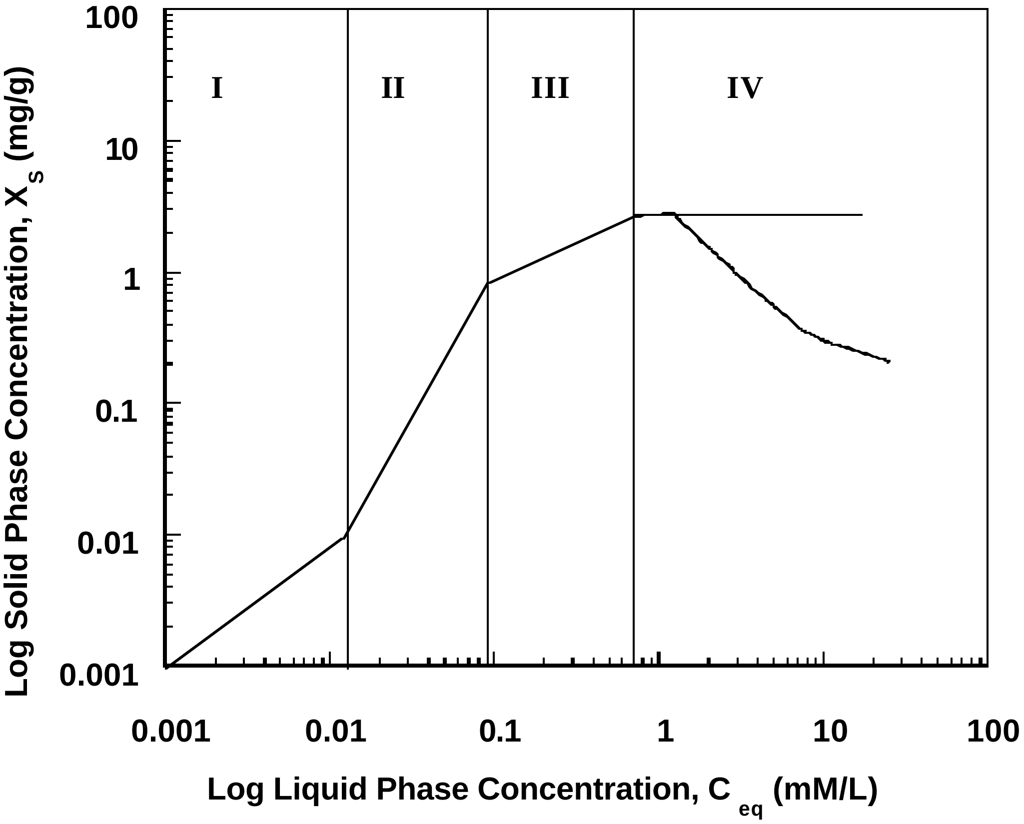


Figure-2.3: Schematic presentation of typical four-regime adsorption isotherm.

typical isotherm of adsorption of surfactants on the solid-liquid interface in a rather wide range of concentration of surfactants going beyond the CMC. In general, a typical isotherm can be subdivided into four regions when plotted on a log-log scale (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Chander et al., 1983). In region I, the adsorption obeys Henry's law, adsorption increases linearly with concentration. Region II shows a sudden increase in adsorption due to surface aggregation of the surfactants, while region III shows a slower rate of adsorption than region II. Region IV is the plateau region above the CMC (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988). However, depending upon several factors the region IV may show a maximum (Fava and Eyring, 1956; Meader and Fries, 1952; Pagac et al., 1998; Ginn et al., 1961; Biswas and Chattoraj, 1997; Sexsmith and White, 1959a, 1959b; Vold and Sivaramakrishnan, 1958; Furst et al., 1996; Trogus et al., 1978; Arnebrant et al., 1989; Evans, 1958). The systems that have shown this four region adsorption isotherms are: adsorption of anionic surfactant on alumina (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Tamamushi and Tamaki, 1959; Chandar et al., 1987), cationic surfactant on silica gel (Gao et al., 1987), cationic surfactant on poly styrene latex (Connor and Ottewill, 1971), both anionic and cationic surfactants on metal oxide (Koopal et al., 1995).

The explanations for the nature of adsorption curve in the first three regimes are well accepted. The sudden rise in adsorption in region II is due to formation of surface aggregate of the surfactant molecules on the solid surface. These surface aggregates are known as 'hemimicelles' (Gaudin and Ferstenau, 1955); which form beyond a critical concentration below the CMC, and is known as critical hemimicellar concentration (HMC). Hemimicellization was first hypothesized (for the adsorption of dodecylammonium ions on quartz) by Gaudin and Ferstenau (1955); the later by others (Somasundaran et al., 1964; Somasundaran and Fuerstenau, 1966; Vanjara and Dixit, 1996; Dixit et al., 2002; Chandar et al., 1987; Gao et al., 1987; Gu et al., 1988). They have mentioned that the forces causing ionic association on the solid surface will be same as those operating in the bulk. Because of the high surface charge, the dodecylammonium ions must necessarily be oriented with the charged head towards the surface and with tail striking out into the liquid. Then the associative van der Waals force in the chains will form hemimicelle. Mane et al. (1994) have reported the first direct AFM imaging of ‘hemimicelle’ on graphite surface using cationic surfactant (CTAB). In region III, there occurs a slowdown of surface cluster formation and hence there is a reduction in slope of isotherm. Gao et al. (1987) have proposed an empirical equation to calculate the average aggregation number of the hemimicelle, n_{hm},

$$n_{hm} = \frac{\Gamma_\infty}{\Gamma_{hm}} \tag{2.8}$$

where Γ_∞ and Γ_{hm} are the amounts adsorbed at saturation and H.M.C respectively. Chandar et al. (1987) have experimentally measured the hemimicellar aggregation number for adsorption of sodium dodecylsulfate (SDS) at alumina-water interface using fluorescence probe. They have found the aggregation number is 121-128 in region II and 166-356 in region III. Table 2.2 shows the reported hemimicellar aggregation number in different studies. From the table it is observed that alumina shows higher aggregation number. Because negatively charged surfactant strongly adsorbed on positively charged alumina at pH 6.5. Hemimicellar equilibrium constant and free energy also can be calculated using following equations (Gu et al., 1988)

$$K_{hm} = \frac{\Gamma_\infty - \Gamma_{hm}}{C^{n_{hm}-1}(n_{hm}\Gamma_{hm} - \Gamma_\infty)} \tag{2.9}$$

$$-\Delta G^0_{hm} = RT \ln K_{hm} \tag{2.10}$$

where K_{hm} is the equilibrium constant and ΔG^0_{hm} is the standard free energy change for hemimicellization.

The adsorption mechanism in region IV is not well understood. Ideally, the adsorption is expected to remain unchanged beyond the CMC since the concentration of monomer does not increase beyond CMC and the micelles that formed do not adsorb on the surface (Brinck et al., 1998a). The observation of a maximum in region IV has drawn attention of some researchers and attempts have been made to explain this occurrence.

Table-2.2: Hemimicellar aggregation number of different systems.

Surfactant	**Medium**	**Adsorbent**	**Aggregation Number**
DPB	Water	Silica gel	12[a]
TPB	Water	Silica gel	13[a]
TPC`	Water	Silica gel	6[a]
SDS	0.1M KCl, pH=6.5	Alumina	121-128 (region-II)[b] 166-356 (region-III)[b]
C_{16}TAB	0.001 M KCl	PTFE	7[c]
C_{14}TAB	0.001 M KCl	PTFE	6[c]
C_{12}TAB	0.001 M KCl	PTFE	7[c]
CPC	0.001 M KCl	PTFE	4[c]
DPC	0.001 M KCl	PTFE	4[c]
C_{16}TAB	0.001 M KCl	Polystyrene	8[d]

DPB, TPB and TPC are dodecyl pyridinium bromide, tetradecyl pyridinium bromide and tetradecyl pyridinium chloride respectively. CPC and DPC are cetylpyridinium chloride and dodecylpyridinium chloride respectively.

[a] = Gao et al., 1987; [b] = Chander et al., 1987; [c] = Vanjara et al., 1996; [d] =Dixit et al., 2002.

Presence of trace surface-active impurities in the surfactant sample have been attributed to the occurrence of this maximum. These would be adsorbed below the CMC but would be solubilized in the micelles above the CMC (Pagac et al., 1998; Furst et al., 1996; Trogus et al., 1978). In some cases reported in the literature, additional surfactant purification was found to decrease the amplitude of the adsorption maximum but could not completely eliminate it (Arnebrant et al., 1989). In an another explanation, it is stated that, ionic strength of the solution reduces the electrical repulsion between adsorbed ions and the repulsive interaction becomes less than the van der Waals attraction between the paraffin chains, leading to the formation of surface micelles. Desorption of both simple monomer ions and surface micelles occur on collision of micelles in solution with the adsorbing surface and thus decreasing the amount of adsorption on the surface (Vold and Sivaramakrishnan, 1958). Sexsmith and White (1959b) have explained the adsorption maxima using the principle of mass action of micellization and the total mole balance equations. The equilibrium among counter ions, anionic or cationic surfactants and micelles can be shown to result in a decrease in the monomer concentration with increasing total concentration above the CMC. They write the mass action equation considering ideal solution

$$K = \frac{C_M}{C_Q^n C_x^{mQ}} \qquad (2.11)$$

where K is an equilibrium constant, C_M molar concentration of micelle, C_Q and C_x are the monomer concentration of counter ion and surfactant respectively, n and m_Q are the micellar aggregation number and number of counter ion per micelle respectively. The conservation of total solute, C_T, present

$$C_T = n\,C_M + C_Q = m_Q\,C_M + C_x \qquad (2.12)$$

The equation can be solved for C_Q as a function of C_T and a maximum in C_Q will occur at the CMC if $n > m_Q \geq 2$. Thus, if one assumes that adsorption depends on the monomer concentration, the adsorption maximum occurs because the monomer concentration exhibits a maximum. The observation of maximum in case of cotton surface has been attributed to the presence of wax, which gets solubilized beyond CMC (Ginn et al., 1961).

2.4.2 Adsorption of nonionic surfactant

The adsorption of non-ionic surfactants on the solid-liquid interface has not been studied as extensively as the ionic surfactants (Corkill et al., 1966; Schott, 1967; Zhu and Gu, 1991; Partyka et al., 1984, 1993; Portet et al., 1997; Levitz, 1991; Levitz et al., 1984a, 1984b; Levitz and Damme, 1986; Kibbey and Hayes, 1998; Zhu et al., 1988; Nevskaia et el., 1998, 1995; Tiberg, 1996; Gracía et al., 2000; Douillard et al., 1992). The adsorption isotherms of non-ionic surfactants are generally Langmurian or L2 (Clunie and Ingram, 1983), like those of most other highly surface-active solutes adsorbing from the dilute solution. However, the isotherms are often the stepped L4 types of Langmuir isotherm (Giles et al., 1960) rather than simple L2 type.

Nonionic surfactants are physically adsorbed rather than electrostatically or chemisorbed. However, they differ from many other surfactant in that, quite small changes in concentration, temperature, or molecular structure of the adsorbent can have a large effect on the adsorption. This is due to adsorbate-adsorbate and adsorbate-solvent interactions which cause surfactant aggregation in bulk solution and which lead to change in orientation and packing of surfactant at the surface. Figure-2.4(a) shows a general scheme of the most likely orientation changes undergo in the adsorption of nonionic surfactants from solution onto solid surface and Figure 2.4(b) shows three adsorption isotherms corresponding to the different adsorption sequences shown in Figure-2.4(a) (Clunie and Ingram, 1983).

In the first stage of the adsorption [Figure-2.4(a) I] the surfactant is adsorbing on a surface where there are very few molecules which are adsorbed obeying Henry's law and because the molecules are far away from each other adsorbate-adsorbate interactions are negligible. Adsorption in this region occurs because of van der Waals interaction, and therefore, it is mainly determined by the hydrophobic moiety of the surfactant. The second region [Figure-2.4(a) II] is accompanied by gradual decrease in the slope of the adsorption isotherm due to saturation of monolayer.

The subsequent stages of adsorption are sudden increasing amount adsorbed dominated by adsorbate-adsorbate interactions, although it is the adsorbate-adsorbent

(a)

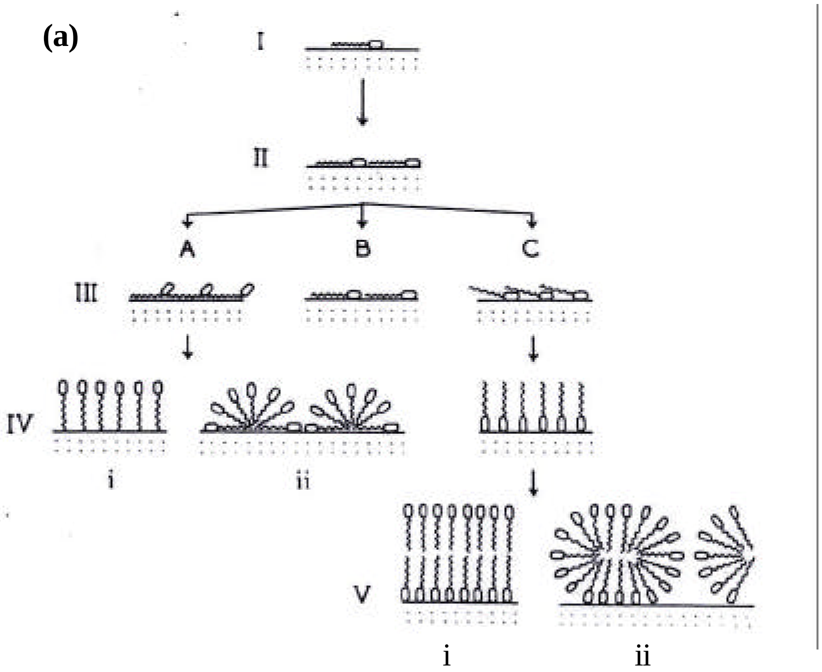


Figure 2.4(a): Adsorption of nonionic surfactant, showing the orientation of surfactant molecules at the surface. I-V are the successive stages of adsorption (Clunie and Ingram, 1983).

(b)

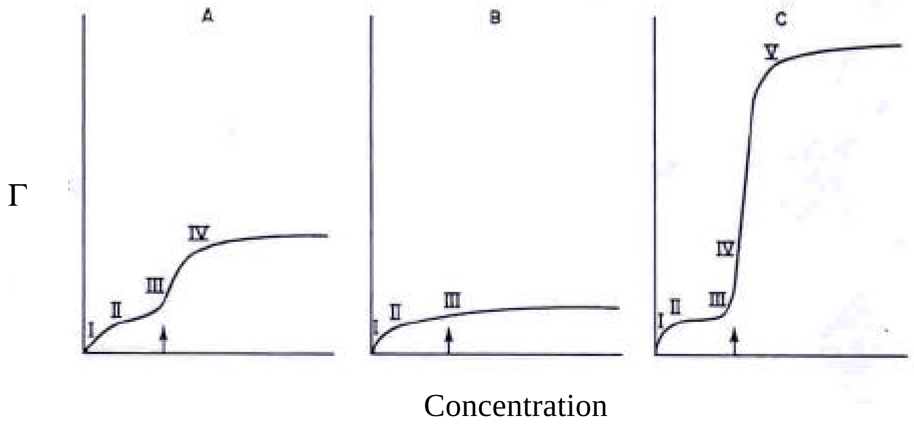


Figure-2.4 (b): Adsorption isotherms corresponding to the three adsorption sequences shown in 2.4 (a) I-V, indicating the different orientations; CMC is indicated by an arrow (Clunie and Ingram, 1983).

interaction that initially determines how the adsorption progresses when stage II is complete. The adsorbate-adsorbate interaction depends on the nature of the adsorbent and on the hydrophilic-lipophilic balance (HLB) in the surfactant. When the hydrophilic group is weekly adsorbed (when adsorbent is hydrophobic and hydrophilic group of surfactant is short) it will be displaced from the surface by the alkyl chains of the adjacent molecules [Figure-2.4(a) IIIA]. However, if there is a strong attraction between the hydrophilic group and the surface with hydrophilic adsorbent like silica or oxides, the alkyl chain is displaced [Figure-2.4(a) IIIC]. The intermediate situation when neither type of displacement is favored and the surfactant then remains flat on the surface [Figure-2.4(a) IIIB].

Finally, in region IV adsorption approaches a plateau above the CMC, there will be a tendency for the alkyl chains of the adsorbed molecules to aggregate (hemimicelle). This will cause the molecules to become vertically oriented and there will be a large increase in adsorption. This occurs for the hydrophobic adsorbent. Figure-2.4(a) IVC shows the case of adsorption nonionic surfactant on hydrophilic solid.

2.4.2.1 Effect of molecular structure

The molecular structure of the surfactant influences the shape of the isotherm in various ways. Within a homologous series it is found that increasing length of the hydrocarbon chain generally increases the magnitude of adsorption, Γ_{max}, at the plateau and diminishes with increasing size of the hydrophilic head group on the hydrophobic solid (Corkill et al., 1966). Partyka et al. (1984) have found that rate of adsorption of series of oxyethylene (EO) alkylphenol surfactant on the silica gel increases with increase in the chain length of hydrophilic group (EO). For the adsorption isotherm with increasing chain length of EO group the amount adsorbed at the plateau decreases. Similar observation was found by Portet et al. (1997) in study of the effect of chain length of hydrophilic group on adsorption.

2.4.2.2 Effect of temperature

The adsorption of nonionic surfactant on solid surface in general, increases with increasing temperature (Corkill et al., 1966; Partyka et al., 1984). Corkill et al. (1966) have studied the effect of temperature on adsorption of C_8E_3 and C_8E_6 on carbon black. They found in both the cases, the amount of adsorption increases with increasing temperature but the effect is strong in the case of C_8E_3. Partyka et al. (1984) have found the adsorption of the homologous series of oxyethylene alkyl phenol the quantity Γ_{max}, the amount adsorbed at the plateau of the isotherm varies linearly with the temperature. However, adsorption of the surfactants increased with increasing temperature. This could not have been predicted from the calorimetric measurements and is not seen in physical adsorption from single component phases, i.e. gas on solid. Corkill et al. (1966) suggested that the adsorbing species is actually the solvated surfactant molecule, which is essentially different at each temperature because the surfactant-solvent interaction, like polyethoxylated surfactants which are very sensitive to temperature. Increasing temperature gradually desolvates the head group, making it less hydrophilic and more compact, and this increases surface activity and saturation adsorption values

2.4.2.3 Effect of salt

Electrolytes can alter the solubility, surface activity, aggregation properties of nonionic surfactant, and thereby it may have an effect on adsorption at the solid/liquid interface (Rosen, 1978; Clunie and Ingram, 1983). Thus an electrolyte that 'salts out' a surfactant would probably increase its adsorption. Denoyel and Rouquerol (1991) found that the presence of NaCl shifts plateau position of TX-100 adsorbed on quartz towards lower equilibrium concentrations, which means that there is a decrease of the CMC. At the same time, these authors observed a rise in adsorption at the plateau. They explained this behavior to an increase in lateral interactions between polar chains, when salinity increases. Similar observation was also found for the adsorption of nonionic surfactant on silica gel (Partyka, et al., 1984, 1993). It has been shown that pH has some influence on the adsorption of nonionic surfactants on the surfaces with hydroxyl groups (Denoyel and

Rouquerol, 1991). At neutral pH, adsorption of TX-100 on quartz is low but it is increased at lower pH. This effect was attributed to the hydrogen bonding between polar chain of the surfactant and the silanol groups of the surface. Nevskaia et al. (1998) have studied the effect of added NaCl and $CaCl_2$ on adsorption of TX-100 on three different quartz (increasing order of hydroxyl group, QA > QB > QC), kaolin and dolomite. Basically three different observations have been found when NaCl is added. The amount of adsorption of TX-100 decreases when NaCl is added to the QA sample; the amounts increases on QB and kaolin samples; no alteration is observed for QC and dolomite samples. They explained that decreasing adsorption was due to the strong adsorption of inorganic ions on the polar surface and the resulting displacement of the nonionic surfactant molecules.

2.4.3 Adsorption of mixed surfactant

Adsorption of more than one surfactant significantly enhance the efficiency of many interfacial properties compared to the adsorption of a single surfactant. Although the adsorption of single surfactants at solid-liquid interface has been investigated intensively, there have been only a few studies of mixed systems, in spite of their great importance (Huang et al., 1989; Scamehorn et al., 1982c; Gao et al., 1984; Somasundaran et al., 1992; Somasundaran and Huang, 1997, 2000; Somasundaran and Krishnakumar, 1997; Ma and Xia, 1992a, 1992b; Xu et al., 1991; Esumi et al., 1990; Wang and Kwak, 1999). Adsorption of surfactants from the mixed systems mainly depends on the solution properties of mixed surfactant system. Many researchers have studied the solution properties of mixed surfactant systems and the resulting adsorption.

2.4.3.1 Anionic-cationic surfactant mixture

Only a few reported studies are available on the adsorption from a solution of anionic-cationic mixed surfactant. Huang et al. (1989) have studied the adsorption of cationic and anionic surfactants on silica from the mixture of anionic and cationic surfactants. They have found that the individual cationic surfactants can be strongly adsorbed onto the silica gel, but no significant adsorption of anionic surfactant can be detected. However, in the mixed systems, the adsorption amount of both the cationic and anionic surfactant ions are enhanced, and the excess adsorption of cationic surface-active ions are exactly equal to the adsorption of anionic surface-active ions. From the observations they assumed that the excess adsorption of cationic and anionic surface-active ions are in the from of ion pairs. Patist et al. (1999) have studied the change in interfacial properties anionic-cationic mixed surfactant at 1:3 and 3:1 molecular ratio due to formation of two-dimensional compact hexagonal arrangement at the air-liquid interface. At the 1:3 and 3:1 molar raio of SDS/CPC (cetylpyridinium chloride), minimum surface tension, maximum surface viscosity, maximum foam stability, maximum surface viscosity, and minimum rate of evaporation were observed. Figure 2.5 shows the 2-D hexagonal arrangements of molecules at the 1:3 and 3:1 molecular ratios in the mixed surfactant systems proposed by Patist et al., (1999). Similar observation has been made for the mixture of stearic acid - stearyl alcohol and decanoic acid – decanol mixtures at the air-liquid interface (Shah, 1971).

2.4.3.2 Anionic-nonionic surfactant mixture

Adsorption of anionic-nonionic surfactant has been studied by many researchers at the solid-liquid interface (Scamehorn et al., 1982c; Gao et al., 1984; Somasundaran et al., 1992; Somasundaran and Huang, 1997, 2000; Somasundaran and Krishnakumar, 1997; Ma and Xia, 1992a, 1992b; Xu, et al., 1991; Esumi et al., 1990). Adsorption of anionic and nonionic surfactants from their mixture on positively charged alumina has been reported (Somasundaran et al., 1992; Somasundaran and Huang, 1997; Wang and Kwak, 1999) and kaolinite (Xu et al., 1991). It is observed that adsorption of nonionic surfactant is enhanced where nonionic alone shows trace adsorption and adsorption of anionic surfactant slightly decreases. Another feature of adsorption isotherm is that with increasing the molar ratio of nonionic surfactant the continuous shift of plateau of isotherm of anionic surfactant towards lower concentration and the hemimicellization concentration of anionic surfactant also shifts towards lower concentration. Adsorption of

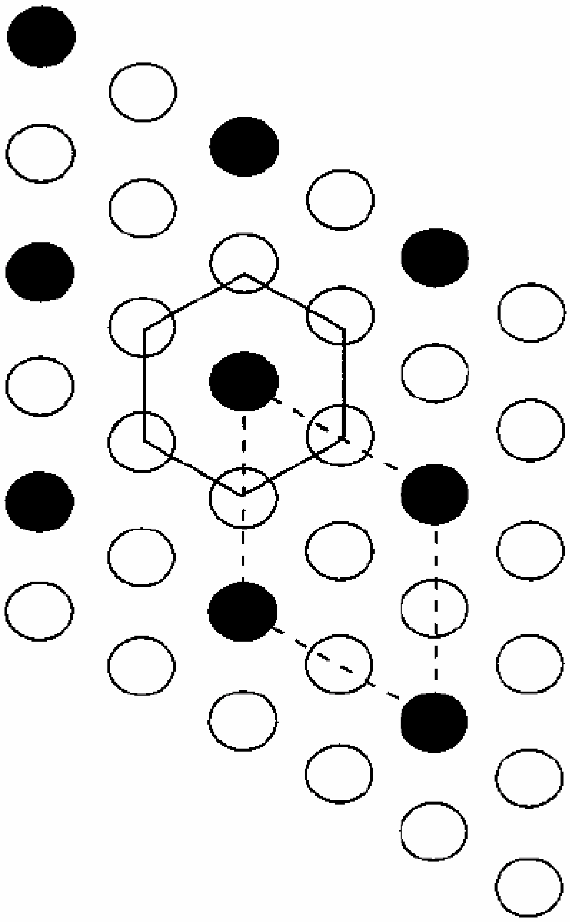


Figure-2.5: Proposed 2-D hexagonal arrangement of molecules at the 1:3 and 3:1 molecular ratios in mixed surfactant systems (Patist et al., 1999).

nonionic surfactant (TX-100) from the mixture of anionic-nonionic surfactant on negatively charged silica gel shows the decreasing amount adsorbed of TX-100 above the CMC with increasing concentration of anionic surfactant and there is no change in isotherm below the CMC between mixed system and the pure TX-100 (Gao et al., 1984). The decrease of limiting adsorption is greater at the same concentration of anionic surfactant with longer alkyl chain length. Somasundaran and Huang (2000) have found that in the case of adsorption of anionic/nonionic surfactant on kaolin, when the hydrocarbon chain length of nonionic surfactant is equal or longer than that of anionic, isotherms of anionic surfactant do not change with changing the chain length of nonionic surfactant. But, if the chain length of nonionic surfactant is shorter than that of anionic, however, different isotherms of anionic surfactant are obtained due to less shielding of anionic surfactant.

2.4.3.3 Cationic-nonionic surfactant mixture

Adsorption of mixture of cationic and nonionic surfactants on a negatively charged alumina (Huang et al., 1996; Somasundaran and Huang, 2000; Somasundaran and Krishnakumar, 1997), silica gel (Huang and Gu, 1987) and on kaolinite (Xu et al., 1991) shows similar effect that of anionic and nonionic surfactant mixture. In case of adsorption of cationic and nonionic surfactant on negatively charged alumina from their mixture, it is observed that nonionic surfactant alone adsorbed negligibly. In the mixed surfactant system, adsorption of nonionic surfactant increases in the presence of cationic surfactant, and the adsorption behavior depends upon the ratio of the two surfactants. The adsorption of cationic surfactant decreases under conditions of saturation due to bulkiness of the co adsorbed nonionic surfactant. However, below saturation adsorption conditions, the adsorption of cationic surfactant was increased due to repulsion among the cationic head groups.

2.5 Detergency

Detergency can be defined as removal of unwanted substance (soil) from a solid surface brought into contact with a liquid (Kissa, 1987). Detergency is a complex process involving a variety of components in a detergent formulation, which can lead to different mechanisms. A commercial detergent product will usually contain a surfactant system, a builder system, consisting of Ca^{++} and Mg^{++} sequesterants, and a buffer system, as well as minor components to improve aesthetics such as perfumes and brighteners (Roubingh, 1991). The complexity is necessitated by the fact that there are a variety of soils to be removed. A useful simplification is to classify soils into two types: oily and particulate soils. While both builders and surfactant are important to remove all the soils, it is generally true that oily soils respond to surfactants while particulate soils respond more to changes in the builder systems.

2.5.1 Mechanisms of particulate soil removal

The particulate soils are siliceous minerals, such as clays, as well as carbonaceous materials such as soot and carbon black, and inorganic oxide such as iron oxide. Detail description of the components of the laundry soil is given by Powe (1972). The removal mechanism also may differ depending on the type of soil. Anionic surfactants generally increase particulate soil removal. Removal of particulate soil in aqueous medium occur by the following mechanisms (Rosen, 1978):

(1) Wetting of the substrate and the soil particles: Adhesion of small solid particles to the solid substrate is generally diminished by immersion in water, because of interaction of the water with substrate and particles, in particular reducing the van der Waals attraction (Batra et al., 2001). The presence of water results in the formation of electrical double layer at the substrate/liquid and soil/liquid interfaces. These electrical double layers almost always result in change of similar sign on the substrate and particle with a resulting mutual repulsion, which reduces the net adhesion of soil.

(2) Adsorption of surfactant and other bath component (e.g. inorganic ions) at the substrate/liquid and particle/liquid interface: This causes a decrease in the work required

to remove the particle from the substrate. The role of surfactant appears to be twofold. First, wetting of particulate agglomerate and fiber by adsorbing surfactant. The net effect of this is to separate the particles and to decrease the attractive interactions between them. This effect is particularly important for hydrophobic particulate soil where little wetting occurs in absence of surfactant. Since most of the soils and fabrics are already negatively charged at the basic pH of the laundry environment. The second effect of adsorption of anionic surfactant is to increase the net negative charge on the particle and the fabric surface. Such increase results in greater electrostatic repulsive force between particles within agglomerate or between soil particles and fabric. This repulsive force can be quantified using DLVO theory for forces between double layers. There are some studies related to ξ potential and particulate soil removal (Yoneyama and Ogino, 1982; Batra et al., 2001). The two-step soil removal process is presented in Figure-2.6.

A soil particle on the substrate is subjected to van der Waals attraction and electrical forces assuming a sphere-plate model presented in Figure-2.7. The potential energy of the van der Waals attraction is E_A, the electrical double layer repulsion is E_R, and the resultant $E_S = E_A + E_R$. The curve depicts an energy barrier E_B, the height of which depends largely on the zeta potential of the fiber and the particulate. The height of this barrier is one of the factors controlling the kinetics of soil removal and redeposition.

2.5.2 Kinetics of particulate soil removal

A kinetic study usually involves the determination of soil concentrations on the fabric or in the bath at various times. A plot of soil concentration against time yields a curve that can provide useful information about the detersive process being studied (Bacon and Smith, 1948; Schott, 1975, 1976; Kissa, 1975, 1978, 1979; Vaughn et al., 1941). The kinetics of soil removal is complicated by the heterogeneity of the soil, shape, size, chemical composition and location of soil. In an empirical approach, kinetics of soil removal can be presented mathematically (Kissa, 1987),

$$\frac{dS}{dt} = -k_S S^{ns} \qquad (2.13)$$

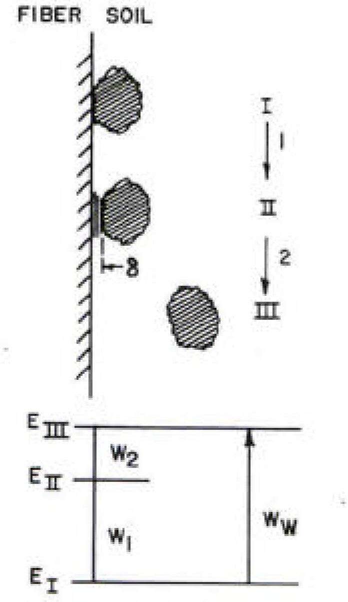


Figure 2.6 Stepwise removal of soil particle from a substrate in water. E_I, E_{II}, E_{III} are potential energies in step I, II, and III respectively. W_1, W_2 and W_W are work needed to separate the particle in step-1, step-2 and total respectively (Lange, 1972).

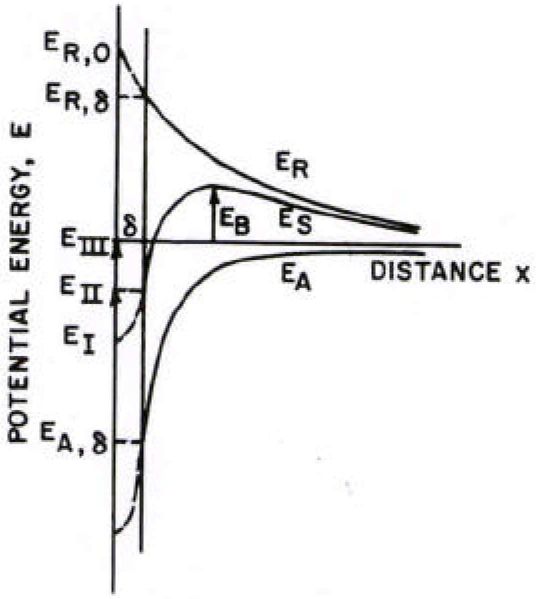


Figure 2.7 Potential energy of a particle-substrate system as a function of distance x (Lange, 1972).

where S is the amount of soil on the substrate at any time t, n_s is the order of the process, k_S is the average soil removal coefficient. The order n_s is independent of time and the rate coefficient k_S is not a constant, rather, decreases with increasing time (Schott, 1976). Most of the reported results of kinetics of particulate soil removal follow first order kinetics (Bacon and Smith, 1948; Hart and Compton, 1952).

2.5.3 Effect of physical parameters on particulate soil removal

Kissa (1979) has studied the effect of soiling conditions on particulate soil detergency. The soil removal rate decreases with increasing soiling time and intensity of mechanical action during soiling. Removal of particulate soil decreases with increasing pressure on the fabric during soiling. Morris and Prato (1982) have studied the effect of temperature on particulate soil removal. They found that with increasing temperature soil removal increases. The removal of soil also increases with increasing mechanical action during laundering (Bacon and Smith, 1948).

2.5.4 Oily soil removal

The detergency of oily soils involves several mechanisms, but in general, the oily soils are removed by (i) rolling-up and (ii) solubilization mechanism (Kissa, 1987). The mechanism of oily soil is also reviewed by Miller and Raney (1993). The driving force causing the oily soil to separate from the fiber surface is the roll-up results from tension at the interfaces between oil, water, and the fiber. In the presence of surfactant, the apparent contact angle of the oil on the fibers increases from 0 to 90 and 180^o, and the oily soil rolls up. The surfactant helps an oily soil to roll up by lowering the water/fiber and water/oil interfacial tensions. Solubilization of oily soil occurs when the concentration of surfactant is above CMC and sufficient surfactant is present, very small droplets of oily soil goes inside the micelle. Removal of oily soil increases with increasing temperature and mechanical action (Scott, 1963). Addition of electrolyte initially decreases the oily soil removal, but at higher concentration of electrolyte it increases and divalent ions are much more effective than the univalent ions (Scott, 1963).

2.5.5 Synergism between oily and particulate soil

The composite soils are the mixture of oily and particulate soils. The multicomponent soils (particulate/oily or oily/particulate) are less effectively removed from the fabric than either particulate or only oily soil (Webb and Obendorf, 1988). It appears that the oil acts as a fatty matrix to bind the particulate to fabric surface. Webb and Obendorf (1988) observed that if the specimens are soiled first with oil and then with particulate, then more soil was removed by laundering than the specimens soiled with particulate first and then oil. The detergency is difficult for composite soil due to encapsulation of particulate by the oil and absorption of oil by the particulates.

2.6 Concluding Remarks

Adsorption of surfactants on the solid-liquid interface has been studied extensively because of the continuing wide rage of applications. Adsorption of surfactants at the solid-liquid interface depends mainly on the nature of the surfactant, the solvent and the nature of the substrate. Adsorption kinetics of surfactants at the fluid-fluid interface shows diffusion control and mixed diffusion-kinetic control (Liggieri et al., 1996; Lin et al., 1996) characteristics depending on the nature of surfactant and the bulk concentration. Adsorption kinetics at the fluid-fluid interface is influenced by the presence of electrolyte (MacLeod and Radke, 1994; Danov et al., 1999). If the diffusion coefficient of counter ion is larger than the surfactant ion diffusion coefficient, then the surfactant transport rate in adsorption increases in presence of counter ion. But, at high electrolyte concentration, the counter ion diffusion does not influence the rate of surfactant transport. Studies have been reported on adsorption kinetics at the solid-liquid interface primarily on the adsorption of nonionic surfactant on silica and limited studies on cationic surfactant on silica and anionic surfactant on cotton. Systematic studies on the adsorption of surfactant on negatively charged cellulose-water interface is needed to improve the basic understanding of the detergency process. Yet, to the best of the authors knowledge no specific study has been attempted on adsorption kinetics of surfactants on cellulose-water interface for a wide range of system parameters such as different types of surfactants, effect of different electrolytes, solid-liquid ratio and so on.

Equilibrium studies of surfactant adsorption on the solid-liquid interface mostly shows four-regime isotherm. Four-regime isotherm was mainly observed for adsorption of ionic surfactant on oppositely charged solid surface and adsorption of nonionic surfactant on silica surface. Region IV of the adsorption isotherm is commonly a plateau region above the CMC, it may also show a maximum above the CMC (Fava and Eyring, 1956; Meader and Fries, 1952; Pagac et al., 1998; Ginn et al., 1961; Biswas and Chattoraj, 1997; Sexsmith and White, 1959a, 1959b; Vold and Sivaramakrishnan, 1958; Furst et al., 1996; Trogus et al., 1978; Arnebrant et al., 1989; Evans, 1958). Many researchers have made attempts to explain the decreasing trend of this isotherm in region IV, but there seems to be a lack of clear understanding on this matter. Therefore, systematic studies of adsorption of surfactants at the cellulose-water interface are required for a wide range of conditions such as surfactant type, electrolyte concentration, pH and so on.

Mixture of surface-active materials can show synergistic interactions, which can be manifested as enhanced surface activity, spreading, foaming, detergency and many other phenomena. The synergistic behaviour of mixed surfactant systems can be exploited to reduce the total amount of surfactant used in a particular application resulting in the reduction of cost. There are a very few adsorption studies on mixed surfactant system at the solid-liquid interface. Specially, there are no studies on the mixed surfactant system at the cellulose-water interface. From the application point of view, anionic-cationic surfactant mixture can be used in laundry detergent with inbuilt fabric softener and other application (Rubingh, 1991). Another important aspect is cationic surfactant have the unique possibility of providing germicidal effects along with their cleaning action (Patterson and Grindstaff, 1977). This makes them useful in applications where antiseptic conditions must be maintained. The mechanism of adsorption of anionic-cationic mixture below CMC of the mixture is not clearly understood and therefore it needs to be studied.

Chapter-3

Kinetics of Adsorption of Surfactants from its Solution at the Cellulose-Water Interface

3.1 Introduction

Adsorption kinetics is an important step for studying the equilibrium studies of adsorption or the adsorption isotherm. In the previous chapter a literature review is presented that leads to adsorption kinetics of surfactants on the solid liquid interface. In this review, it is shown that most of the studies on adsorption kinetics onto solid-liquid interface are on the silica-water interface. There are limited studies on the cellulose water interface. Adsorption of surfactant at the solid-liquid interface in presence of varying salt concentration and mixture of salt has not been studied yet. The effect of electrolyte at the fluid-fluid interface has been studied well and it is well known that the existence of an electric double layer essentially influences the equilibrium (Tajima et al., 1970; Tajima, 1970; Tajima, 1971; Cross and Jayson, 1994; Licassen-Reynders, 1966; Hachisu, 1970; Borwankar and Wasan, 1988; Hall, 1994; Kalinin and Radke, 1996) and dynamic (Fainerman, 1991; Fainerman et al., 1994; Joos et al., 1992; Bonfillon et al., 1994; Hua and Rosen, 1991) interfacial properties of the ionic surfactant solutions. The reported theoretical studies are based on the diffusion controlled kinetics.

A study on the kinetics of adsorption of three types of surfactants, anionic, nonionic and cationic at the cellulose-water interface is presented in this chapter. The objective is to compare the nature of adsorption kinetics of three different surfactants on the cellulose-water interface. In addition, the effects of varying electrolyte, valancy of co-ion and mixture of salt are also investigated. Further more, a simple Langmuir type two-site kinetic model is developed to explain the experimental observations and also to determine the adsorption rate constants under different conditions.

3.2 Experimental Section

3.2.1 Materials

Anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) was obtained from Fluka Chemicals. Nonionic surfactant, polyoxyethylene (number of segments 9.5) glycol tert-octylphenyl ether (Triton X-100 or TX-100) was obtained from Sigma Chemicals. NaDBS and TX-100 were used as received, without any further purification. Cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) was obtained from Ranbaxy Fine Chemicals Ltd., India. It was recrystalized twice from an acetone : methanol (3:1) mixture before use (Desai and Dixit, 1996). Calcium chloride di-hydrate and chloroform from E. Merk (India) Ltd. Potassium chloride, sodium sulfate and methylene blue were obtained from s. d. fine-chem Ltd, India. Adsorbent used was Whatman-40 ashless filter paper of 9 cm dia from Whatman International Ltd., England. The BET multipoint surface area of this filter paper (N_2 adsorption) was 16.5 m^2/g. Double distilled water of pH 5.6 and conductivity 1.2 μS (μ Mho) was used for the experiment.

3.2.2 Methods

3.2.2.1 Washing of filter paper

The filter paper was washed thoroughly with double distilled water to remove the dust and soluble ions from the filter paper till the conductivity of the washed water became equal to that of the distilled water. Then it was dried in an oven for 1 - 1.5 hours at 50-55^{o}C until the weight of the filter paper became constant.

3.2.2.2 Surfactant analysis

The concentrations of NaDBS and TX-100 were determined by measuring UV absorbance at 223 nm wavelength using UV-Vis spectrophotometer (Shimadzu, UV-160A model). Quartz glass cells (Hellma) of 10 mm path length were used. A calibration plot (absorbance vs. concentration) was obtained by measuring absorbance of surfactant solution of known concentration. Figures- 3.1(a) and (b) show the calibration plots of NaDBS and TX-100 respectively. Concentration of unknown solution was measured using the calibration plot. The concentration of CTAB was measured by two-phase titration technique (Rosen and Goldsmith, 1972; ASTM, 1959) by using methylene blue indicator. In this method, indicator was prepared in a solution of 0.3 g of methylene blue, 12 g of concentrated H_2SO_4, and 50 g of Na_2SO_4 per liter. An aliquot of CTAB was pipetted in a stoppered conical flux, then 10 ml indicator solution and 8 ml chloroform were added to that flux and titrated with the standard SDS solution. The flux was shaken vigorously after each addition. When the colour in both the phases is equal in reflected light (after 1 min rest), the titration is complete.

3.2.2.3 Adsorption experiments

In the adsorption study, surfactant solution was prepared by diluting the concentrated stock solution. Amount of adsorbent and the volume of solution were kept constant for each set of experiments. For each set of experiments, 0.580 g of filter paper was used

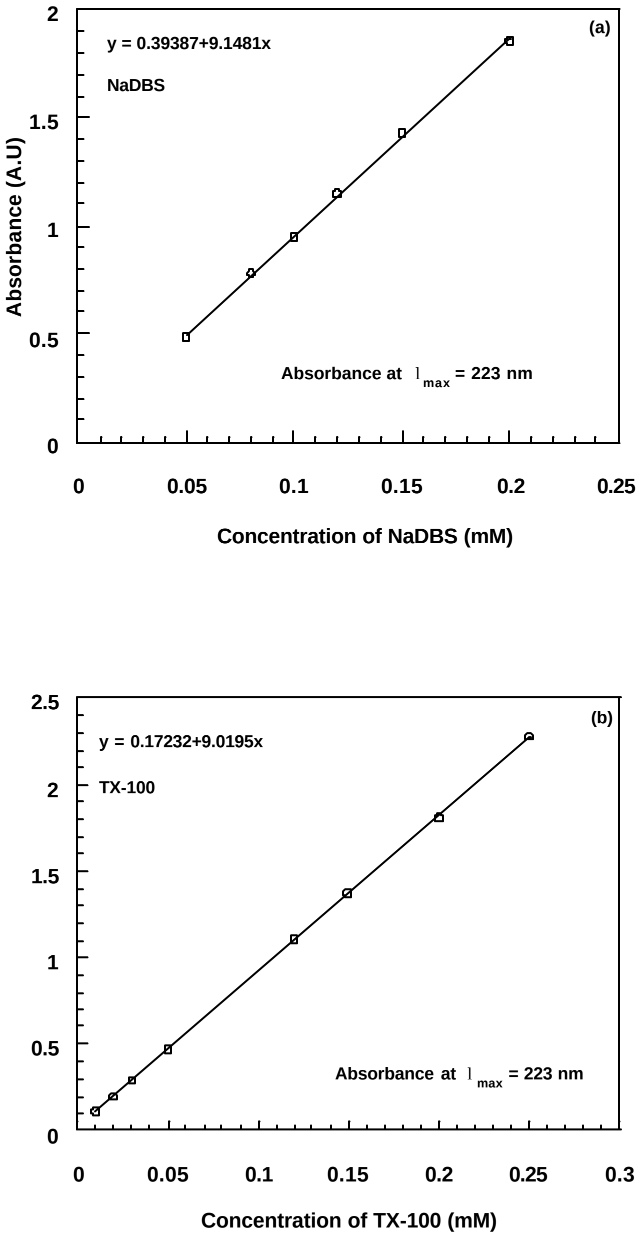


Figure-3.1: (a) Calibration plot (absorbance vs. concentration) of NaDBS. (b) Calibration plot (absorbance vs. concentration) of TX-100.

after cutting into small pieces of size 5-10 mm. 10 ml surfactant solution was used for each set of experiments. The system was stirred slowly at regular intervals. All the experiments were done at the room temperature (25^{o}C). Amount of surfactant adsorbed was calculated according to,

$$X_S = \frac{(C_{b0} - C_t)M.V}{1000.m} \tag{3.1}$$

where X_S is the solid phase concentrations of surfactant (amount adsorbed) in g/g, C_t and C_{b0} are the concentration of surfactant in moles/liter at time t and initially respectively. M is the molecular weight of surfactant, V is the volume of solution used, and m is the mass of filter paper used. Solution was taken out for UV absorbance by using a micropipette and the solution was pored back after analysis for TX-100 and NaDBS. Separate batch was used for analysis of CTAB at different time intervals.

3.3 Results and Discussion

3.3.1 Experimental studies of adsorption kinetics

3.3.1.1 Effect of external mass transfer on kinetics of NaDBS

Figure-3.2 presents the effect of bulk (external) mass transfer on the kinetics of NaDBS adsorption on filter paper surface. The figure presents the comparison between two conditions, one is without stirring and another is with stirring. The main objective of this experiment is to determine whether mass transfer is the controlling step in kinetics of adsorption. The adsorption can be described as a two-step process, where the first step is diffusion from the bulk to solution to a sub-surface (mass transfer) and the second step is the transport from sub-surface to the surface and the concomitant adsorption. From Figure-3.2 it is clear that initially there is a very week effect of stirring (mass transfer), in presence of stirring the rate of adsorption is slightly faster but the effect is not very significant. Also it is found that the extent of adsorption at equilibrium is not dependent on the stirring. All the experiments were carried out under identical stirring conditions.

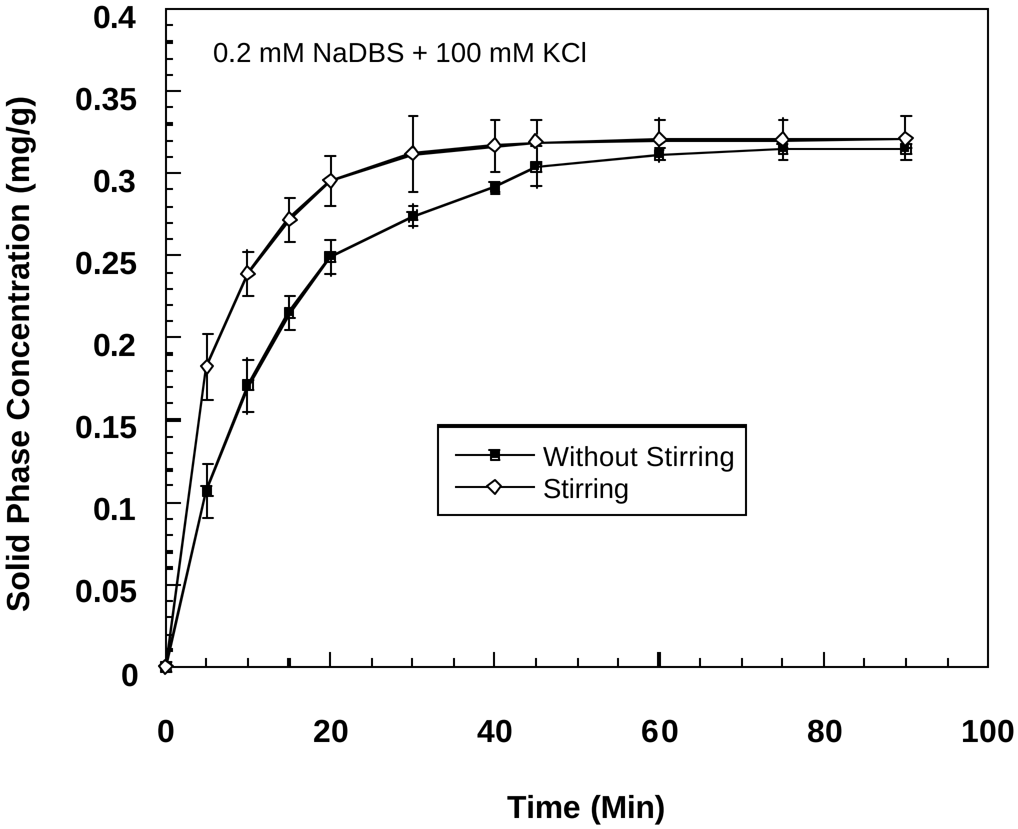


Figure-3.2: The effect of stirring on adsorption kinetics of NaDBS. 100 mM KCl was used as background electrolyte.

The difference is the kinetics of adsorption can therefore be attributed to the surface during adsorption.

3.3.1.2 Adsorption kinetics of NaDBS, TX-100 and CTAB

Adsorption kinetics of three different surfactants NaDBS, TX-100 and CTAB was studied on the cellulose-water interface. Figures-3.3, 3.4 and 3.5 graphically present the kinetics of adsorption of NaDBS, TX-100 and CTAB respectively at three different initial concentrations. Following observations can be noted from these figures. The nature of the plots is similar, that is, having a somewhat non-linear increase in the amount of adsorption followed by a clear leveling off to indicate equilibrium. The amount of adsorption increases with increase in the concentration. Both these trends are expected. Comparing adsorption kinetics between the surfactants, it is noted that the rate of adsorption increase in the following order NaDBS ≈ TX-100 < CTAB. The average rate of adsorption of NaDBS, TX-100 and CTAB are determined from the slope at $t_{1/2}$ (half equilibrium time) of the adsorption curve. A qualitative explanation to the above observations is offered. The cellulosic material such as filter paper is negatively charged (zeta potential ~ -28 mV) in the neutral aqueous medium (Schott, 1972). It is further assumed there are two types of sites present in the cellulose surface, hydrophilic and hydrophobic sites, and the hydrophilic sites are negatively charged. CTAB being a cationic surfactant adsorbs rapidly onto the negatively charged sites. Anionic surfactants and nonionic surfactants are adsorbed on the hydrophobic sites. Anionic surfactants in presence of salt and cationic surfactant are adsorbed on the hydrophilic sites as well as on the hydrophobic sites. It has been discussed in detail in the chapter-4.

3.3.1.3 Adsorption kinetics of NaDBS in presence of salt

Figure-3.6 shows the adsorption kinetics of NaDBS at four different KCl concentrations. It has been observed from the figure that, there are enhancements in both the rate of adsorption as well as in the equilibrium extent of adsorption at all four KCl

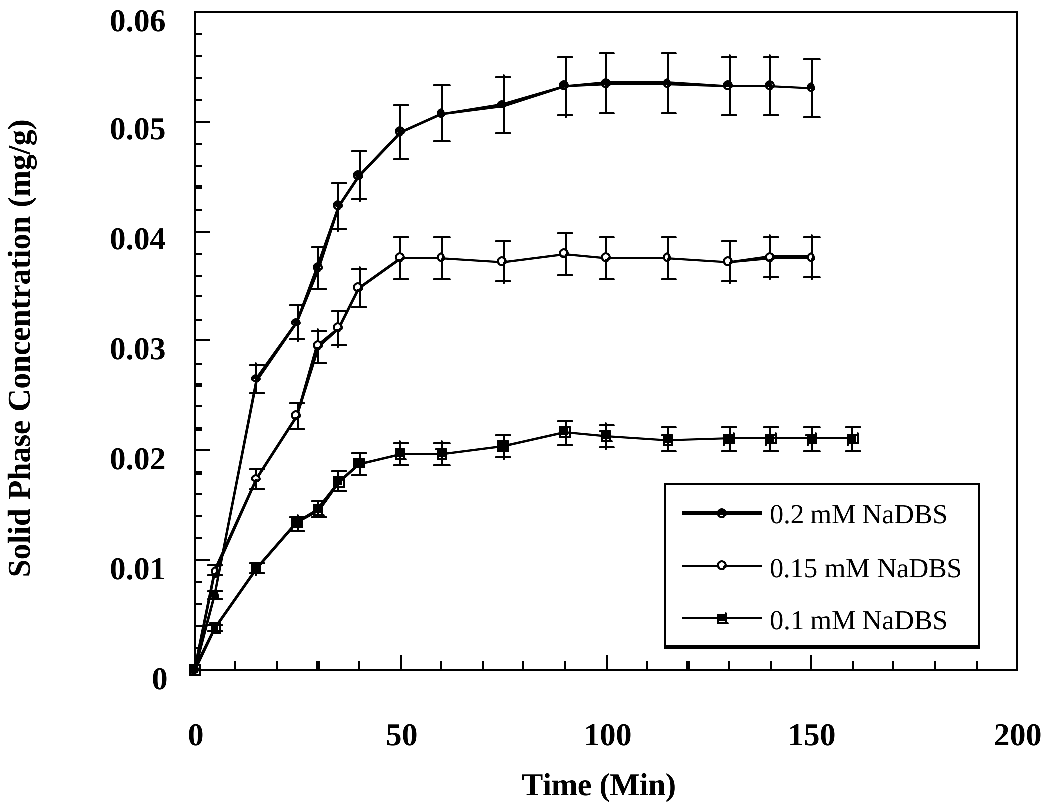


Figure-3.3: Adsorption kinetics of NaDBS.

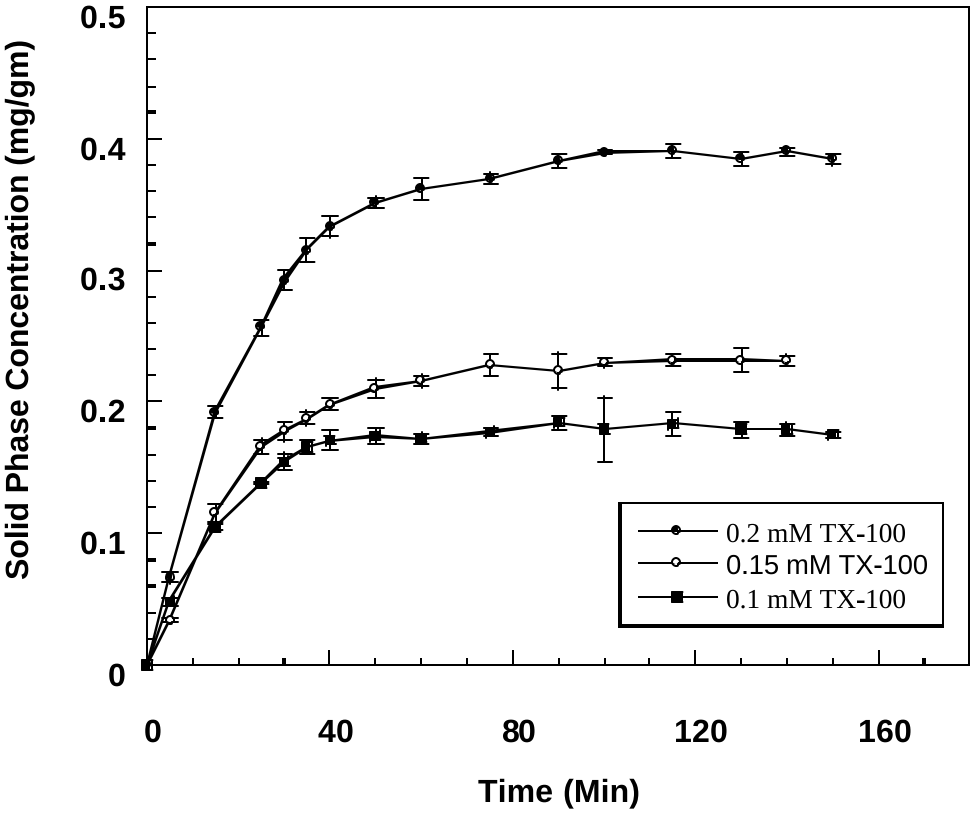


Figure-3.4: Adsorption kinetics of TX-100.

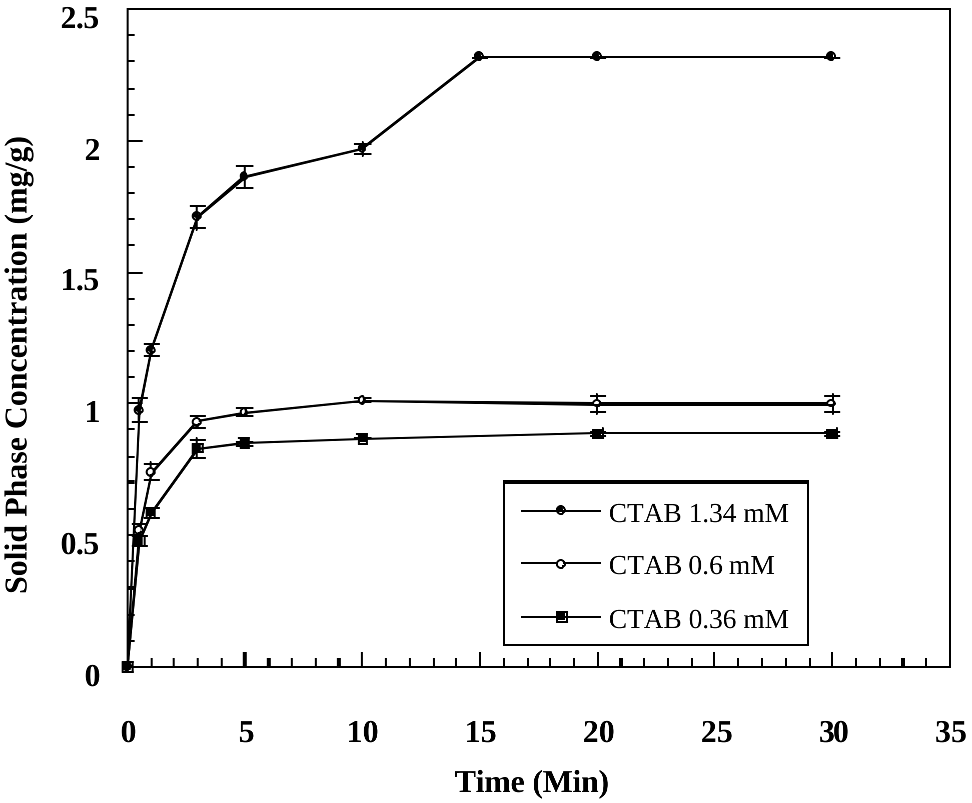


Figure3.5: Adsorption kinetics of CTAB.

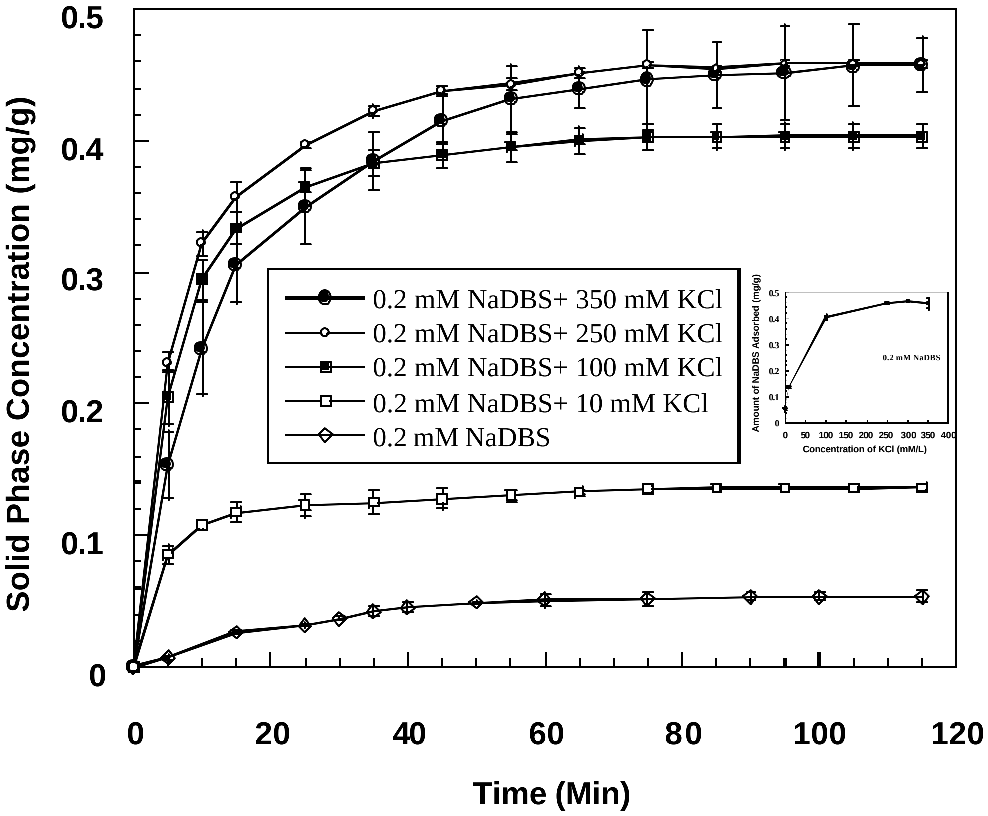


Figure-3.6: Adsorption kinetics of NaDBS at different KCl concentration.

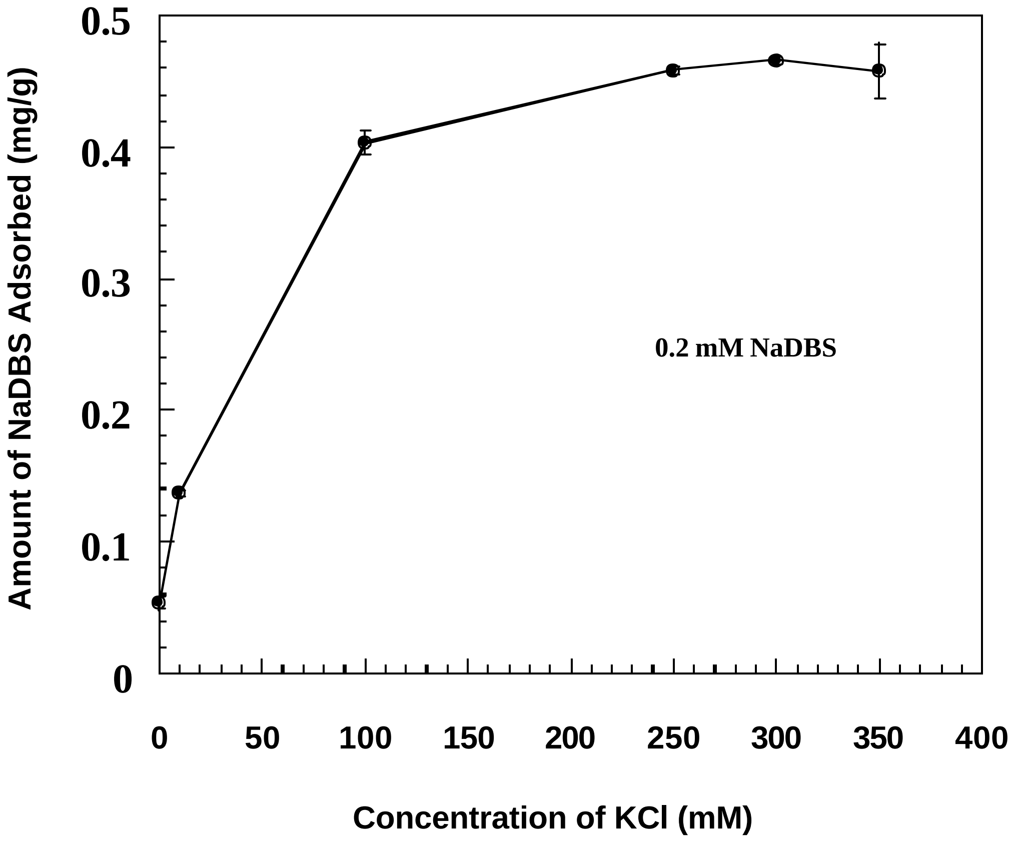


Figure-3.7: Amount of NaDBS adsorbed at different KCl concentration from 0.2 mM NaDBS solution.

concentrations shown. Comparing the plots, it is observed that the adsorption kinetics is significantly enhanced both for the concentration of 10 mM and 100 mM KCl while for higher concentrations of 250 and 350 mM, there is no further enhancement as compared to that for 100 mM KCl solution. Figure-3.7 shows the amount of NaDBS adsorbed at different KCl concentration from 0.2 mM NaDBS solution. The figure shows that the extent of adsorption enhancements varies with the electrolyte concentration and enhancement is higher at low concentration of KCl but levels off at high KCl concentration. With increasing concentration of KCl, CMC of NaDBS changes, which in turn changes the rate and equilibrium extent of adsorption. Table-3.1 shows different CMC values of NaDBS in presence of salts.

To study the effect of valency of counter ion (cation for negatively charged cellulosic surface), measurements have been conducted using $CaCl_2$ solution. The results are presented in Figure-3.8. It is observed from this figure that there is significant enhancement with an increase in concentration of $CaCl_2$, but this occurs at lower concentrations. This observation is consistent with classical theories such as DLVO and *Schulze-Hardy* rule, which state that higher valent counter ions are more effective in shielding the charge on the surface. The results presented in Figures-3.6 and 3.8 strongly indicate that the electric double layer of charged cellulosic surface has significant effect on the adsorption. The rate as well as the extent of adsorption is higher for high electrolyte concentration and for higher valency of counter ions.

Figure-3.9 shows the effect of co-ions on the adsorption at two different concentrations. The figure depicts that there is no difference in effects of co-ion Cl^- with those of SO_4^{2-}. Such observations further support the importance of electric double layer effects in adsorption on negatively charged cellulosic surface.

3.3.1.4 Adsorption kinetics of NaDBS in presence of mixed salt

Figures-3.10 (a) and (b) show the adsorption kinetics in presence of mixture of KCl and $CaCl_2$. Mixing was done at two different $CaCl_2$ and KCl concentrations. Figure-3.10 (a) presents the adsorption plots at 0.1 mM $CaCl_2$ while Figure-3.10 (b) presents the plots at 0.5 mM $CaCl_2$. It is observed from Figure-3.10 (a), that addition of 0.1 mM $CaCl_2$ to 10

Table-3.1: CMC values of surfactants under different concentrations.

Surfactant	**Salt**	**Salt Conc. (mM)**	**CMC (mM)**
NaDBS	-	-	1.2
NaDBS	KCl	10	0.8
NaDBS	KCl	20	0.4
NaDBS	KCl	100	0.15
NaDBS	KCl	250	0.1
NaDBS	Na_2CO_3	10	0.8
NaDBS	$CaCl_2$	0.1	0.8
NaDBS	$CaCl_2$	0.5	0.3
NaDBS	KCl + $CaCl_2$	10 + 0.5	0.3
NaDBS	KCl + $CaCl_2$	100 + 0.5	0.15
TX-100	-	-	0.25
SDS	-	-	8
SDS+TX100 (80:20)	-	-	0.6
SDS+TX100 (70:30)	-	-	0.4
SDS+TX100 (80:20)	KCl	100	0.4
SDS+TX100 (70:30)	KCl	100	0.3

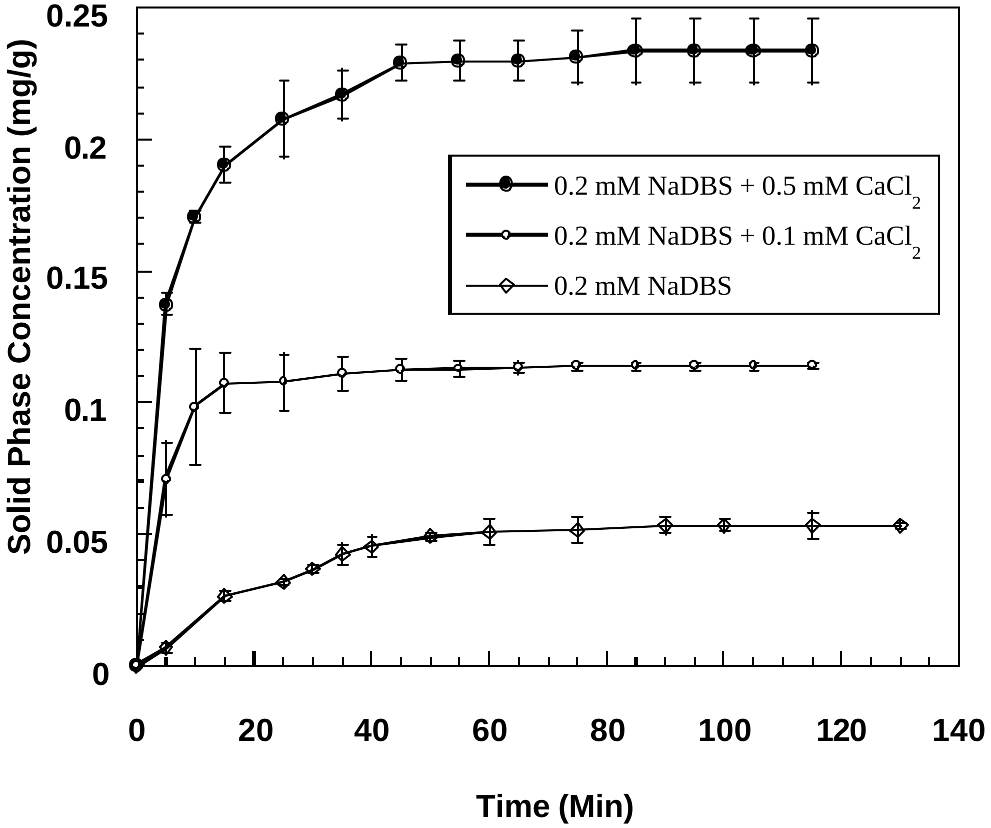


Figure-3.8: Adsorption kinetics of NaDBS at different $CaCl_2$ concentration.

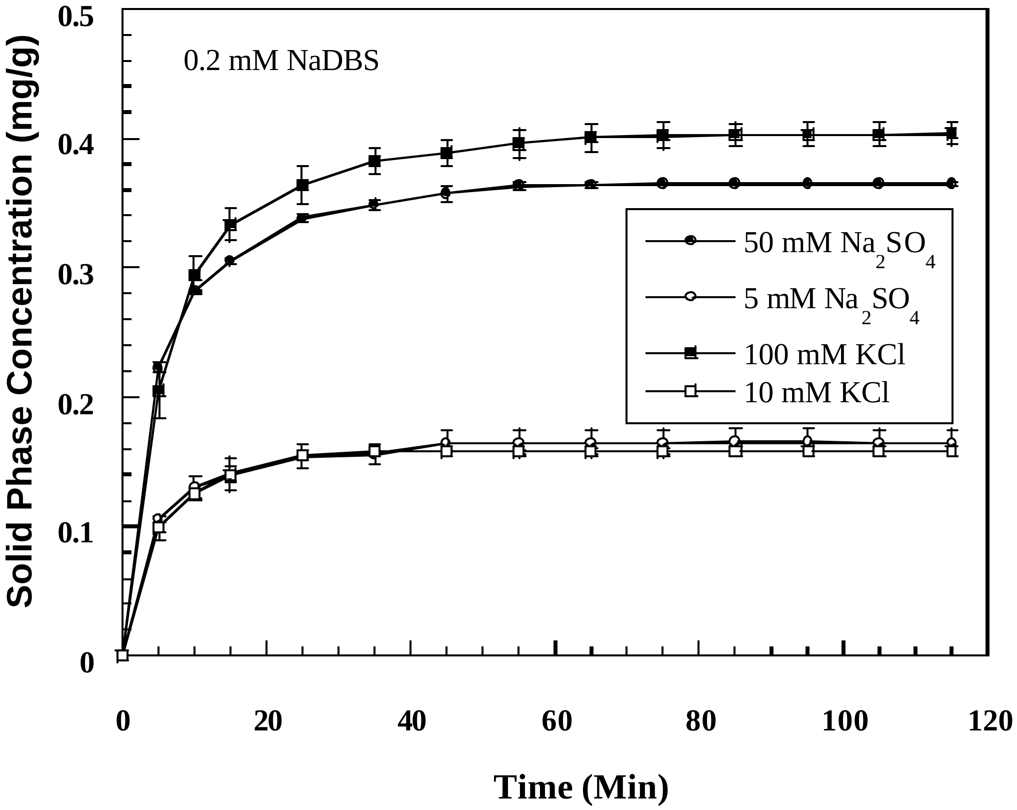


Figure-3.9: Comparison of adsorption kinetics NaDBS in presence of Na_2SO_4 and KCl.

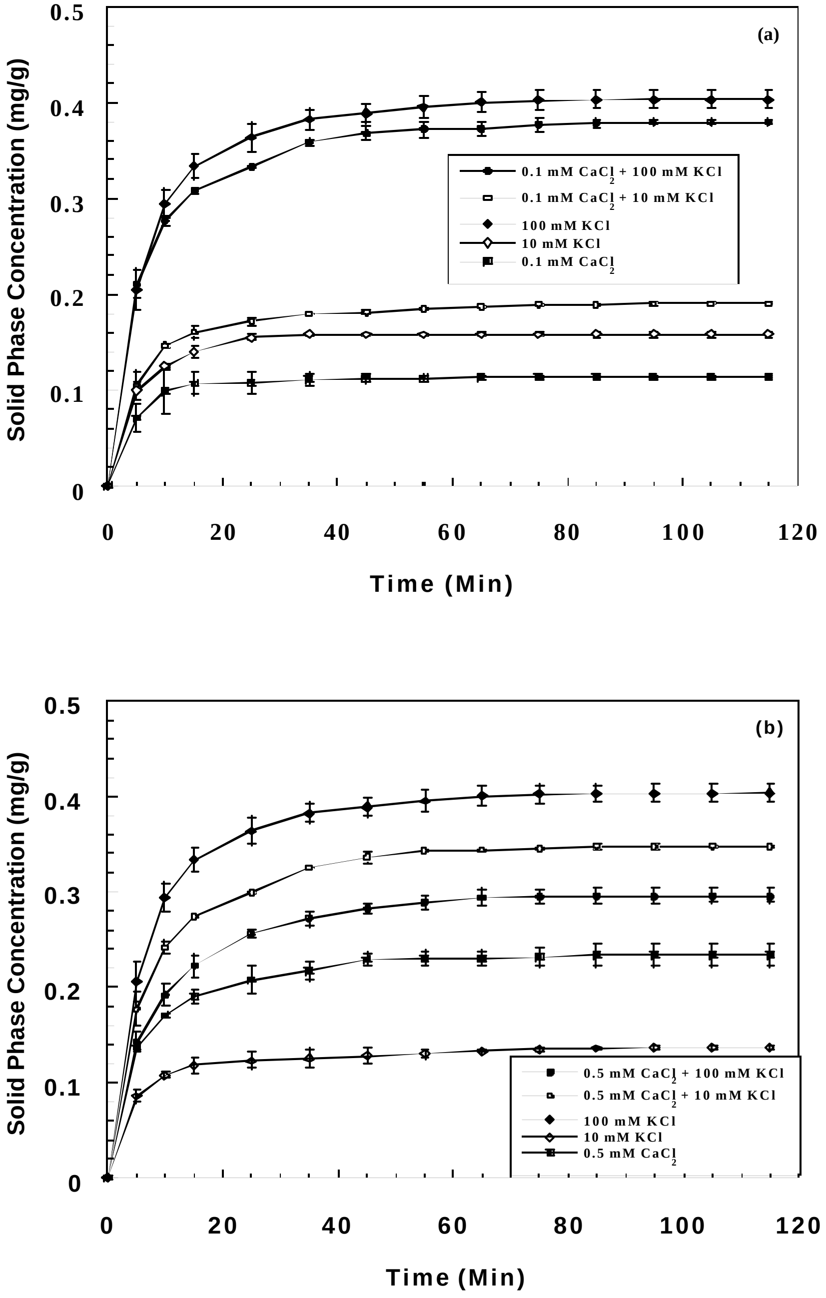


Figure-3.10: Adsorption kinetics of NaDBS in presence of mixture of KCl and $CaCl_2$.

mM of KCl solution enhances the rate and equilibrium extent of adsorption, though there is no significant difference in adsorption due to the difference in KCl concentration (100 mM). Figure-3.10 (b) shows an interesting result. It is observed from this figure that the extent of adsorption actually slightly decreases for (100 mM KCl + 0.5 mM $CaCl_2$) mixture. Similar result was found in a mixture of 250 mM KCl + 0.5 mM $CaCl_2$ but the difference is less than that of 100 mM KCl + 0.5 mM $CaCl_2$. For the mixture of 250 mM KCl + 0.1 mM $CaCl_2$, enhancement is same as for 250 mM KCl. This may be due to the change in the properties of surfactant at high salt concentration. It is known that at high salt concentration, the hydrophilicity of the surfactant head group decreases (Ruckenstein and Beunen, 1984) which may give rise to decrease in adsorption.

The 'charged phase model' of ionic surfactant in presence of electrolyte is used to explain the bulk properties of surfactant solution (Hall, 1981). From the similar approach, 'ion association constant' for micelle and the adsorbed layer is important for the adsorption of surfactant at an interface. The association constant for surface is close to unity, there is some un-neutralized charge based on the measurement of negative surface excess of chloride ions in presence of anionic surfactant (Tajima, 1971). At very high concentration of KCl the shape of surfactant micelle will be more towards in the sequence sphere → rod → disc i.e. to decrease the average curvature (Aveyard et al., 1985). Electrostatic repulsive force is higher between the ions on a planer surface compared to that between the ions in a spherical micelle. The difference in association constants between surface and micelle, for the reason stated above, will decrease or even tend to zero, then the effect of electrolyte concentration will be nominal. The association constant for nonionic micelles and surface layers can be approximated to zero and hence it is, again, not surprising that there is nominal effect of electrolyte on ionic surfactant adsorption.

3.3.1.5 Effect of adsorbent concentration

Figure-3.11 (a) shows the effect of adsorbent concentration on the kinetics of NaDBS with three different adsorbent concentrations, 30 g/l, 60 g/l and 80 g/l. The following observations are observed from the figure. First, there is no change in kinetics initially

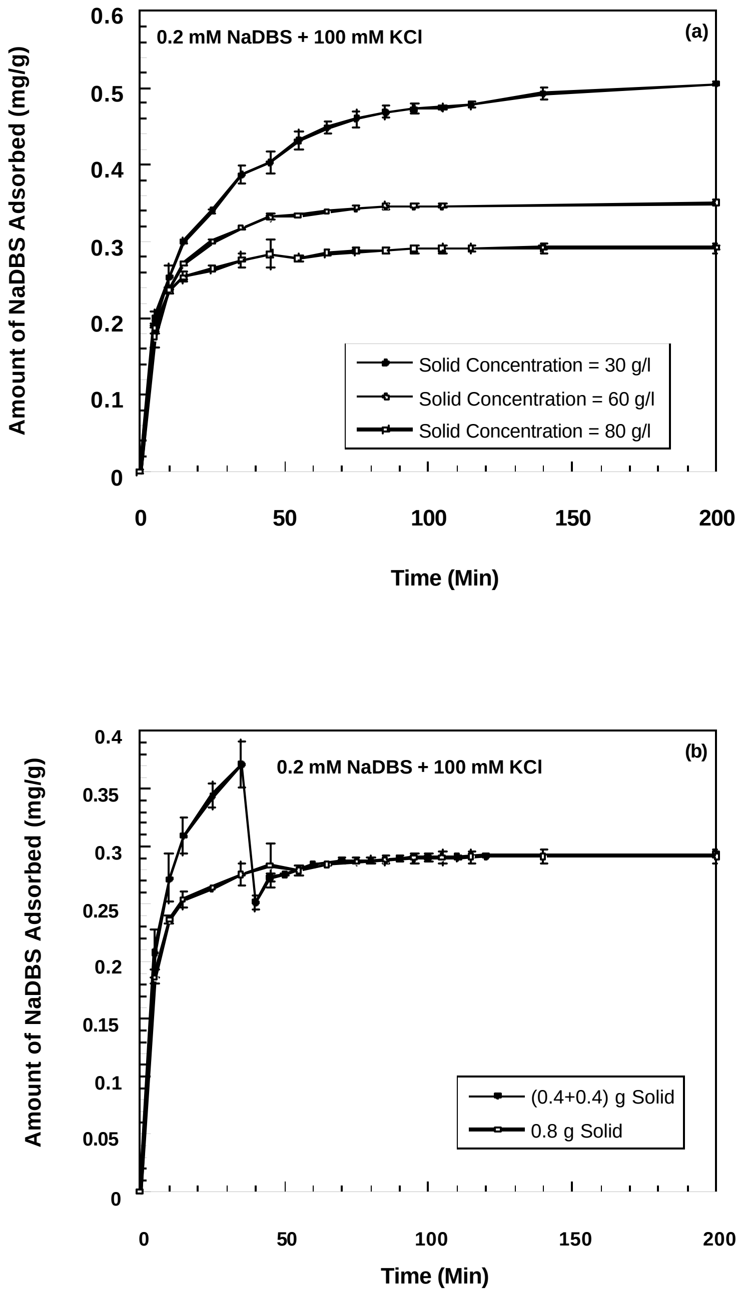


Figure-3.11: (a) Effect of adsorbent concentration on the kinetics of NaDBS. (b) Effect of stepwise addition of adsorbent on the kinetics of NaDBS. 100 mM KCl was used as background electrolyte.

with changing the concentration of adsorbent concentration. Second, with increasing adsorbent concentration equilibrium amount adsorbed decreases and the time of equilibrium also decreases. Figure-3.11 (b) shows the effect of addition of adsorbent on the kinetics. In Figire-3.11 (b), 80 g/l adsorbent was added in one case and in another case 40 g/l adsorbent was added initially and then another 40 g/l of adsorbent was added to the same system after the equilibrium is reached. From the figure it is clear that in both the cases final equilibrium amount adsorbed is the same. Therefore, as expected the amount adsorbed in a particular solid-liquid ratio does not depend on path, like stepwise addition of adsorbent, but depends on the total amount of adsorbent present in the system.

3.3.2 Modeling studies

3.3.2.1 Adsorption kinetics model

A simple two-site model is proposed to describe adsorption of surfactant on a cellulosic surface. One can write equations for system containing V m^3 of solution of surfactant at a concentration of C_{b0} and m kg of fresh filter paper pieces added to it. Assuming the cellulose surface containing two sites,

$$X_S = X_{Sh} + X_{Se} \tag{3.2}$$

$$X_{Sm} = X_{Smh} + X_{Sme} \tag{3.3}$$

X_S is the total concentration of surfactant on the cellulose surface at time t in kg/kg. X_{Sh} and X_{Se} are the concentrations of surfactant on the hydrophobic and hydrophilic site respectively at time t. X_{Sm} is the maximum amount of total surfactant adsorbed on cellulose surface and X_{Sme} and X_{Smh} are that of hydrophilic and hydrophobic sites.

Now considering the mole balance of surfactant at any time “t”

$$V.C_{b0} = V.C_b + \frac{m(X_{Sh} + X_{Se})}{M} \tag{3.4}$$

solving for C_b, obtain

$$C_b = C_{b0} - \frac{m(X_{Sh} + X_{Se})}{V.M} \tag{3.5}$$

C_{b0}, C_b are the concentrations of surfactant in solution at time t = 0 and t = t, respectively in k mole.m^{-3} and M is the molecular weight of surfactant.

The over all rate of adsorption can be expressed as

$$\frac{dX_S}{dt}=\frac{d\left(X_{Sh}+X_{Se}\right)}{dt}=\frac{dX_{Sh}}{dt}+\frac{dX_{Se}}{dt} \qquad (3.6)$$

The rate of adsorption can be expressed for both hydrophilic and hydrophobic sites using Langmuir equation.

$$\frac{dX_{Sh}}{dt}=k_{ah}(X_{Smh}-X_{Sh})C_b-k_{dh}X_{Sh} \qquad (3.7)$$

$$\frac{dX_{Se}}{dt}=k_{ae}(X_{Sme}-X_{Se})C_b-k_{de}X_{Se} \qquad (3.8)$$

subscripts h and e are used for hydrophobic and hydrophilic sites respectively, k_a and k_d adsorption and desorption rate constants respectively.

Substituting the value of C_b from equation 3.5 in equations 3.7 and 3.8, obtain,

$$\frac{dX_{Sh}}{dt}=k_{ah}X_{Smh}C_{b0}+\frac{k_{ah}.m}{V.M}X_{Sh}^2-\left(\frac{k_{ah}.X_{Smh}.m}{V.M}+k_{ah}C_{b0}+k_{dh}\right)X_{Sh}-\frac{k_{ah}.X_{Smh}.m}{V.M}X_{Se}$$
$$+\frac{k_{ah}.m}{V.M}X_{Sh}X_{Se} \qquad (3.9)$$

$$\frac{dX_{Se}}{dt}=k_{ae}X_{Sme}C_{b0}+\frac{k_{ae}.m}{V.M}X_{Se}^2-\left(\frac{k_{ae}.X_{Sme}.m}{V.M}+k_{ae}C_{b0}+k_{de}\right)X_{Se}-\frac{k_{ae}.X_{Sme}.m}{V.M}X_{Sh}$$
$$+\frac{k_{ae}.m}{V.M}X_{Se}X_{Sh} \qquad (3.10)$$

The equations 3.9 and 3.10 are first order non-linear differential equation and difficult to solve analytically. A numerical method (Euler's method) was used to solve the simultaneous differential equations, to obtain X_S as a function of time.

3.3.2.2 Comparison of measurements with the predictions of the model

Figures-3.12 – 3.14 show the comparison between model and experimental data of adsorption kinetics of NaDBS, TX-100 and CTAB respectively. The values for rate constants were obtained by fitting the experimental data. Although there are four rate constants in the model for each case some of the parameters value are assume to be zero, such as for the case of NaDBS with out salt we assume k_{ae} and k_{de} are zero as the adsorption occurs mainly at hydrophobic sites. In this case k_{ah} and k_{dh} are used as the fitting parameters. In further, NaDBS adsorption in presence of salt, we used same values

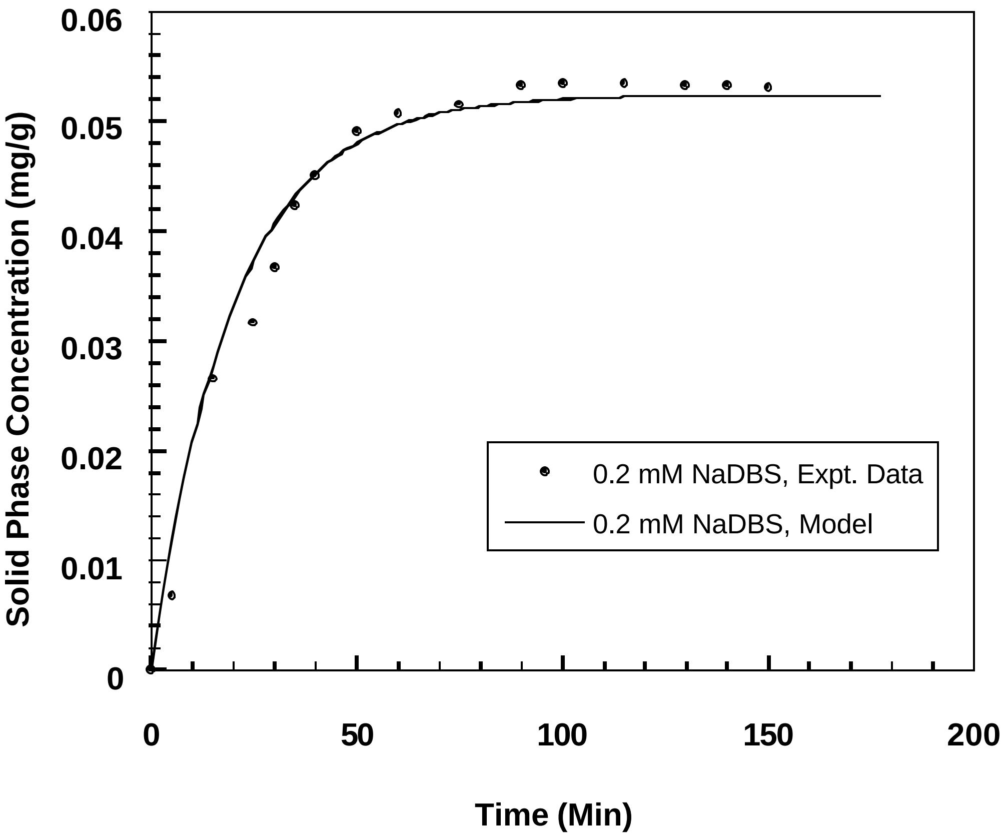


Figure-3.12: Fitting of the experimental data of adsorption kinetics of NaDBS with model.

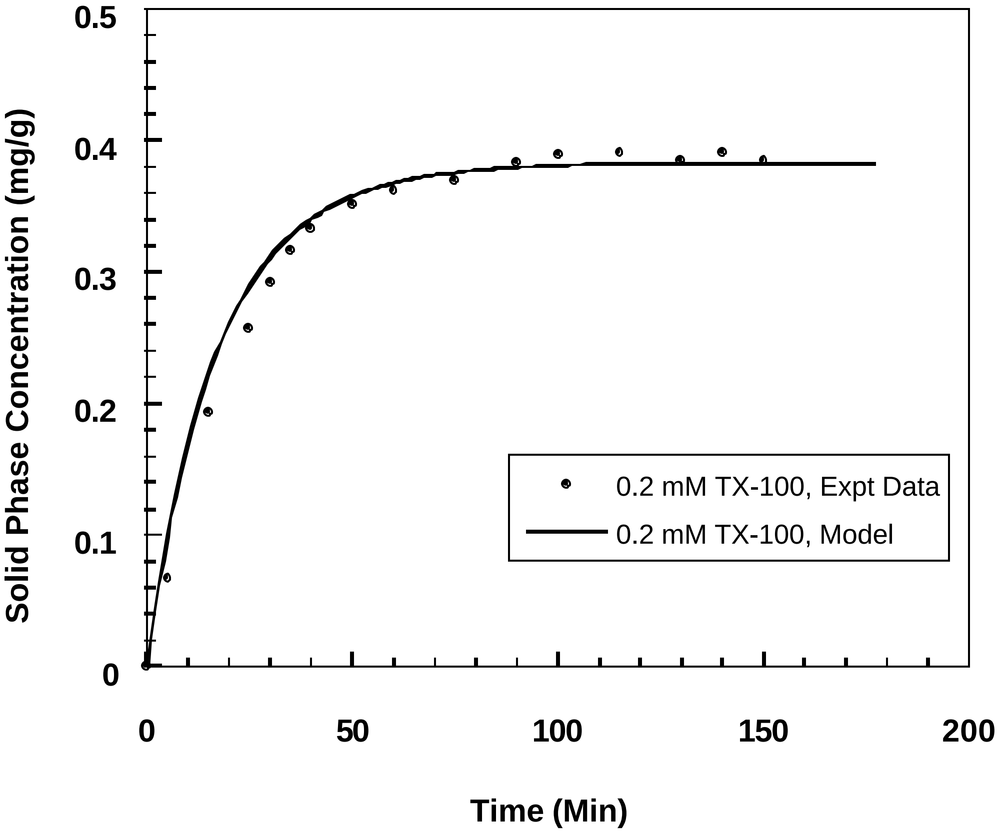


Figure-3.13: Fitting of the experimental data of adsorption kinetics of TX-100 with model.

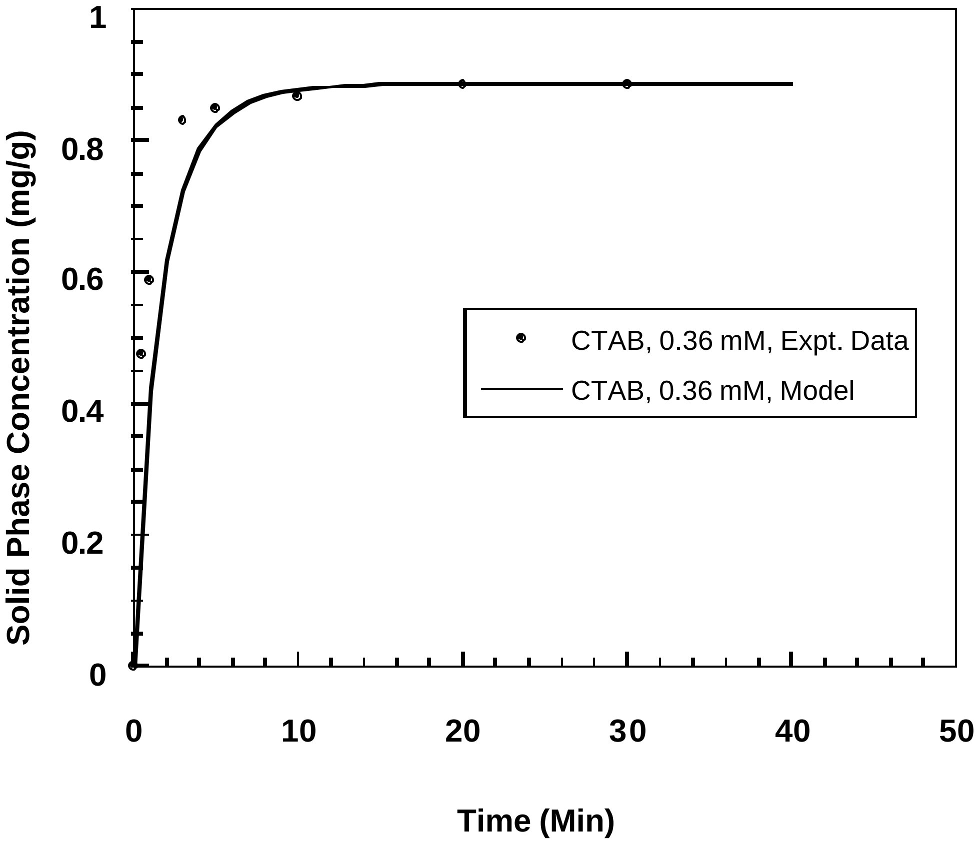


Figure-3.14: Fitting of the experimental data of adsorption kinetics of CTAB with model.

Table-3.2: Different model parameters obtained from the fitting of the experimental data with the theory.

Surfactant	Conc. of salt (mM)	k_{ah}(m^3.k mol^{-1} min^{-1}$\times10^3$)	k_{dh}(min^{-1})	k_{ae}(m^3.k mole^{-1} min^{-1}$\times10^3$)	k_{de}(min^{-1})
NaDBS(0.2mM)	0	300	0.002		
TX-100 (0.2mM)	0	300	0.001		
CTAB (0.36mM)	0			2000	0
NaDBS(0.2mM) + KCl	10	300	0.002	800	0
	100	300	0.002	850	0
	250	300	0.002	750	0
	300	300	0.002	450	0
	350	300	0.002	400	0
NaDBS(0.2mM) + $CaCl_2$	0.1	300	0.002	900	0
	0.5	300	0.002	1150	0
NaDBS (0.2mM) + Pre-adsorbed CTAB (0.02mM)	0	400	0.001		

of k_{ah} and k_{dh} as obtained earlier then k_{ae} used as the fitting parameter assuming in presence salt k_{de} is negligible. Similarly we have fitted the other surfactant data to obtain the different parameter. Sum of the standard deviation of experimental and theoretical plots were kept minimum for fitting. Different rate constants obtained from the fitting are presented in Table-3.2. For the adsorption of NaDBS and TX-100 in the absence of salt, it is considered that the adsorption occurs only at the hydrophobic sites. Adsorption rate constants of NaDBS and TX-100 are found to be same where as desorption rate constant is slightly different. In case of adsorption of CTAB, it is assumed that CTAB adsorbs onto negatively charged sites (hydrophilic) and desorption can be neglected due to strong electrical attraction between the site and adsorbed CTAB molecules. Rate constant for the adsorption of CTAB is found to be higher than NaDBS or TX-100, which is expected due to favorable electrical effects.

Figure-3.15 shows the fitting of adsorption kinetics of NaDBS on filter paper, which is pre-adsorbed with CTAB. In this experiment, CTAB was pre-adsorbed to modify the filter paper surface. The surface is expected to become more hydrophobic with higher extent of adsorption. First, the filter paper was pre-adsorbed with 0.02 mM CTAB solution, and then it was rinsed with distilled water, dried and was used to study kinetics of NaDBS. As the surface becomes more hydrophobic, rate constant of adsorption on the hydrophobic site increases compared to that on the pure filter paper surface.

Figure-3.16 shows the fitting of kinetics of NaDBS in presence of KCl. It is assumed that desorption rate constant is negligible on the hydrophilic site in presence of salt. For the fitting of NaDBS in presence of salt, two sites were used and the rate constant for hydrophobic sites was used as determined previously for NaDBS in absence of salt. The rate constant for adsorption on the hydrophilic site for 10 mM KCl is 800×10^{3} m^{3}.k $mole^{-1}$ min^{-1}, with increasing KCl concentration to 100 mM there is an enhancement in k_{ae}. This result is consistant with the DLVO theory and can be explained in terms of energy barrier of total interaction energy between the surface and surfactant molecules in presence of salt. The rate of adsorption depends on the height of the energy barrier in total interaction energy vs. distance curve. In the absence of salt, the energy barrier is high. With increasing salt concentration, the energy barrier decreases and

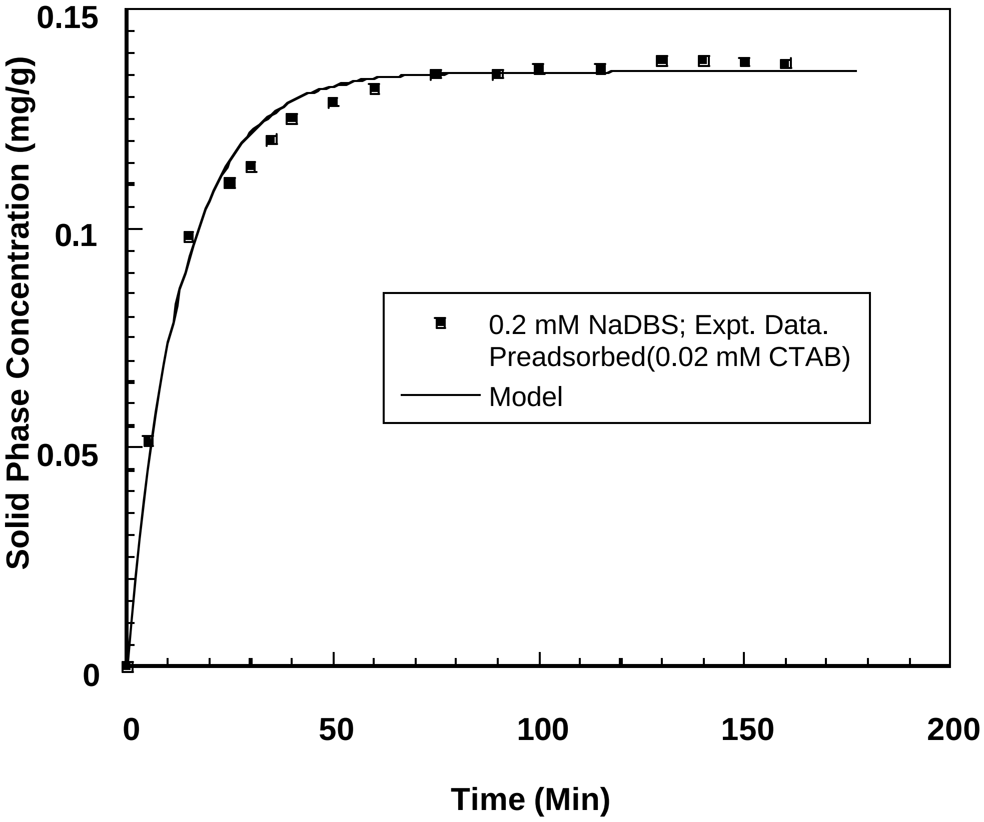


Figure-3.15: Fitting of the experimental data of adsorption kinetics of NaDBS on pre-adsorbed CTAB filter paper with model.

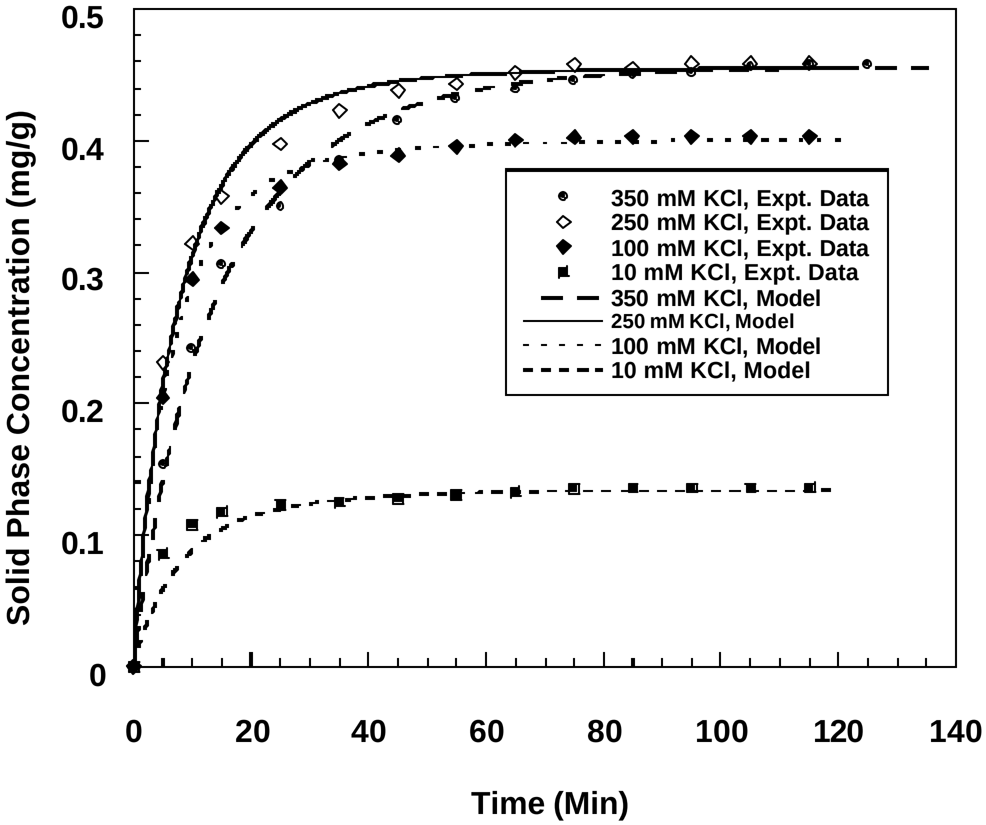


Figure-3.16: Fitting of the experimental data of adsorption kinetics of NaDBS in presence of KCl with model.

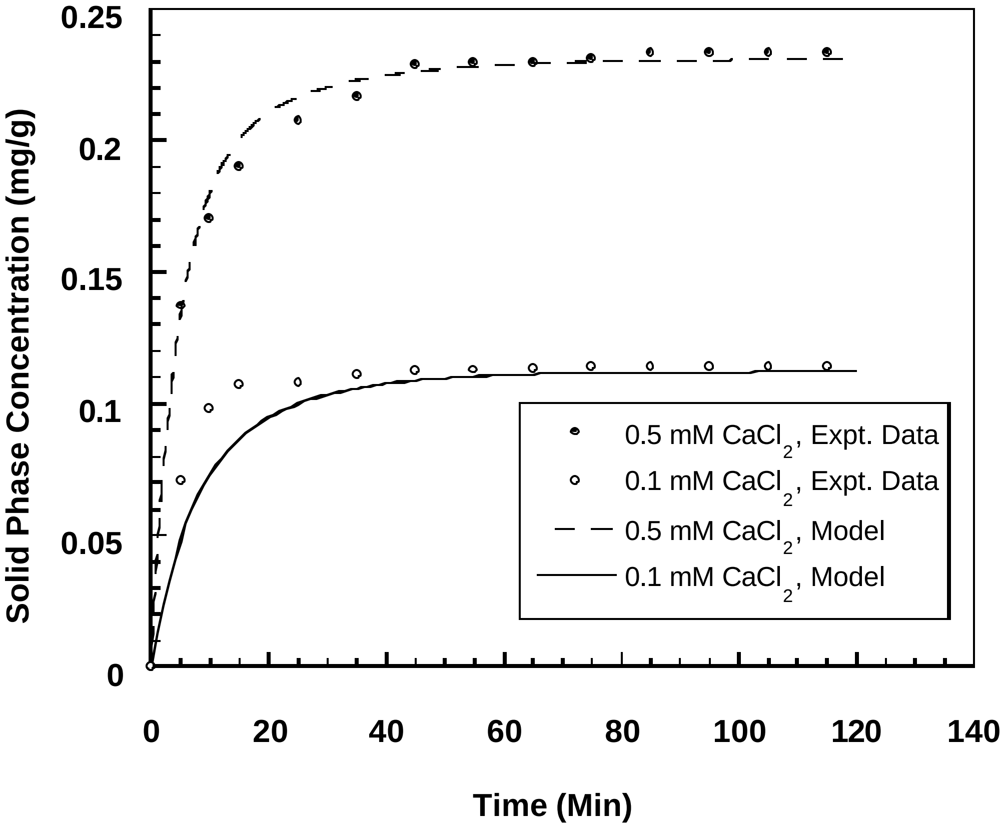


Figure-3.17: Fitting of the experimental data of adsorption kinetics of NaDBS in presence of $CaCl_2$ with model.

becomes almost zero at 100 mM KCl (Ruckenstein and Prieve, 1976). Interestingly, at very high concentration, 250 mM and 350 mM of KCl, rate constants in the hydrophilic site decrease, as hypothesized earlier. Another reason may be at 250 mM and 350 mM KCl concentration surfactant is above the CMC (CMC values are given in the Table-3.1), so the monomer concentration of surfactant decreases at that concentration, as a result rate of adsorption decreases. Similar observations are found in presence of $CaCl_2$ also. The fitting with experimental data in case of $CaCl_2$ is shown in Figure-3.17.

The rate constants obtained in this work are compared with those reported in the literature. Studies reporting the values for adsorption and desorption rate constant are very few in literature. The values are dependent on the nature of surfactants and adsorbent. Studies on the adsorption of TX-100 and $C_{14}E_6$ on two hydrophobic surfaces, carbon black (Gracía et al., 2000) and silica (Tiberg, 1996) respectively report the values of adsorption equilibrium constant. For the carbon black, k_a/k_d is $\approx 20 \times 10^3$ m^3 /k mole and for silica, it is 2.9×10^6 m^3/k mole. The value for the adsorption equilibrium constant for TX-100 on the filter paper is 3×10^8 m^3/k mole in this study, which is higher than the reported values.

3.4 Conclusions

1. Adsorption kinetics of NaDBS, TX-100, and CTAB, on cellulose water interface show CTAB is adsorb rapidly and to a higher extent than NaDBS and TX-100, with NaDBS showing the least adsorption. Adsorption of CTAB is rapid due to adsorption of cationic surfactant onto a negatively charged cellulose surface. It is also assumed that cellulose surface contains two types of sites, negatively charged hydrophilic sites and neutral hydrophobic sites. Cationic surfactants are preferably adsorbed on the hydrophilic site, anionic, and nonionic and surfactants adsorb on the hydrophobic site. Whereas anionic surfactants in presence of salt adsorb on both the sites.
2. Adding electrolytes such as KCl and $CaCl_2$, however, can enhance the extent of adsorption of NaDBS. At a particular concentration of surfactant with increasing concentration of electrolyte, the extent of adsorption is enhanced, ultimately it

levels off with further increasing electrolyte concentration. The valency of co-ion does not have any effect on adsorption of NaDBS on cellulose-water interface.

3. At low concentration of KCl, addition of $CaCl_2$ enhances the extent of adsorption of NaDBS but at high concentration of KCl addition of $CaCl_2$ decreases the extent of adsorption of NaDBS.
4. The extent of adsorption of NaDBS is enhanced with decreasing value of solid-liquid ratio.
5. A two site kinetic model is developed using Langmuir approach. From the two-site model the rate constant of NaDBS for hydrophilic and hydrophobic sites on cellulose-water interface can be determined in presence of electrolyte.

Chapter-4

Adsorption from Solutions Containing one Surfactant in Presence of Electrolyte at the Cellulose-Water Interface

4.1. Introduction

Studies of adsorption of surfactants at the solid/liquid interfaces find practical applications in many areas, such as, detergency, flotation of ore, oil recovery, and dispersions such as paints and pigments. In particular, adsorption is an important step for removal of particulates and oily soils in detergency. This chapter is focused on the adsorption isotherm of surfactants on the cellulosic surface. In chapter-3 kinetic aspects of different surfactants on the cellulose-water interface under different conditions are presented.

In general, the adsorption of surfactants on solid-liquid interface can be subdivided into four regions (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and

Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Chander et al., 1983). In region I adsorption obeys Henry's law, that is, adsorption increases linearly with concentration. Region II shows a sudden increase in adsorption, while region III shows a slower rate of increase in adsorption than region II. Region IV is the plateau region above the CMC (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988). However, depending upon several factors this IV region may show a maximum (Fava and Eyring, 1956; Meader and Fries, 1952; Pagac et al., 1998; Ginn et al., 1961; Biswas and Chattoraj, 1997; Sexsmith and White, 1959a, 1959b; Vold and Sivaramakrishnan, 1958; Furst et al., 1996; Trogus et al., 1978; Arnebrant et al., 1989; Evans, 1958).

Although the mechanism of adsorption in the first three regions is well known but that in region IV is not well understood. Ideally, the adsorption is expected to remain unchanged beyond the CMC since the concentration of monomer does not increase beyond the CMC and the micelles formed do not adsorb on the surface. The observation of a maximum in region IV has drawn attention of some researchers and attempts have been made to explain this occurrence. Presence of trace surface-active impurities in the surfactant sample has been attributed to the occurrence of this maximum. These would be adsorbed below the CMC but would be solubilized in the micelles above the CMC (Pagac et al., 1998; Furst et al., 1996; Trogus et al., 1978). In an another explanation, it is stated that ionic strength of the solution reduces the electrical repulsion between adsorbed ions and the repulsive interaction becomes less than the van der Waals attraction between the paraffin chains, leading to the formation of surface micelles. Desorption of both simple monomer ions and surface micelles occur on collision of micelles in solution with the adsorbing surface and thus decreasing the amount of adsorption on the surface (Vold and Sivaramakrishnan, 1958). The observation of maximum in case of cotton surface has been attributed to the presence of wax, which gets solubilized beyond CMC (Ginn et al., 1961). There seems to be a lack of clear understanding of the adsorption of surfactants on to cellulosic surface beyond the CMC (region IV).

The effect of electrolyte on the adsorption of surfactant onto cellulosic surface has not been studied systematically. It is shown that presence of an electrolyte enhances the adsorption of anionic surfactant onto a gas/liquid (Cross and Jayson, 1994) or solid/liquid (Meader and Fries, 1952; Nevskaia et al., 1998, 1995) interface. In case of a non-ionic surfactant, such as TX-100, the adsorption onto a solid/liquid interface containing OH group (quartz, kaolin, silica) changes in presence of electrolyte, when it occurs by means of hydrogen bonding (Nevskaia et al., 1998, 1995).

The overall objective of this study is to generate information and generic understandings on the adsorption of surfactants onto cellulosic surface under a wide range of conditions such that practical application such as detergency can be enhanced. There are situations where removal of soils is extremely difficult due to strong bonding of soil to the fabric and poor penetration and adsorption of surfactant molecules onto soil-surface interface. To solve such problems of difficult detergency, one requires the knowledge of adsorption of surfactants under variety of conditions. This chapter presents a systematic and comprehensive study of the adsorption of surfactants under a wide range of conditions such as type of surfactant, presence of electrolyte, presence of wetting agents and so on.

4.2. Experimental Section

4.2.1 Materials

Anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) was obtained from Fluka Chemicals. Nonionic surfactant, polyoxyethylene (number of segments 9.5) glycol tert-octylphenyl ether (Triton X-100 or TX-100) was obtained from Sigma Chemicals. NaDBS and TX-100 were used as received, without any further purification. Cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) was obtained from Ranbaxy Fine Chemicals Ltd., India. It was recrystallized twice from an acetone : methanol (3:1) mixture before use (Desai and Dixit, 1996). Calcium chloride di-hydrate and chloroform were received from E. Merk (India) Ltd. Potassium chloride, sodium sulfate, sodium carbonate and methylene blue were received from s. d. fine-chem Ltd, India. Adsorbent used was Whatman-40 ashless filter paper of 9 cm dia from Whatman International Ltd., England. The BET multipoint surface area of this filter paper (N_2 adsorption) was 16.5

m^2/g. Double distilled water of pH 5.6 and conductivity of 1.2 μS (μ Mho) were used for the experiment.

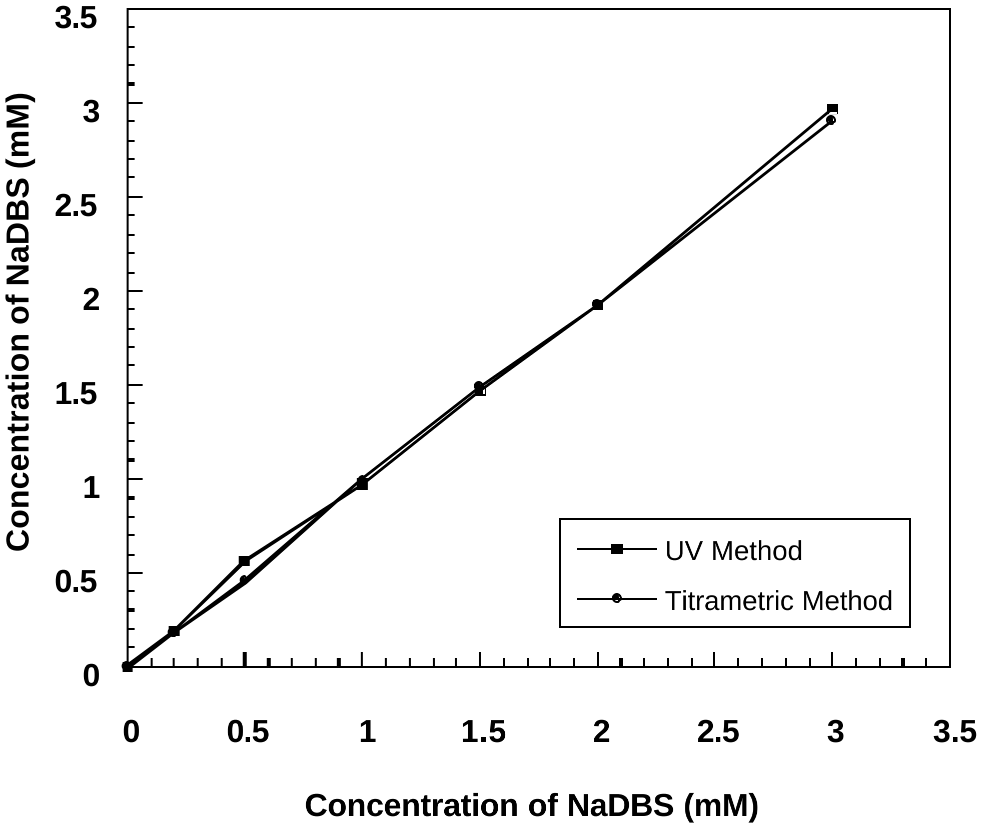
4.2.2 Methods

4.2.2.1 Washing of filter paper

The filter paper was washed thoroughly with double distilled water to remove the dust and soluble ions from the filter paper till the conductivity of the washed water became equal to that of the distilled water. Then it was dried in oven for 1 - 1.5 hours at 50-55°C until the weight of the filter paper became constant.

4.2.2.2 Surfactant analysis

The concentrations of NaDBS and TX-100 were determined by measuring UV absorbance at 223 nm wavelength using UV-Vis spectrophotometer (Shimadzu, UV-160A model). Quartz glass cells (Hellma) of 10 mm path length were used. A calibration plot (absorbance vs. concentration) was obtained by measuring absorbance of known concentration surfactant solution. Concentration of unknown solution was measured using the calibration plots mentioned in Chapter-3. Absorbance of concentrated solutions was measured after diluting the solution. The concentration of NaDBS was measured by two-phase titration technique (Rosen and Goldsmith, 1972; ASTM, 1959) by using methylene blue indicator. In this method, indicator was prepared in a solution of 0.3 g of methylene blue, 12 g of concentrated H_2SO_4, and 50 g of Na_2SO_4 per liter. An aliquot of NaDBS was pipetted in a stopper conical flux, then 10 ml indicator solution and 8 ml chloroform was added to that flux and titrated with the standard CTAB solution. The flux was shaken vigorously after each addition. When color in both the phases is equal in reflected light (after 1 min rest), the titration is complete. Figure-4.1 shows the comparison of concentrations determined by UV and titrametric method. In TX-100 and SDS mixture, TX-100 concentration was measured by UV and SDS was by titrametric



4.1: Comparison of concentration of NaDBS determined by UV and Titrametric method.

method. Concentrations of CTAB and SDS were determined by the titrametric method mentioned in Chapter-3.

The critical micelle concentration (CMC) at room temperature (25°C) was determined from the break in the surface tension vs. concentration plots using a Du-Noüy ring tensiometer (Fisher surface tensiomat, Model 21).

4.2.2.3 *Adsorption experiments*

In the adsorption study, surfactant solution was prepared by diluting the concentrated stock solution. Amount of adsorbent and the volume of solution were kept constant for each set of experiments. For each set of experiments, 0.580 g of filter paper was used after cutting into small pieces of size 5-10 mm. A 10 ml surfactant solution was used for each set of experiments. The system was stirred slowly at regular intervals. Results presented in Chapter-3 show that the time taken for adsorption to reach equilibrium at various conditions is approximately equal to one hour. For the adsorption isotherm, system was kept for 3-4 hours for equilibration. All the experiments were done at the room temperature (25°C). Amount of surfactant adsorbed was calculated according to,

$$X_S = \frac{(C_0 - C_t)M.V}{1000.m} \qquad \text{(4.10}$$

where X_S is the solid phase concentration of surfactant (amount adsorbed) in g/g, C_t and C_{b0} are the concentration of surfactant in moles/liter at time t and initially respectively, M is the molecular weight of surfactant, V is the volume of solution used, and m is the mass of filter paper used.

Absorbance of concentrated solution was measured after proper dilution and waiting for 1 hour. In some cases absorbance method can give rise to errors due to suspended particles. To get an independent check on the concentration of NaDBS, the concentration was also measured by two-phase titration technique. The precipitation phase diagram (clear to turbid boundary) was determined by measuring turbidity of the solution. Acidic and alkaline pH were maintained by adding dilute HCl and Na_2CO_3 respectively. All the experiments were done at the room temperature (25°C).

4.3. Results and Discussion

4.3.1 Measurements of CMC and molecular area calculation at air-water interface

Critical micelle concentration of surfactant was determined by surface tension measurements. The CMC of pure TX-100 and NaDBS are 0.25 mM and 1.2 mM respectively. From the surface tension data of nonionic and anionic surfactants, surface area occupied by a surfactant molecule at the air-water interface (a_{air}) was calculated by using Gibb's surface excess equation (Rosen, 1978),

$$\Gamma = -\frac{1}{2.303RT}\frac{d\gamma}{d(\log C)} \tag{4.2}$$

$$a_{air} = \frac{1}{\Gamma N_A} \tag{4.3}$$

For 1:1 ionic surfactant in Γ_1 will be,

$$\Gamma_1 = -\frac{1}{2\times 2.303RT}\frac{d\gamma}{d(\log C)} \tag{4.4}$$

where Γ and Γ_1 are the surface concentrations (mole/area); γ is the surface tension for a molar concentration of C; N_A is the Avagadro's number and RT is the product of ideal gas constant and absolute temperature. For TX-100, calculated surface area is 106 $Å^2$ per molecule, which compares well with the reported value of 120.8 $Å^2$ per molecule calculated from the molecular volume (Kushnar and Hubbard, 1954). Surface area occupied by one molecule of dodecylbenzenesulfonate is calculated as 54.12 $Å^2$ in absence of salt and 49 $Å^2$ in presence of 100 mM KCl, this value compares well with the reported value of 45 $Å^2$ per molecule (Rosen, 1978).

4.3.2 Adsorption isotherms

Figures-4.2, 4.3 and 4.4 show the adsorption isotherm curves for TX-100, NaDBS and CTAB respectively on the filter paper surface, which is negatively charged (zeta potential ~ - 28 mV) in neutral aqueous medium (Schott, 1972). We observe from these figures

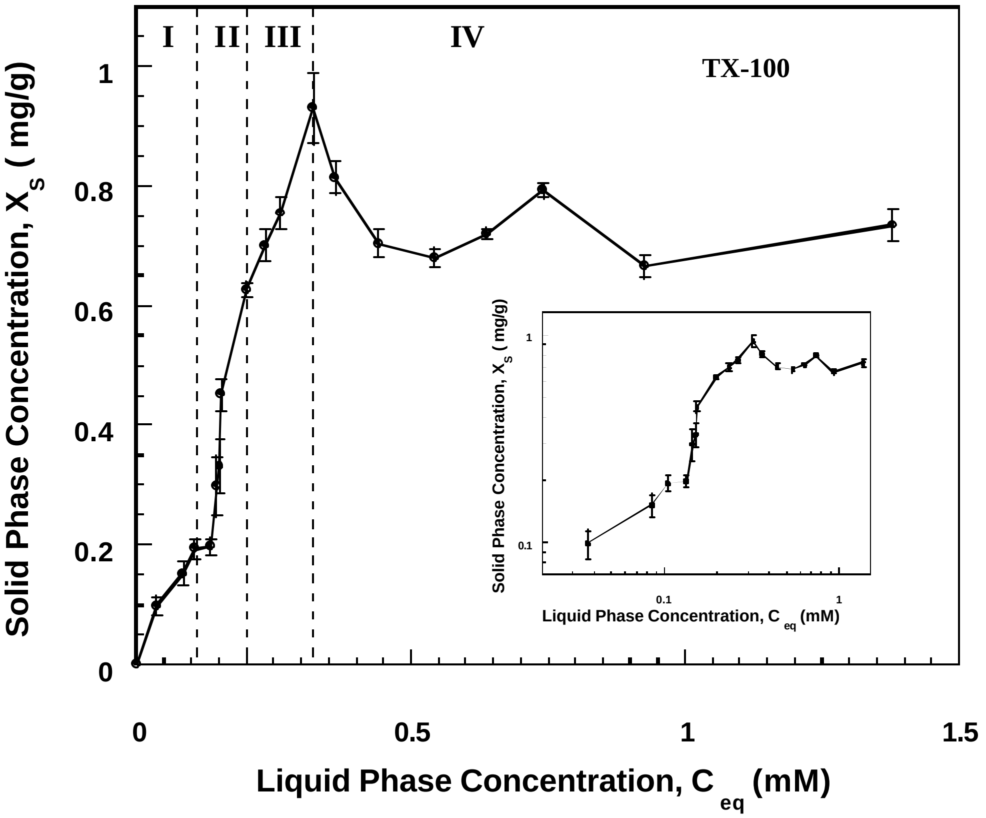


Figure-4.2: Adsorption isotherm of TX-100 on filter paper. The inset shows the log-log plot.

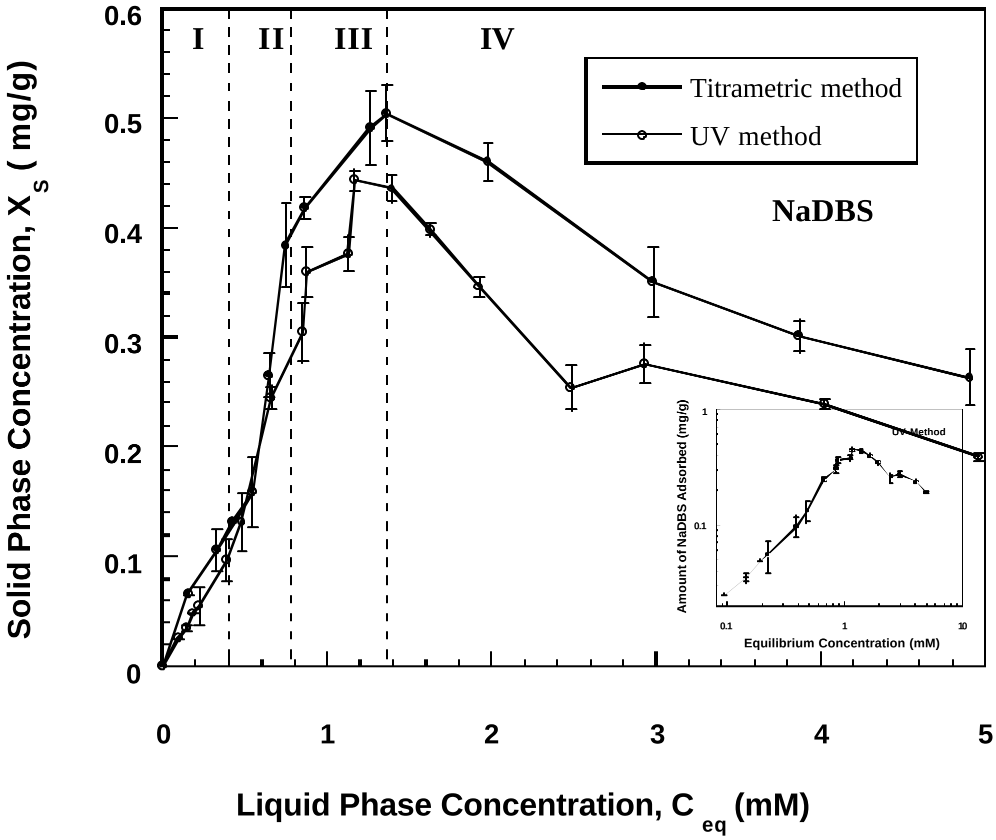


Figure-4.3: Adsorption isotherm of NaDBS by UV and titrametric method on filter paper. The inset shows the log-log plot.

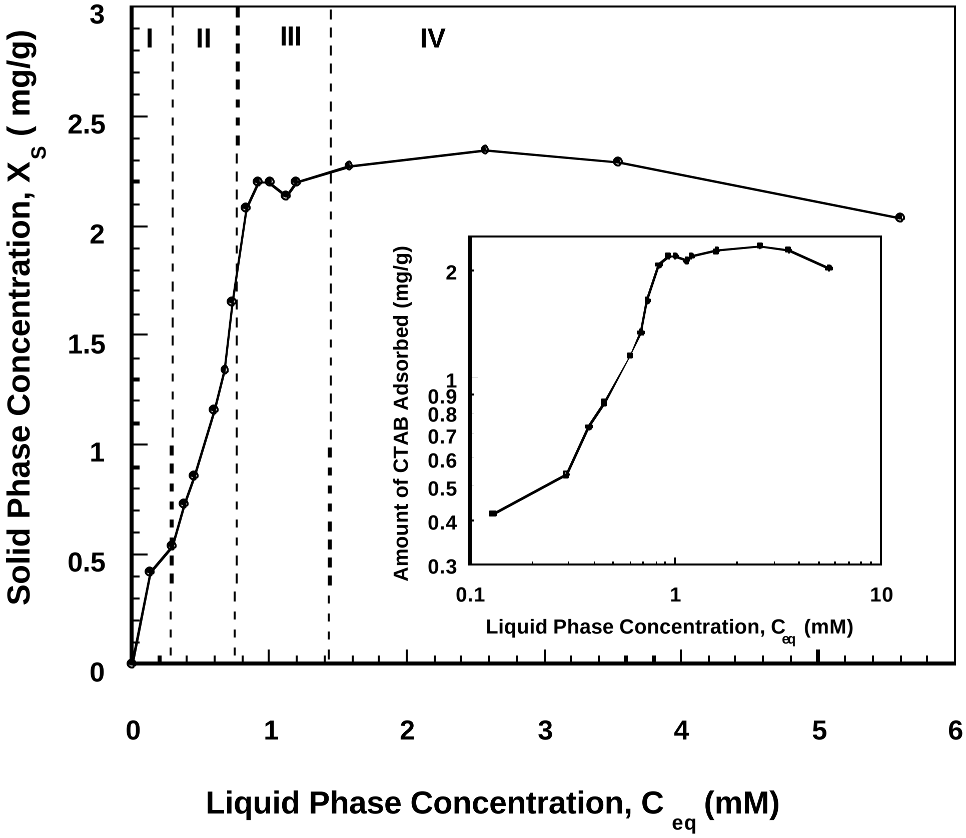


Figure-4.4: Adsorption isotherm of CTAB on filter paper. The inset shows the log-log plot.

that adsorption isotherm can be divided into four regions, both for NaDBS and TX-100. Such adsorption behavior has been reported earlier (Somasundaran and Fuerstenau, 1966; Scamehorn et al., 1982a, 1982b; Gao et al., 1987; Wang and Kwak, 1999; Koopal et al., 1995; Harwell and Scamehorn, 1993; Harwell et al., 1988; Lopata et el., 1988; Chander et al., 1983). In further, it is observed from the figures that even though the four-region adsorption seems to occur for the three cases, there are indeed some differences. For non-ionic TX-100, and cationic CTAB, the distinctness between region II with that of region I is sharper as compared to that for NaDBS. This indicates that the phenomenon distinguishing region II is more intense in case of non-ionic and cationic surfactants. In region III, the slope of X_S vs. C_{eq} plot is lower for NaDBS as compared to that for the case of TX-100, indicating presence of some inhibiting factor for ionic surfactants. One other significant difference is in the region IV. For NaDBS, the solid phase concentration, X_S, actually decreases with concentration beyond the CMC, resulting in a maximum at around CMC. The existence of such a maximum is, however, not as definite in case of TX-100 and CTAB although there seems to be some decrease in the extent of adsorption.

In region I of low concentrations, as expected NaDBS, CTAB and TX-100 molecules adsorb in a linear fashion. Beyond a particular concentration, the adsorption is suddenly enhanced as compared to that of molecular adsorption. Such enhanced adsorption can be attributed to the cluster mode adsorption termed as hemimicellization, initiated by some adsorbed surfactant molecules on the surface (Gaudin and Fuerstenau, 1955). Hemimicellization occurrs through hydrophobic interaction between the surfactant chain in bulk and in adsorbed molecules. The concentration beyond which enhancement occurs is known as hemimicellization concentration, HMC. Adsorption isotherms of TX-100 and CTAB show that hemimicellar concentration (HMC) is approximately 0.15 mM and 0.4 mM respectively. For NaDBS, there seems to be no sharp difference between regions I & II, and hence, HMC cannot be determined accurately. According to Gao et al. (1987) the average hemimicellar aggregation number h is equal to the ratio of the amount of adsorption at the two plateaus, Γ_∞ and Γ_{hm} of the adsorption isotherm.

$$n_{hm} = \frac{\Gamma_\infty}{\Gamma_{hm}} \tag{4.5}$$

For TX-100 and CTAB adsorption, our measurements indicate the hemimicellar aggregation number to be 5.

In region III, the rate of adsorption becomes smaller both for NaDBS as well as for TX-100. It is believed that in this region either the cluster mode adsorption due to surface micellization (hemimicellization) stops or the rate decreases significantly and adsorption proceeds more or less in a regular way. Anionic NaDBS adsorbes at slower rate than nonionic TX-100 and cationic CTAB.

In region IV, adsorption shows a maximum near CMC and there is a subsequent decrease in the extent of adsorption. We believe that the maximum is due to the presence of lower chain length surfactant molecules as impurities. Lower chain surfactants are adsorbed to a less extent on the solid surface than the higher chain surfactants. If we assume a solution of binary mixture of different chain length, one long (L) and the other short (S) then, the CMC of the mixed solution will be (Holland and Rubingh, 1983),

$$\frac{1}{\mathrm{CMC}_{\mathrm{Mix}}} = \frac{a_{\mathrm{L}}}{\mathrm{f}_{\mathrm{L}}\mathrm{CMC}_{\mathrm{L}}} + \frac{a_{S}}{\mathrm{f}_{\mathrm{S}}\mathrm{CMC}_{\mathrm{S}}} \tag{4.6}$$

$\mathrm{CMC}_{\mathrm{Mix}}$ is the CMC of the mixed solution, f is the activity coefficient of surfactant in the mixed micelle, equal to one for ideal system, α is the mole fraction of surfactant in total surfactant. The subscripts L and S represent long and short chain surfactant molecules respectively. Below the $\mathrm{CMC}_{\mathrm{Mix}}$ ($C_T \leq \mathrm{CMC}_{\mathrm{Mix}}$) the monomer concentration of long chain will be,

$$C_L = \alpha_L C_T \tag{4.7}$$

Above the CMC of the mixture ($C_T \geq \mathrm{CMC}_{\mathrm{Mix}}$) monomer concentration of long chain in the bulk can be written as (Holland and Rubingh, 1983),

$$C_L = y_L \mathrm{CMC}_L \tag{4.8}$$

$$C_S = (1 - y_L)\,\mathrm{CMC}_S \tag{4.8a}$$

Micellar mole fraction of long chain component can be written as,

$$y_L = \frac{C_L}{\mathrm{CMC}_L} = \frac{(\alpha_L C_T - C_L)}{C_T - C_L - C_S} \tag{4.9}$$

Eliminating C_S from equation 4.9 we get the concentration of monomer of long chain component above the mixed CMC (Clint, 1975; Nishikido, 1993),

$$C_L = \frac{-(C_T - \Delta) + \left\{(C_T - \Delta)^2 + 4.\alpha_L.C_T.\Delta\right\}^{\frac{1}{2}}}{2\left(\frac{\Delta}{CMC_L}\right)} \quad (4.11)$$

where $\Delta = CMC_S - CMC_L$, C_T is the total surfactant concentration, y_L is the mole fraction of long chain component in mixed micelle. Figure-4.5 shows the plot of C_T vs. C_L, C_S for a binary mixture of surfactants. With the increase in the C_T above the mixed CMC of the mixture, monomer concentration of long chain component decreases and that of short chain increases. As micelles do not adsorb and short chain surfactants are less adsorbed, there will be a decrease in the amount of adsorption. Therefore, we conclude that the existence of a maximum at around CMC in adsorption isotherm is due to the presence of short chain surfactant molecules. It is important to mention that the 'impurity' of the surfactant supply will not, in this case, show the minimum in a surface tension-concentration plot as this minimum is generated by a hydrophobic impurities which can not self-assemble (i.e. does not form micelle on its own). In addition, to produce a minimum, the impurity must be more surface active than the major component and be solubilized in the micelles of the major component. Thus, the absence of minima is necessary but not sufficient criterion of purity of surface-active agents (Elworthy and Mysels, 1966).

Adsorption isotherms of TX-100 and SDS from their mixture on the filter paper surface were carried out to test the effects of bulk mixed micelle formation on adsorption at the solid-liquid interface. In this case, TX-100 and SDS has the different CMC's and both the compounds form micelles individually. No surface tension minimum was observed in the SDS-TX-100 mixed surfactant system. The CMC values of SDS-TX-100 mixture are given in Table-3.1. Figures-4.6 (a) and (b) show the adsorption isotherm of TX-100 and NaDBS from their 80:20 and 70:30 mixture respectively. Both the cases TX-100 isotherms show maximum in adsorption nearer to concentration of mixed CMC and SDS isotherms show increasing amount adsorbed above the mixed CMC of the solution. The experimental results are consisting with theory.

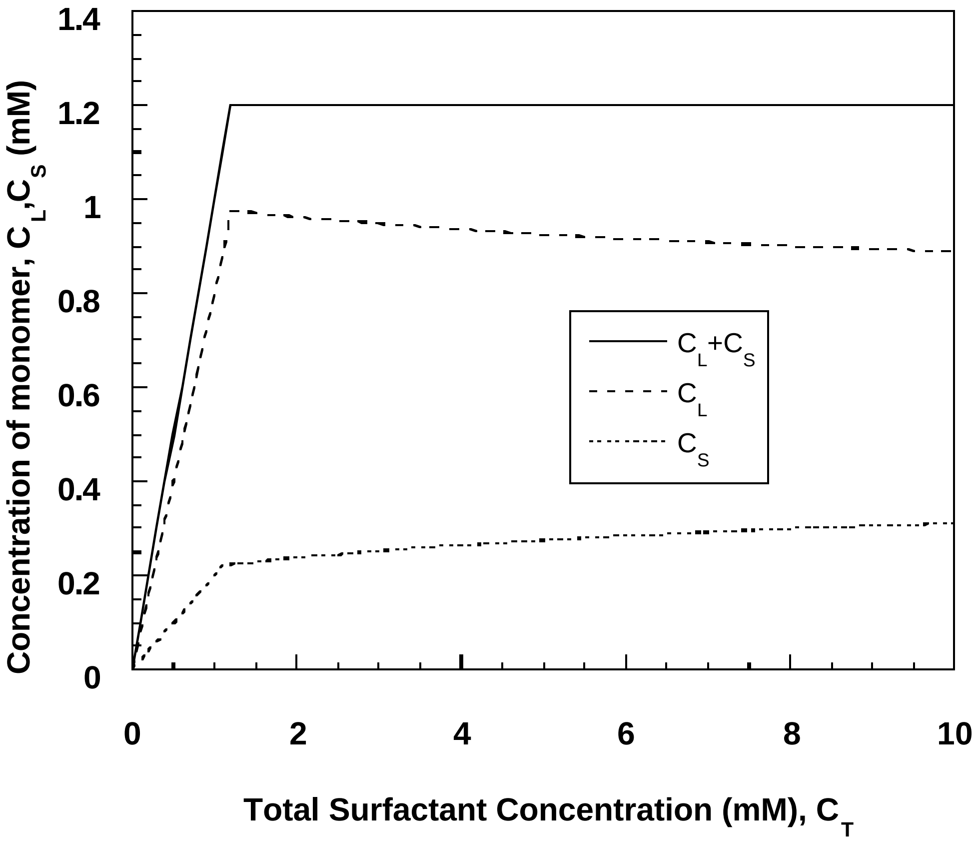
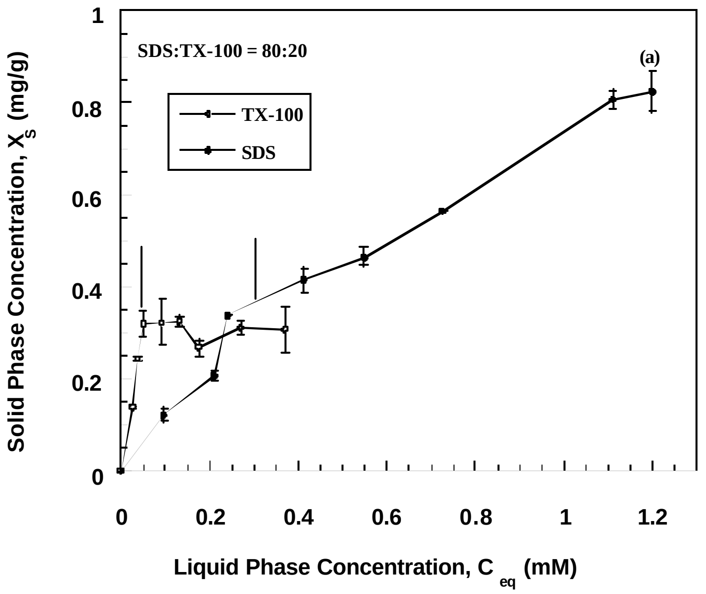


Figure-4.5: Plot of total surfactant concentration vs. monomer concentrations, assuming binary surfactant system of ideal mixed micelle. $CMC_L = 1$ mM, $CMC_S = 10$ mM, $CMC_{Mix} = 1.2$, $\alpha_L = 0.8$, $\alpha_L + \alpha_S = 1$.



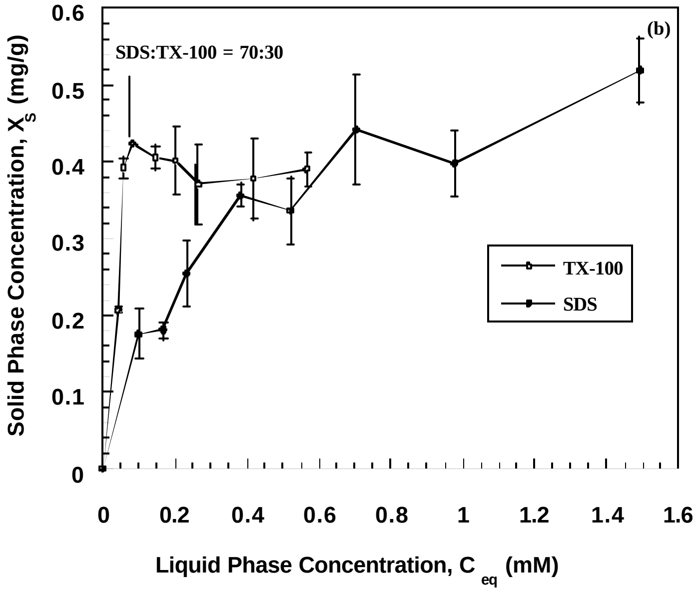


Figure-4.6: (a) Adsorption isotherms of SDS and TX-100 from their 80:20 mixtures. (b) Adsorption isotherms of SDS and TX-100 from their 70:30 mixtures. Arrow indicates the CMC of surfactant in the mixture.

To detect the presence of short chain surfactant molecules, high performance liquid chromatographic (HPLC) measurements of NaDBS solution at a concentration of 0.5 mM have been conducted. The chromatograph is presented in Figure-4.7. One can observe from this figure that there are some 21 perceptible peaks, which clearly indicate the presence of surfactant molecules of different chain lengths. Retention times are supposed to be associated with chain length of the surfactant molecules. Based on the retention time vs. percent area data, we have taken the percentage of surfactant molecules having short chain lengths as 20 %.

Furthermore, HPLC measurements were conducted using solutions before and after the adsorption. Using the data, percentage adsorption for short chain and long chain surfactants were calculated. Table-4.1 presents these values at four different concentrations. It is observed from Table-4.1 that short chain surfactants are adsorbed to less extent than the long chain surfactants. The first two lower values are below CMC while the rest are above CMC. Based on the above experimental measurements, we can conclude that the decrease in the extent of adsorption beyond CMC is due to the presence of short chain surfactants.

4.3.3 Effect of solid-liquid ratio on adsorption isotherm

Figure-4.8 (a) and (b) show the adsorption isotherm of NaDBS on filter paper and clean cotton respectively presenting the effect of solid concentration on the decreasing trend of the isotherm. Both the figures indicate that, if the volume of the solution is constant, with increasing the concentration of solid the decreasing trend slowly decreases, indicating that this effect is predominant when the surface area of the solid is less. At higher solid-liquid ratio higher amount of long chain molecules gets adsorbed. As a result CMC of the equilibrium mixture increases and therefore, the maximum shifts to the higher CMC. Adsorption on filter paper shows that with increasing solid concentration maximum amount adsorbed decreases but in case of cotton there is no significant change.

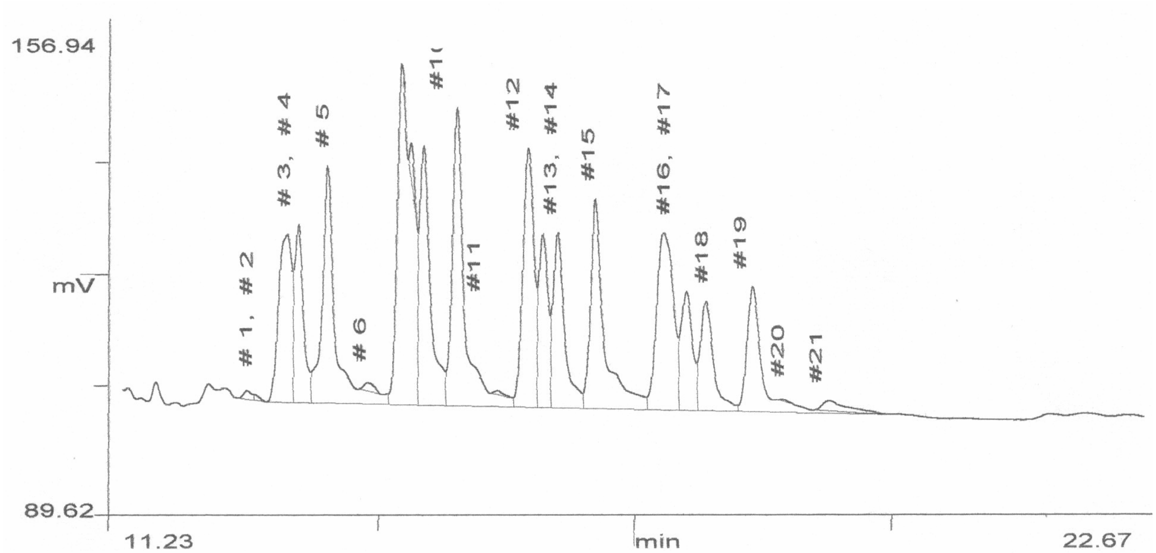


Figure-4.7: HPLC chromatograph of NaDBS at 0.5 mM concentration.

Table-4.1: Percentage of the short and long chain surfactants adsorbed, calculated from HPLC analysis.

NaDBS concentration (mM)	Percentage of lower chain surfactant adsorbed	Percentage of long chain surfactant adsorbed
0.5	1.34	14.94
1.0	3.79	13.16
3.0	2.61	6.06
5.0	1.36	3.25

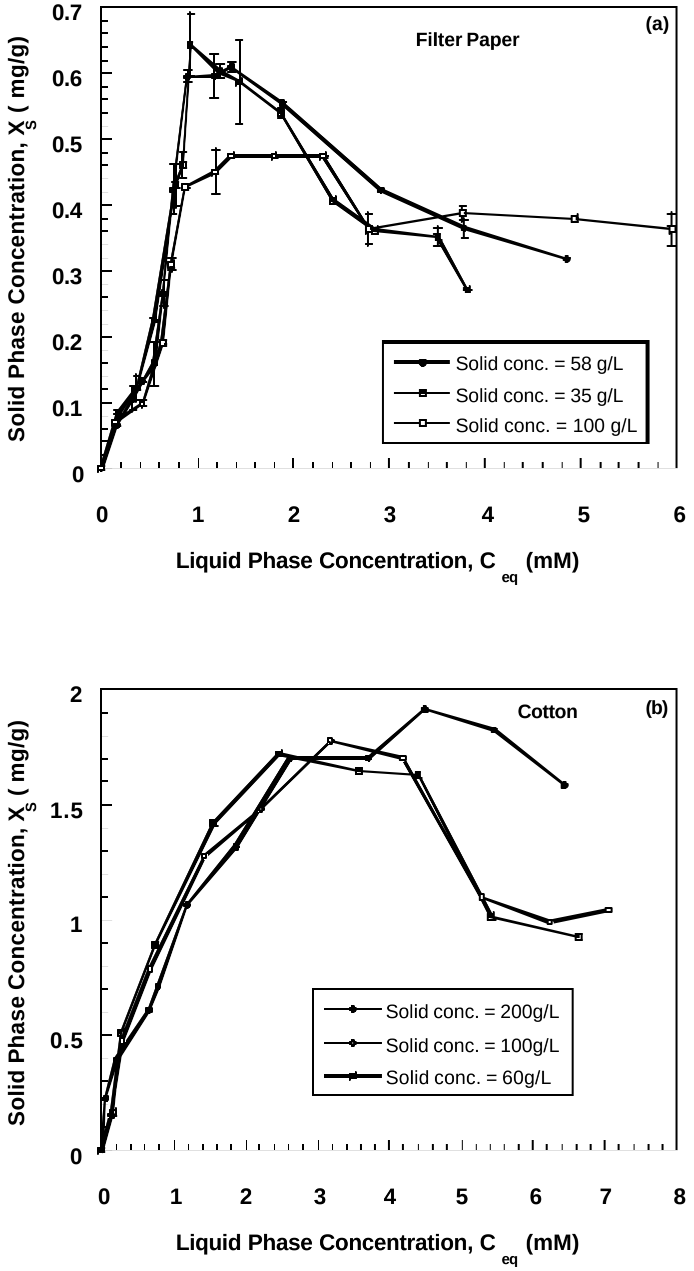


Figure-4.8: (a) Adsorption isotherm of NaDBS on filter paper at different solid-liquid ratio. (b) Adsorption isotherm of NaDBS on cotton at different solid-liquid ratio.

4.3.4 Adsorption isotherm in presence of electrolytes

4.3.4.1 Adsorption isotherm in presence of $CaCl_2$

Figure-4.9 shows the precipitation phase diagram of Ca^{++} ion in presence of NaDBS. It can be observe from the figure that for lower surfactant concentrations calcium ion tolerance is more, and then the tolerance decreases and goes through a minimum near CMC. Beyond this minimum, the borderline is a straight line, that is, the turbid to clear region maintains a particular, surfactant : Ca^{++} ratio. This study is conducted within the clear (no precipitation) regime.

Figure-4.10 shows the adsorption isotherm of NaDBS in presence of calcium ion. It is observed from this figure that, there occurs a significant increase in adsorption in the presence of even a small amount of Ca^{++} ions. Further, it is observed that the extent of increase is higher for higher amount of Ca^{++} ions present. The amount of adsorption at the peak value increases by 167 % and 316 % for the mixtures containing NaDBS and $CaCl_2$ in the ratios of 1:0.125 and 1:0.185 respectively. In addition, the extent of enhancement is found to be higher at lower surfactant concentration. Interestingly, the nature of curves, particularly the existence of maximum remains intact in the presence of Ca^{++} ions, although there is a shift of the location of the peak to a lower concentration of surfactant at higher Ca^{++} ion concentration.

Following explanations can be offered for this observation in presence of Ca^{++} ions. In presence of Ca^{++} ions, the negative charge of cellulosic surface gets neutralized partially and as a result, anionic surfactant adsorption gets enhanced. Conductivity measurements presented in Figure-4.11, show the conductivity of the mixture of NaDBS, $CaCl_2$, and the sum of the individual conductivities of NaDBS and $CaCl_2$ in the same proportion. It shows that the conductivity of the mixture is less than the sum of the conductivities. Therefore, it can be concluded that the negative charge of the surfactant molecules is shielded by the Ca^{++} ions. In addition, the compressed electric double layer at the cellulosic surface shields the charge. Consequent to this charge shielding, the adsorption of surfactant molecules onto cellulosic surface does not experience any

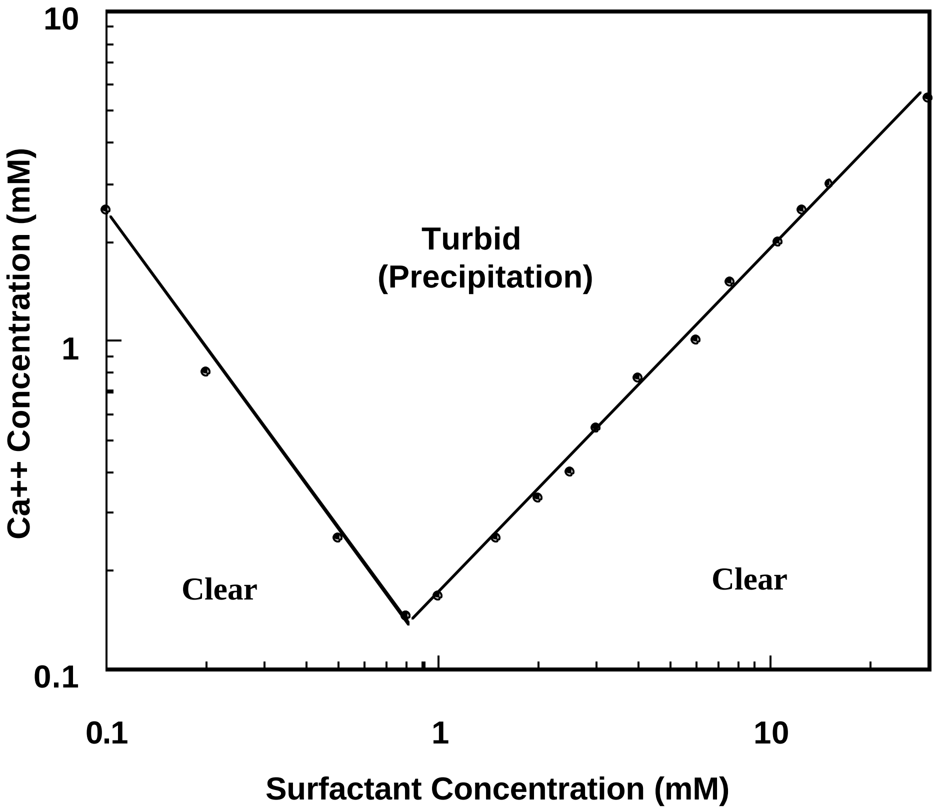


Figure-4.9: Precipitation phase diagram of NaDBS in presence of $CaCl_2$.

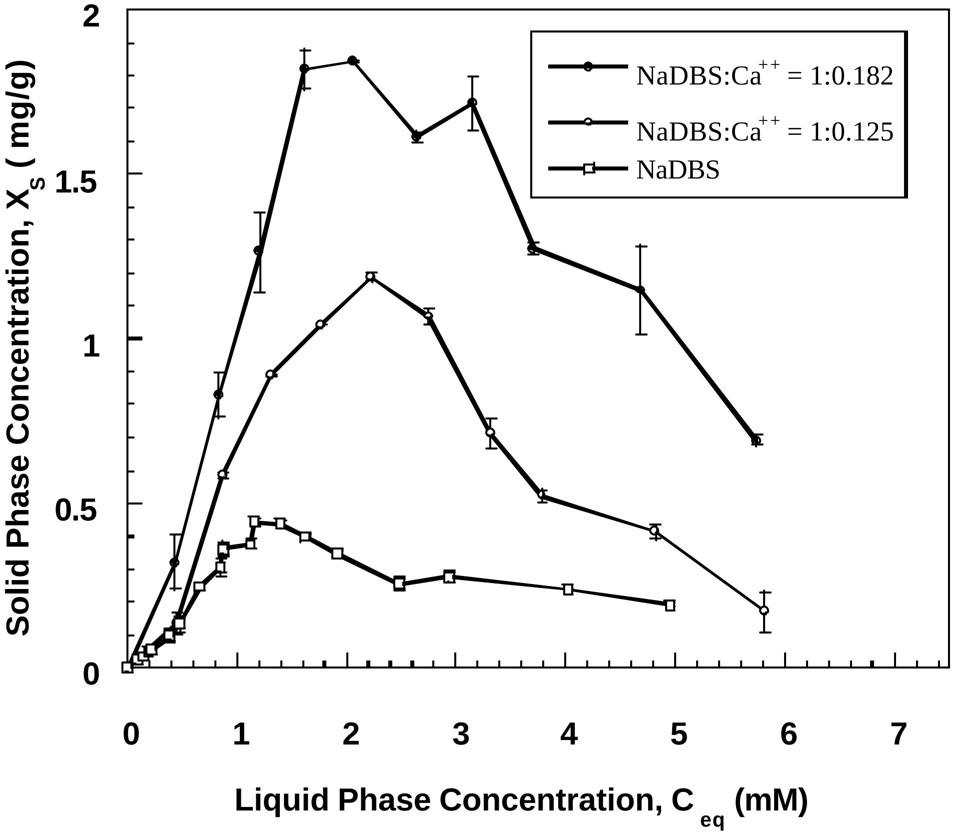


Figure-4.10: Adsorption isotherm of NaDBS in presence of $CaCl_2$.

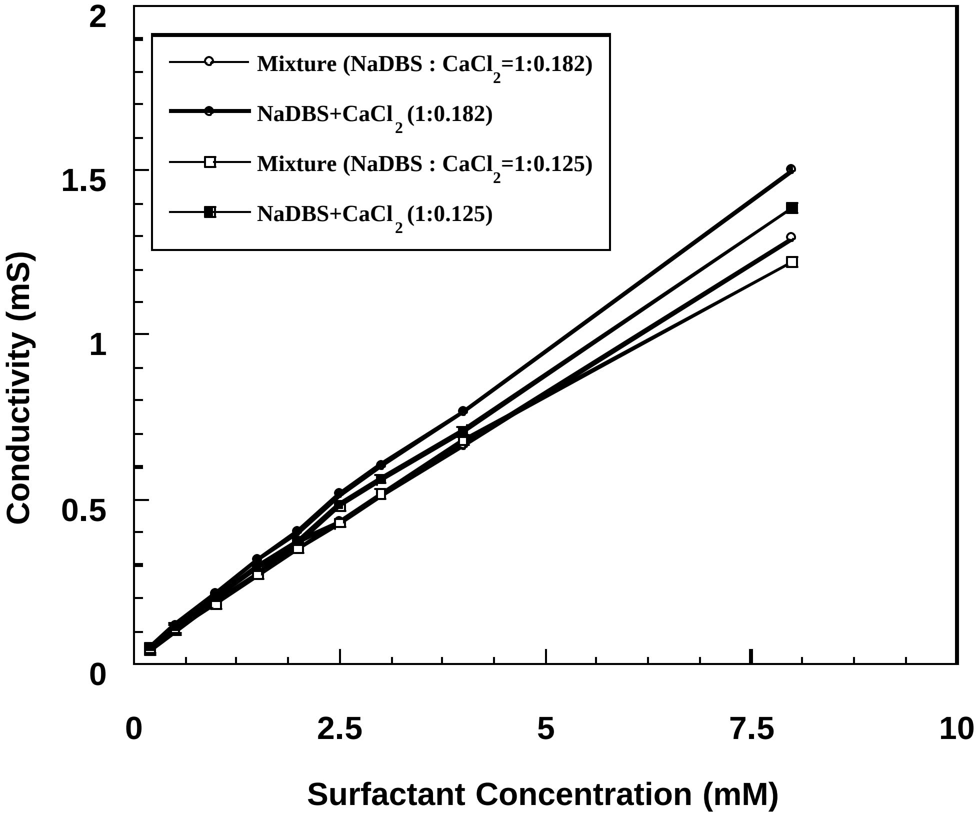


Figure-4.11: Comparison of conductivity of NaDBS and $CaCl_2$ mixture and sum of the conductivities of the individual solutions in same proportions.

inhibition arising out of electrical repulsion. Hence the extent of adsorption increases. As regards to the shifting of the peak, the peak appears at the CMC, which decreases in presence of $CaCl_2$.

4.3.4.2 Adsorption isotherm of NaDBS in presence of KCl

Figure-4.12 shows the adsorption isotherms of NaDBS in presence of KCl. At lower concentration of KCl (NaDBS : KCl = 1:0.364) there is negligible increase in adsorption. At higher concentration of KCl (NaDBS : KCl = 1:11.64), and at constant KCl concentration (20mM and 100 mM KCl) the extent of adsorption, however, is enhanced. Enhancement at this KCl concentration (NaDBS : KCl = 1:11.64) matches with the isotherm for the presence of $CaCl_2$ at a concentration, which is 93 times less (NaDBS : $CaCl_2$ = 1:0.125). Such observation qualitatively agrees with *Schulze-Hardy* rule, which states the importance of the effectiveness of valency of the counter ion in shielding the charge. The shifting of adsorption maximum towards lower concentration due to lowering CMC is clear when ionic strength is constant. Other observations are similar to those mentioned in case of $CaCl_2$ case.

4.3.4.3 Adsorption isotherm of NaDBS in presence of $CaCl_2$ and KCl mixture

Figure-4.13 shows the adsorption isotherms in the presence of mixture of KCl and $CaCl_2$. At the lower concentration of KCl (NaDBS:KCl = 1:0.364) there is no enhancement of amount of NaDBS adsorption. However, at the same concentration of KCl solution, if the $CaCl_2$ solution is mixed in the proportion of NaDBS:KCl:$CaCl_2$ = 1:0.364:0.125, then higher extent of enhancement in adsorption occurs as compared to that in case of $CaCl_2$ alone. This observation is in consistent with the fact that the charge is effectively shielded at higher ionic strength produced by mixing of the electrolytes.

Interestingly, a very high concentration of KCl (1:11.64) does not significantly enhance the adsorption as can be seen in the figure. At higher concentration of KCl, CMC of the solution decreases with a consequent increase in the number of micelles.

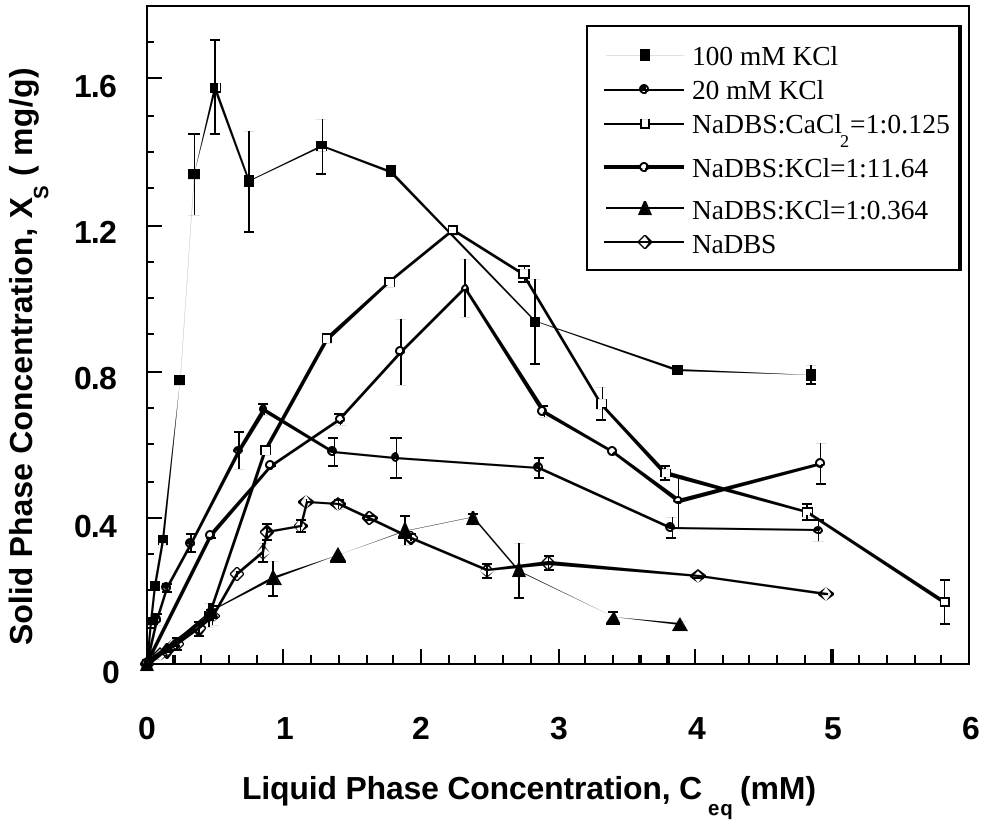


Figure-4.12: Adsorption isotherm of NaDBS in presence of KCl.

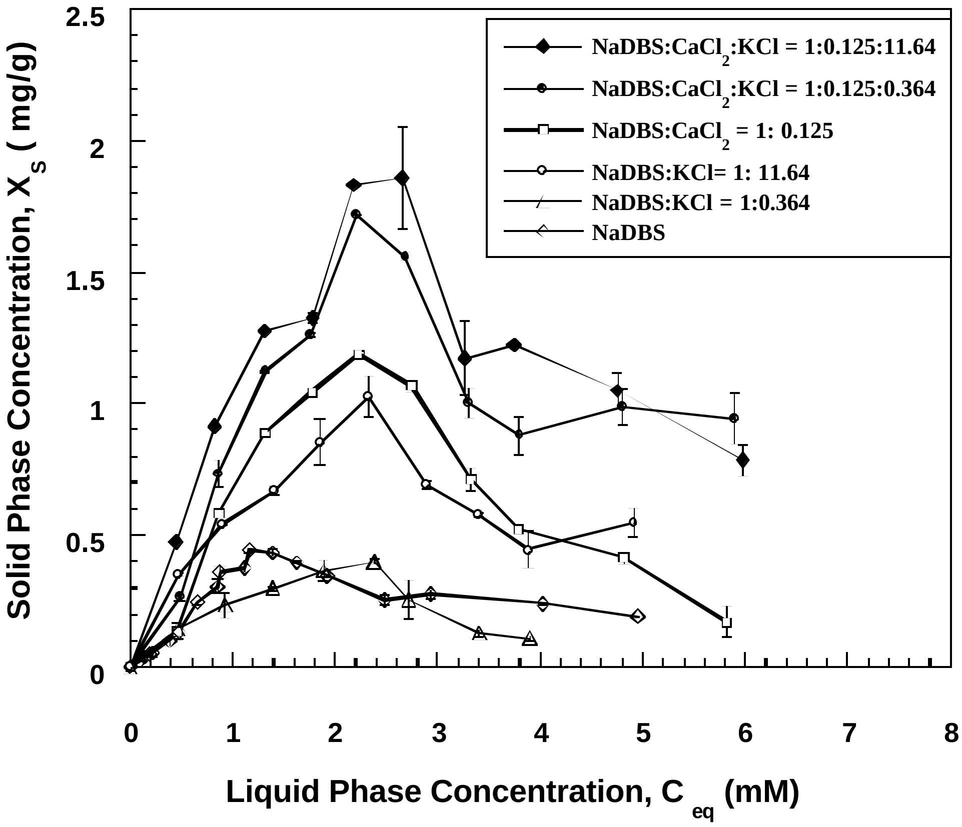


Figure-4.13: Adsorption isotherm of NaDBS in presence of mixture of KCl and $CaCl_2$.

As a result adsorption of surfactant molecules decreases. This result is also consistant with the DLVO theory and can be explained in terms of energy barrier of total interaction energy between the surface and surfactant molecules in presence of salt. The rate of adsorption depends on the height of the energy barrier in total interaction energy vs. distance curve. In the absence of salt, the energy barrier is high. In addition of small amount of salt the energy barrier decreases significantly and further presence of more salt does not show any significant change in adsorption.

4.3.4.4 Adsorption isotherm of TX-100 in presence of $CaCl_2$ and KCl

Figure-4.14 presents the data on adsorption of TX-100 in presence of KCl and $CaCl_2$. The figure shows that there is no significant change in the adsorption isotherms as compared to those with out the presence of electrolyte. Note, TX-100 is non-ionic surfactant and hence is not influenced by the electrostatic effects. The enhancement in the case of NaDBS, as seen is primarily an electrostatic effect and it is absent in case of TX-100 adsorption. Furthermore, we can conclude that, adsorption of TX-100 does not occur due to hydrogen bonding with OH group on the cellulosic surface. If the adsorption was by hydrogen bonding, then, in presence of K^+ or Ca^{++}, the extent of adsorption of TX-100 should decrease due to strong adsorption of K^+ or Ca^{++} ion with free OH group of cellulose (Nevskaia et al., 1998; 1995). Adsorption of TX-100 molecules appears to occur primarily by the interactions between the hydrophobic site and the hydrophobic group of the TX-100.

4.3.4.5 Adsorption isotherm of NaDBS at different pH

Furthermore, the effect of pH on the adsorption isotherm of NaDBS was studied at two different pH of 3 and 11. The isotherms are presented in Figure-4.15. We observe from the Figure-4.15 that the amount of adsorption at equilibrium decreases at pH equal to 11, compared with same electrolyte concentration. At pH of 11, surface becomes increasingly negatively charged and hence there occurs a decrease in adsorption. The adsorption at pH equal to 3.0 is slightly higher arising out of partial neutralization of

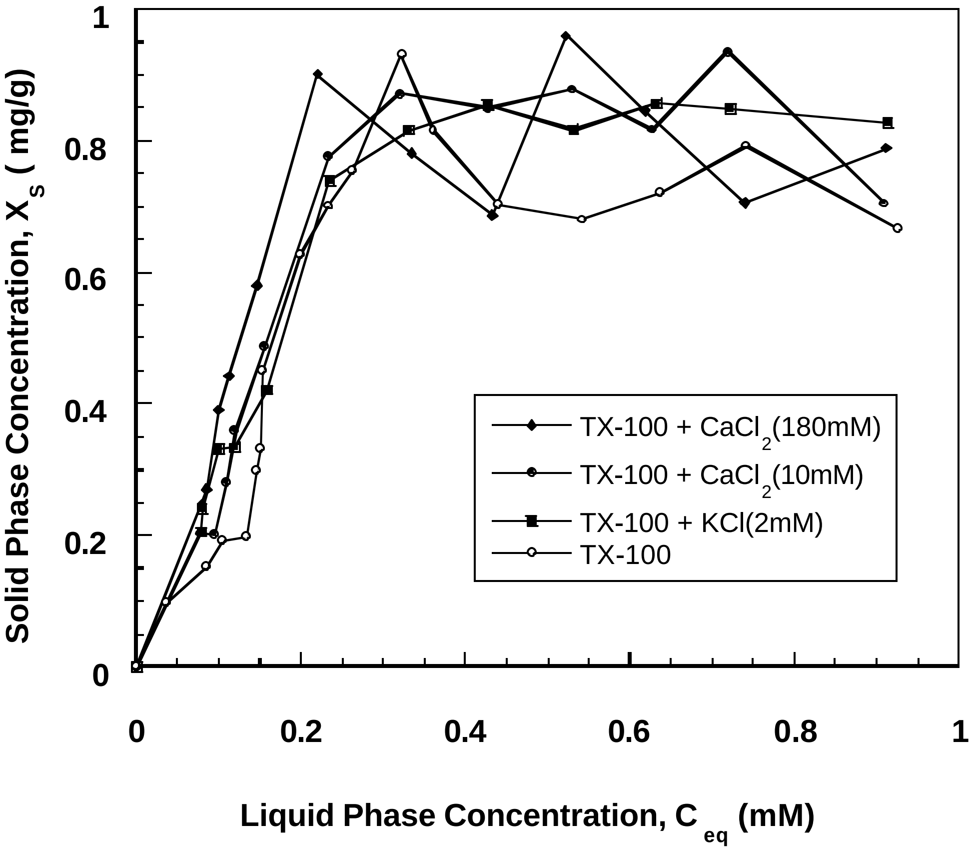


Figure-4.14: Adsorption isotherm of TX-100 in presence of $CaCl_2$ and KCl.

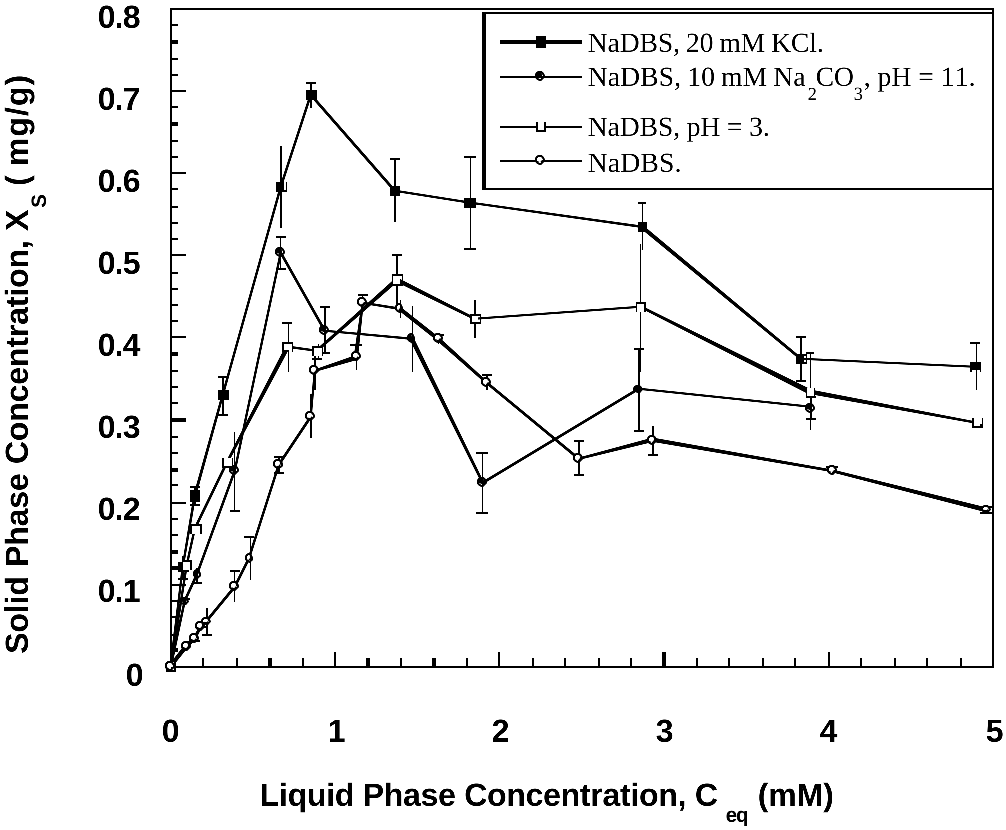


Figure-4.15: Adsorption isotherm of NaDBS in presence of different pH.

negative charge. Therefore the observed pH effect indicates significant electrical effects on the adsorption behavior.

4.4 Estimation of polar and non-polar sites on the cellulosic surface

The observations related to the adsorption of NaDBS and TX-100, indicate the presence of both charged and hydrophobic sites on the cellulosic surface as discussed in chapter-3. The electrical nature of the surface is manifested in the change in adsorption behavior in presence of electrolyte, while the hydrophobic nature is shown through the adsorption of TX-100. Therefore, it is hypothesized that the cellulosic surface consists of two kinds of sites for adsorption: electrically charged sites or polar and hydrophobic sites or non-polar sites.

Hydrophilic site is a characteristic of materials exhibiting affinity for water. The surface chemistry of hydrophilic materials allows adsorption of water form surface function groups. The surface functional groups have the ability to form hydrogen bond with water. The hydrophobic site is a characteristic of material exhibiting opposite response to water compared to hydrophilic site. Hydrophobic site lacks the active groups to form hydrogen bonds with water. Cellulosic material is a natural polymer, a long chain made up of repeating units of β-D glucose monomer molecule as shown in Figure-1.2. The monomer units are joined by single oxygen atoms (acetyl linkage) between the C1 of one monomer ring to C4 of the next ring. The free hydroxyl groups present in the cellulose chain act as hydrophilic sites and the C-C linkage in the ring structure may act as hydrophobic sites

From the adsorption isotherms we have determined the area occupied (nm^2) of different surfactant molecules on the filter paper surface. The values are calculated using the formula

$$a_{sm} = \frac{M \times S_{BET} \times 10^{21}}{\Gamma \times N_A} \qquad (4.12)$$

where M is the molecular weight of the surfactant, S_{BET} is the BET surface area of the filter paper in m^2/g, Γ is the amount of surfactant adsorbed in mg/g, a_{sm} is mean area

Table-4.2: Area occupied by one molecule of surfactant and methylene blue on filter paper surface.

Molecule	Area occupied per molecule (nm^2/molecule)
NaDBS	20.0
TX-100	19.2
NaDBS + Ca^{++} (1 : 0.182)	5.3
NaDBS + Ca^{++} + K^{+} (1 : 0.182 : 11.64)	5.1
NaDBS + KCl (100mM)	6.0
CTAB	4.4
Methylene Blue	7.5

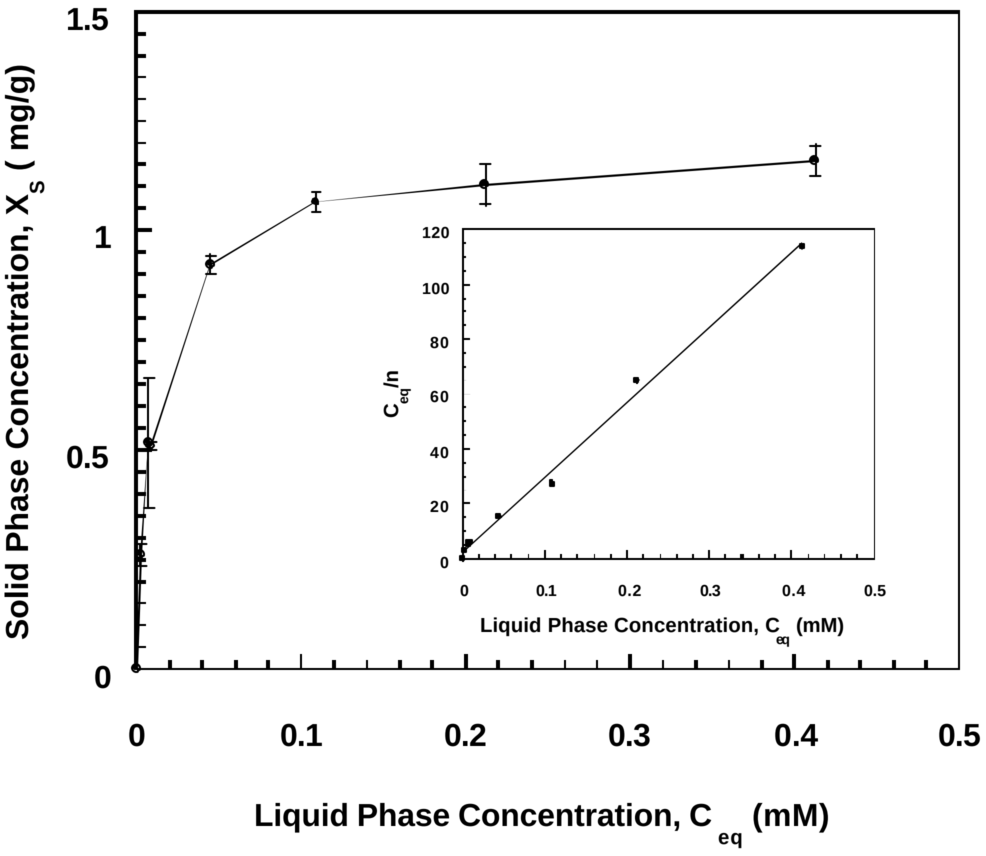


Figure-4.16: Adsorption isotherm of methylene blue. The inset shows the plot of $\frac{C_{eq}}{n}$. vs. C_{eq}, where n is the number of moles of methylene blue adsorbed per gram of filter paper.

occupied per molecule in nm^2. Based on the observations presented earlier, we expect the filter paper surface consists both negatively charged sites as well as neutral hydrophobic sites. Calculations have been conducted to determine the area occupied by surfactant molecules and are presented in Table-4.2. Table-4.2 shows that the area occupied by a molecule of NaDBS and a molecule TX-100 are nearly same. Such agreement may indicate that NaDBS and TX-100 are mainly adsorbed to the same site, that is, on the hydrophobic sites of the filter paper.

In order to prove the presence of the negatively charged sites, we have conducted the adsorption of a cationic dye, methylene blue. The molecules carry positive charge and hence are expected to adsorb on to the negatively charged sites. Figure-4.16 presents the adsorption isotherm. We observe from this figure that unlike the four regime adsorption isotherms of NaDBS, CTAB and TX-100, methylene blue gives a Langmuir type of isotherm. This is expected as both hemimicellization and micellizations are absent in such system.

Referring back to Table-4.2, we note that, the area occupied by a molecule for anionic surfactant in presence of electrolytes, and the area occupied by a cationic surfactant, CTAB are nearly equal to 5 nm^2. The area occupied by a molecule of methylene blue 7.5 nm^2, is higher than that for surfactants in presence of electrolyte and for CTAB. Let us assume that, NaDBS and TX-100 molecules adsorb onto hydrophobic sites only and methylene blue molecule onto negatively charged sites only. NaDBS in presence of electrolyte and CTAB adsorb onto both hydrophobic and negatively charged site. Let us further assume that f is fraction of area occupied by the hydrophobic sites. The area occupied by one molecule as calculated assuming that adsorption occurs on the entire area is, $a_{sm} = 5\ nm^2$. The area occupied by one molecule, as calculated assuming that adsorption occurs on the area consisting of hydrophobic sites only is, $a_{smh} = 20\ nm^2$. The number of molecules adsorbed on unit area in case of adsorption on hydrophobic sites is $\frac{1}{a_{smh}}$, which is also equal to $\frac{f}{a_{sm}}$. Hence, f the fraction of area occupied by hydrophobic sites is equal $\frac{a_{sm}}{a_{smh}}$=0.25. When adsorption occurs only in the area containing negatively charged sites, it can easily be shown that the area occupied by a molecule will be

$\left(\frac{a_{sm}}{1-f}\right) = \frac{5}{0.75} = 7\ \text{nm}^2$. This value of 7 nm^2 agrees well with the calculation of 7.5 nm^2 as shown in Table-4.2. Hence it can be concluded that the filter paper surface consists of approximately 25 % hydrophobic sites and 75 % negatively charged sites.

4.5 Conclusions

1. Equilibrium adsorption isotherms of NaDBS, CTAB and TX-100 do not show Langmuir type adsorption but show a typical four-region isotherm. The presence of maximum in region IV can be attributed to the presence of shorter chain surfactant molecules. CTAB and TX-100 molecules show hemimicelle formation while NaDBS molecules do not form hemimicelles.
2. Adsorption of cationic molecules, CTAB and methylene blue is strong, indicating that the charged sites on filter paper surface is negative and they dominate over the smaller number of hydrophobic sites. Detailed calculations show that 25 % sites are hydrophobic in nature and the rest 75 % sites are negatively charged sites.
3. Studies on the effect of salts, Ca^{++} and K^+ on NaDBS adsorption confirm the above conclusions. Ca^{++} ions may form 'bridges' between the head group of NaDBS and the charged sites of filter paper enhancing the extent of adsorption.
4. Area per molecule estimated from the adsorption isotherm data indicate that methylene blue molecules adsorb densely on the anionic sites of filter paper. NaDBS molecules do so only in presence of Ca^{++} and K^+. NaDBS and TX-100 molecules adsorb on the hydrophobic sites and CTAB molecules adsorb on both hydrophilic and hydrophobic sites.

Chapter-5

Adsorption from Solutions Containing a Mixture of Anionic-Cationic Surfactants at the Cellulose-Water Interface

5.1. Introduction

Adsorption of surfactants at the solid-liquid interfaces has many practical applications such as detergency, ore flotation, oil recovery and preparation of dispersions such as paints. We have conducted a study to investigate the adsorption of surfactants onto a cellulosic surface under various conditions so that the adsorption can be enhanced or inhibited as needed for an application. In case of detergency, we need to optimize adsorption of surfactant when mixture of surfactants is used.

In many cases, adsorption of surfactants is significantly enhanced in a mixed system of surfactants as compared to the adsorption of a single surfactant. Although the self-assembly of mixed surfactants in solution is well known, but there is very little information about the self-assembly of mixed surfactants at the solid-liquid interface.

Mixture of surface-active materials can show synergistic interactions, which can be manifested as enhanced surface activity, spreading, wetting, foaming, detergency and many other phenomena. Some of these synergistic actions have practical applications. The synergistic behavior of mixed surfactant system can be exploited to reduce the total amount of surfactant used in a particular application resulting in reduction in the cost and in environmental pollution. The underlying scientific understandings on these synergistic interactions are not currently available, and therefore, trial and error methods are used to design mixed surfactant systems for practical applications (Shiloach and Blankschtein, 1998).

There have been only a few studies of anionic-cationic mixed surfactant adsorption due to the problem of precipitation. From the application point of view, anionic-cationic surfactant mixture can be used in laundry detergent with in-built fabric softeners (Rubingh, 1991). Another aspect is cationic surfactants have the unique possibility of providing germicidal effects along with their cleaning action (Patterson and Grindstaff, 1977). This makes them useful in applications where antiseptic conditions must be maintained. Huang et al. (1989) have studied the adsorption of cationic surfactant on silica from the mixture of anionic-cationic surfactants. The adsorption of cationic surfactant was enhanced by the presence of small amount of anionic surfactant. Patist et al. (1999) have studied the change in interfacial properties of anionic-cationic mixed surfactant systems at 1:3 and 3:1 molecular ratio due to the formation of two-dimensional compact hexagonal arrangements at the air-liquid interface. Similar phenomena have been observed for stearic acid-stearyl alcohol mixture at the air-liquid interface (Shah, 1977).

In this chapter, the studies concerning adsorption enhancement behavior of anionic-cationic mixture at the cellulose surface (solid-liquid interface) is presented. The studies have been conducted below CMC of the mixed surfactant system to isolate the systems from the effects of micellization. In the absence of micellization, the interactions between the molecules and the surface may govern the adsorption process.

5.2. Experimental Section

5.2.1 Materials

Anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) was obtained from Fluka Chemicals. Nonionic surfactant, polyoxyethylene (number of segments 9.5) glycol tert-octylphenyl ether (Triton X-100 or TX-100) was obtained from Sigma Chemicals. NaDBS and TX-100 were used as received, without any further purification. Cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) was obtained from Ranbaxy Fine Chemicals Ltd., India. It was recrystallized twice from an acetone : methanol (3:1) mixture before use (Desai and Dixit, 1996). Adsorbent used was a Whatman-40 ashless filter paper (9 cm dia) from Whatman International Ltd., England. The BET multipoint surface area (N_2 adsorption) was 16.5 m^2/g. Double distilled water of pH 5.6 and conductivity 1.2 μS (μ Mho) was used for the experiment.

5.2.2 Methods

5.2.2.1 Washing of filter paper

The filter paper was washed thoroughly with double distilled water to remove the dust and soluble ions from the filter paper till the conductivity of the washed water became equal to that of the distilled water. Then it was dried in oven for 1 - 1.5 hours at 50-55^oC until the weight of the filter paper became constant.

5.2.2.2 Surfactant analysis

The concentration of NaDBS and TX-100 was determined by measuring UV absorbance at 223 nm wavelength using UV-Vis spectrophotometer (Shimadzu, UV-160A model). Quartz glass cells (Hellma) of 10 mm path length were used. A calibration plot (absorbance vs. concentration) was obtained measuring absorbance of known concentration surfactant solution. Concentration of unknown solution was measured using the calibration plot mentioned in Chapter-3.

The surface tension was measured using a Du-Noüy ring tensiometer (Fisher surface tensiomat, Model 21). Conductivity was measured by an auto ranging conductivity meter (Equiptronics, Mumbai, India) using cell constant, k = 1.

5.2.2.3 Adsorption experiments

For the adsorption study, single surfactant solution was prepared by diluting from the concentrated solution. The other surfactant was mixed to this solution 10-12 hours prior to each adsorption experiment. For each set of experiment, 0.580 g filter paper was used after cutting into small pieces of size 5-10 mm. A 10 ml surfactant solution was used for each set of experiment. The system was stirred slowly at regular intervals. All the experiments were done at 25^{o}C. The experiments were repeated atleast three times and the average data were plotted.

Adsorption measurements were carried out at concentrations below CMC and at five different mixing ratios, 50:1, 25:1, 20:1, 15:1 and 10:1 (moles of anionic:moles of cationic). The surfactant concentrations were chosen below the CMC of the individual surfactants as well as the CMC of mixed surfactant systems. In anionic-cationic mixture there is a tendency to form precipitate in the mixture. Below the CMC, it is possible to study in a wide range of mixing ratios without forming precipitate in that mixing range.

5.3 Results and Discussion

The equilibrium adsorption of NaDBS in presence of CTAB on the cellulose-water interface enhances significantly. We have calculated the adsorption enhancement according to

$$\mathrm{E} = \frac{\Gamma_{\mathrm{mix}} - \Gamma_{\mathrm{NaDBS}}}{\Gamma_{\mathrm{NaDBS}}} \times 100 \qquad (5.1)$$

where E is adsorption enhancement in %, Γ_{NaDBS} and Γ_{mix} are the equilibrium amount adsorbed in mg/g of NaDBS from the solution containing only NaDBS and from the

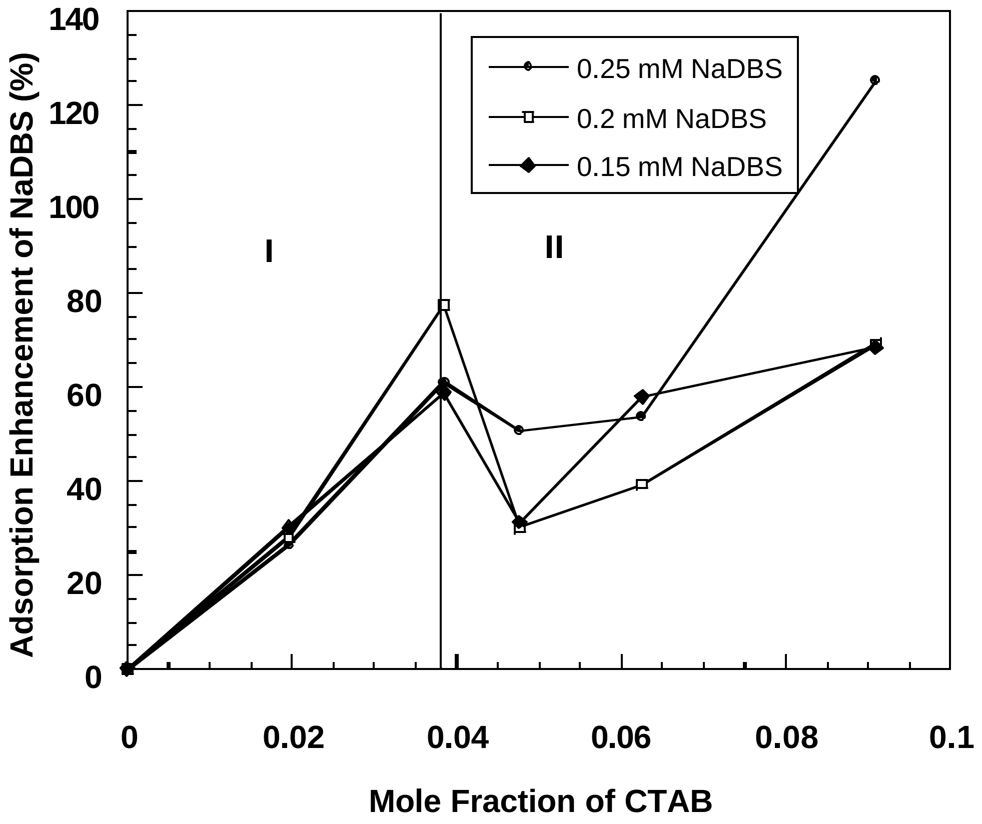


Figure-5.1: Adsorption enhancement (E) of NaDBS at different concentration of CTAB.

solution containing mixture of surfactants respectively for a particular concentration of NaDBS. Adsorption enhancement (E) of NaDBS at three different NaDBS concentrations, 0.15 mM, 0.2 mM and 0.25 mM are plotted against the mole fraction of the CTAB as shown in Figure-5.1.

It can be observed from the Figure-5.1 that the enhancement vs. mole fraction plot is typically non-linear and the curve can be described by two distinct regimes. Initially with increasing the concentration of CTAB the enhancement in adsorption increases almost

linearly, up to the vertical line (25:1 mole ratio). This portion is termed as regime-1 and the rest of the curve as regime-2.

There is a proposed explanation for these two-regime enhancements. This explanation is based on a hypothesized 2-D lattice formation on the surface. This mechanism will be discussed here and later on in details. Essentially, in the first regime the 2-D lattice structure is hexagonal 2-D structure of NaDBS and CTAB. While in the other regime, the 2-D structure adjusts to 1 to 2 molecules ratio of NaDBS and CTAB. The lattice formation results in substantial decrease in the energy of the interface and thus generates higher adsorption potential.

To understand the 2-D lattice formation at the interface, the enhancement (E_{cal}) have been calculated assuming one CTAB molecule induced adsorption of one NaDBS molecule (1:1 enhancement). Where,

$$E_{Cal} = \frac{\Gamma_{Cal} - \Gamma_{NaDBS}}{\Gamma_{NaDBS}} \times 100 \tag{5.2}$$

$$\Gamma_{Cal} = \Gamma_{NaDBS} + \frac{C_{CTAB} \times V \times M}{1000 \times m} \tag{5.3}$$

E_{cal} is the calculated adsorption enhancement in %, Γ_{cal} is calculated amount of NaDBS adsorbed in presence of CTAB in mg/g, C_{CTAB}, V, m, M are the concentration of CTAB in mM/L, volume of solution taken in ml, mass of filter paper in 'g' and molecular weight of NaDBS respectively. The experimental and calculated data at three different NaDBS concentrations are tabulated in Table-5.1. From the data one can observe that up to 25:1 NaDBS/CTAB mole ratio adsorption enhancement is 1:1 (regime-1) and from 20:1 mole ratio it is 2:1 (regime-2), i.e. two moles of CTAB enhances one mole of NaDBS. The critical concentration of the cationic surfactant for transition one regime to another is, Table-5.1: The experimental and calculated adsorption enhancement data and comparison of calculated and experimental concentration of CTAB for transition in the enhancement regime-1 to regime-2 at three different NaDBS concentrations.

NaDBS conc. mM/L	NaDBS : CTAB	E_{cal}	E	E/E_{cal}.	C_{Crit} (mM/L)	C_{exp} (mM/L)
0.15	100:0	0.0000	0.0000	0.0000	0.0130	0.0075
	50:1	27.550	30.300	1.0900		
	25:1	55.110	58.650	1.0600		
	20:1	68.400	31.310	0.45700		
	15:1	91.860	58.05	0.4200		
	10:1	137.79	68.367	0.47000		
0.2	100:0	0.0000	0.0000	0.0000	0.0173	0.01
	50:1	28.040	37.860	1.3500		
	25:1	56.040	91.740	1.6300		
	20:1	70.060	41.050	0.58590		
	15:1	93.410	50.060	0.53590		
	10:1	140.12	73.120	0.52191		
0.25	100:0	0.0000	0.0000	0.0000	0.0197	0.0125
	50:1	30.229	26.210	0.867		
	25:1	60.45	61.049	1.0090		
	20:1	75.57	50.750	0.671		
	15:1	100.76	53.660	0.532		
	10:1	151.146	125.10	0.826		

C_{exp} = Experimental critical concentration of CTAB for transition of regime-1 to regime-2.

$$C_{Crit} = \frac{2 \times \Gamma_{NaDBS} \times m \times 1000}{M \times V} \tag{5.4}$$

where, C_{Crit} is the concentration of the cationic surfactant in mM/L. Table-5.1 shows the comparison of calculated and experimental concentration of CTAB for transition in the enhancement of regime-1 to regime-2 at three different NaDBS concentrations. Experimental critical CTAB concentration shows slightly lower value.

Figure-5.2 shows the adsorption enhancement of NaDBS in presence of MTAB (C_{14}TAB) at a concentration of 0.2 mM NaDBS. We observe from this figure that there are more significant differences between the enhancement curves of CTAB and MTAB. Firstly, the enhancement is negligible at lower concentrations of MTAB. At higher concentrations, however, the enhancement values are significant. Such enhancements in adsorption are due to possible adsorption of MTAB molecule onto the negatively charged site at higher concentration. There is, however, no indication of a two-regime adsorption enhancement in case of MTAB indicating the absence of formation of 2D hexagonal lattice structure at the solid-liquid interface. Noting that, the CTAB molecule is more hydrophobic than MTAB, such observation indicates, the importance of hydrophobicity of surfactant species in adsorption of cellulosic surface.

The plots showing the kinetics of adsorption on plain paper surface and paper surface pre-adsorbed with CTAB are presented in Figure-5.3. The NaDBS concentration of 0.2 mM/L, and 10:1 mixing ratio was used for the mixed solutions. For the pre-adsorbed experiment, the filter paper was pre-adsorbed with 0.02 mM/L CTAB. After equilibrating the system for three hours, one filter paper was rinsed with distilled water for three times and another ten times. Adsorption experiments were carried out in presence of 0.2 mM NaDBS using this pre-adsorbed filter paper. This pre-adsorbed experiment was carried out to observe the mechanism of mixed surfactant adsorption as well as the synergistic behavior of the surfactants in the mixture.

We observe from Figure-5.3 that the amount adsorbed is higher for pre-adsorbed surface and there is a little difference in adsorption between three times washed and ten times washed surface. The rate of adsorption is rapid in both the pre-adsorbed cases than the mixture. The effect of washing is less, because the cationic surfactants are strongly adsorbed on the negatively charged cellulose surface (~ -28 mV) in the neutral aqueous medium (Schott, 1972). The cationic surfactants are adsorbed to the oppositely charged

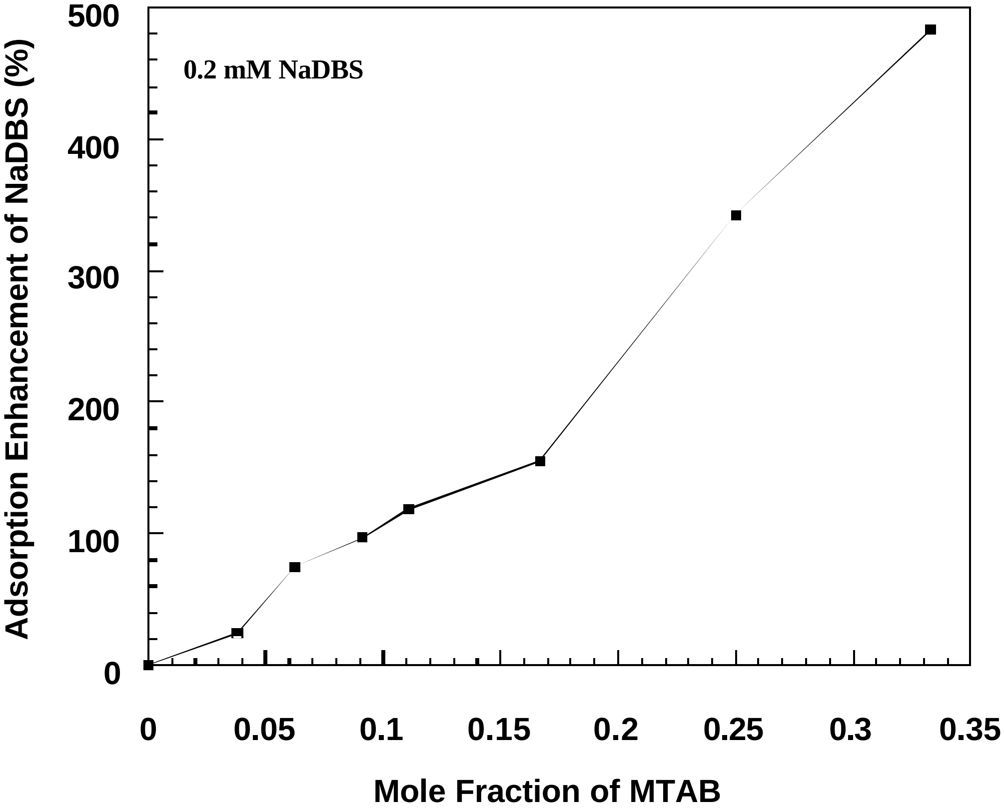


Figure-5.2: Adsorption enhancement (E) of NaDBS at different concentration of MTAB.

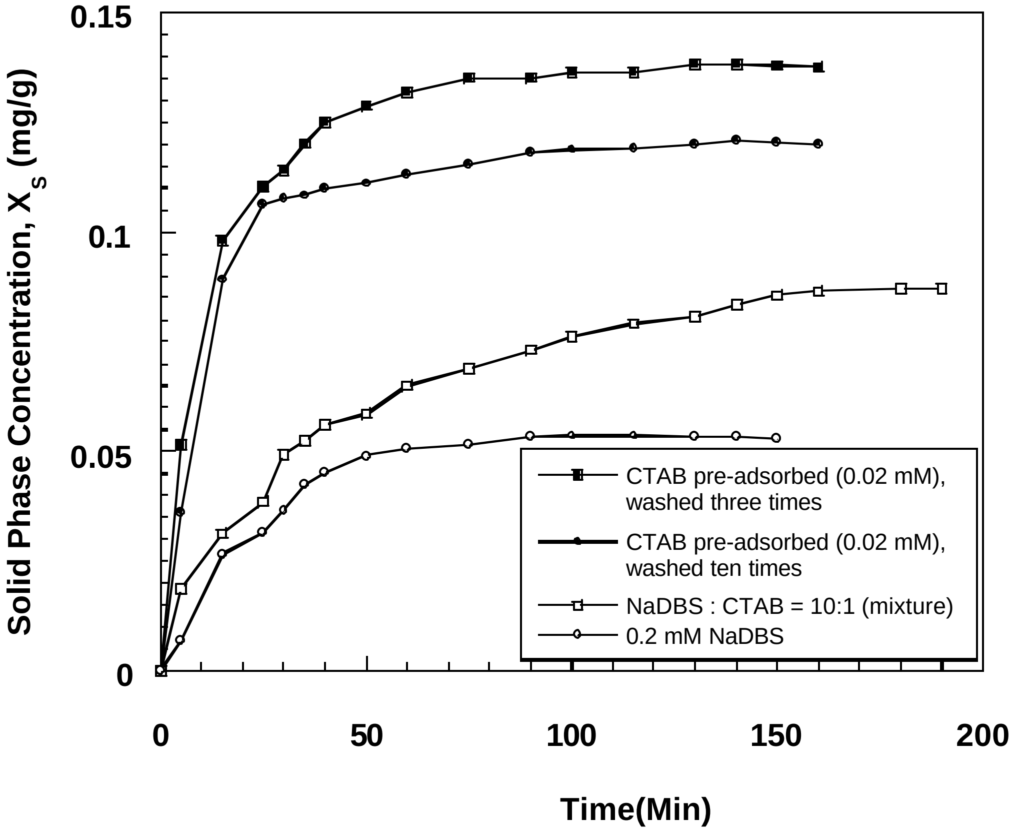


Figure-5.3: Comparison of adsorption enhancement between NaDBS (0.2 mM/L), NaDBS/CTAB mixture (10:1 mole ratio) and NaDBS (0.2 mM/L) with pre-adsorbed filter paper in 0.02 mM/L CTAB.

surface, and make the surface hydrophobic, and possibly positively charged, as a result the anionic surfactants adsorb readily. As a result, anionic surfactant, NaDBS adsorb onto both the hydrophobic and charged sites. We further observe that in case of pre-adsorbed surface, the amount of adsorption is 2-3 times more than that of bare surface. This can be explained by using two-site hypothesis proposed in chapter-4. In chapter-4 it is shown that electrical sites occupy approximately 75 % of the surface. During adsorption of CTAB, the negative electrical sites become hydrophobic or positively charged. Thus in case of pre-adsorbed surface, both sites adsorb NaDBS molecules, resulting in approximately upto four times enhancement in adsorption.

A similar comparison is presented in Figure-5.4 with one difference; this time the pre-adsorbed surfactant is TX-100, a non-ionic surfactant. We observe from this figure that unlike CTAB pre-adsorbed case, there is no enhancement in adsorption between the pre-adsorbed TX-100 and the mixture of NaDBS and TX-100. We believe such difference may indicate the presence of two types of interactions of NaDBS molecules with CTAB. These interactions are: favorable electrostatic interactions of positively charged surface, and a possible ion pair formation between anionic NaDBS and cationic CTAB molecules in the solution.

A mechanism for the two-regime adsorption is proposed. In this mechanism, a two-dimensional hexagonal honeycomb or graphite like arrangement, which may form during adsorption of anionic-cationic mixed surfactant, is shown in Figure-5.5. Organization of surfactant molecules at the solid-liquid interface has been reported earlier (Manne and Gaub, 1995; Wanless and Ducker, 1996). At the low concentration of CTAB (less than the critical concentration, C_{Crit}), it is hypothesized that 2-D hexagonal arrangement is formed with the NaDBS and CTAB molecules at the interface. Each unit cell of the structure contains four NaDBS and two CTAB molecules in regime-1. Reason for 1:1 enhancement may be due to the 2-D hexagonal arrangement. With increasing the cationic surfactant concentration (above the critical concentration, C_{Crit}), single hexagonal arrangement will form a more dense 2-D hexagonal arrangement in regime-2. The transition will be favorable due to less repulsive force between the molecules in the structure, as the anionic : cationic average molecular ratio is 1:1. The transition of the structure is the cause of 2:1 enhancement in regime-2.

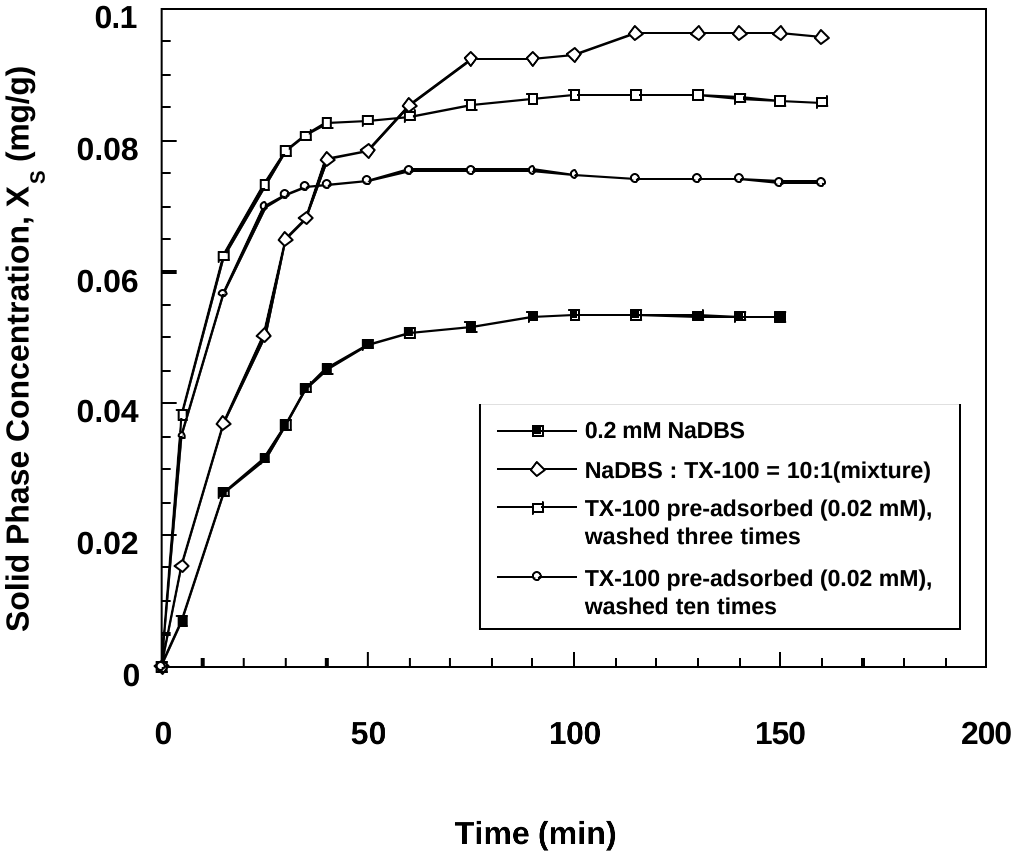


Figure-5.4: Comparison of adsorption enhancement between NaDBS (0.2 mM/L), NaDBS/TX-100 mixture (10:1 mole ratio) and NaDBS (0.2 mM/L) with pre-adsorbed filter paper in 0.02 mM/L TX-100.

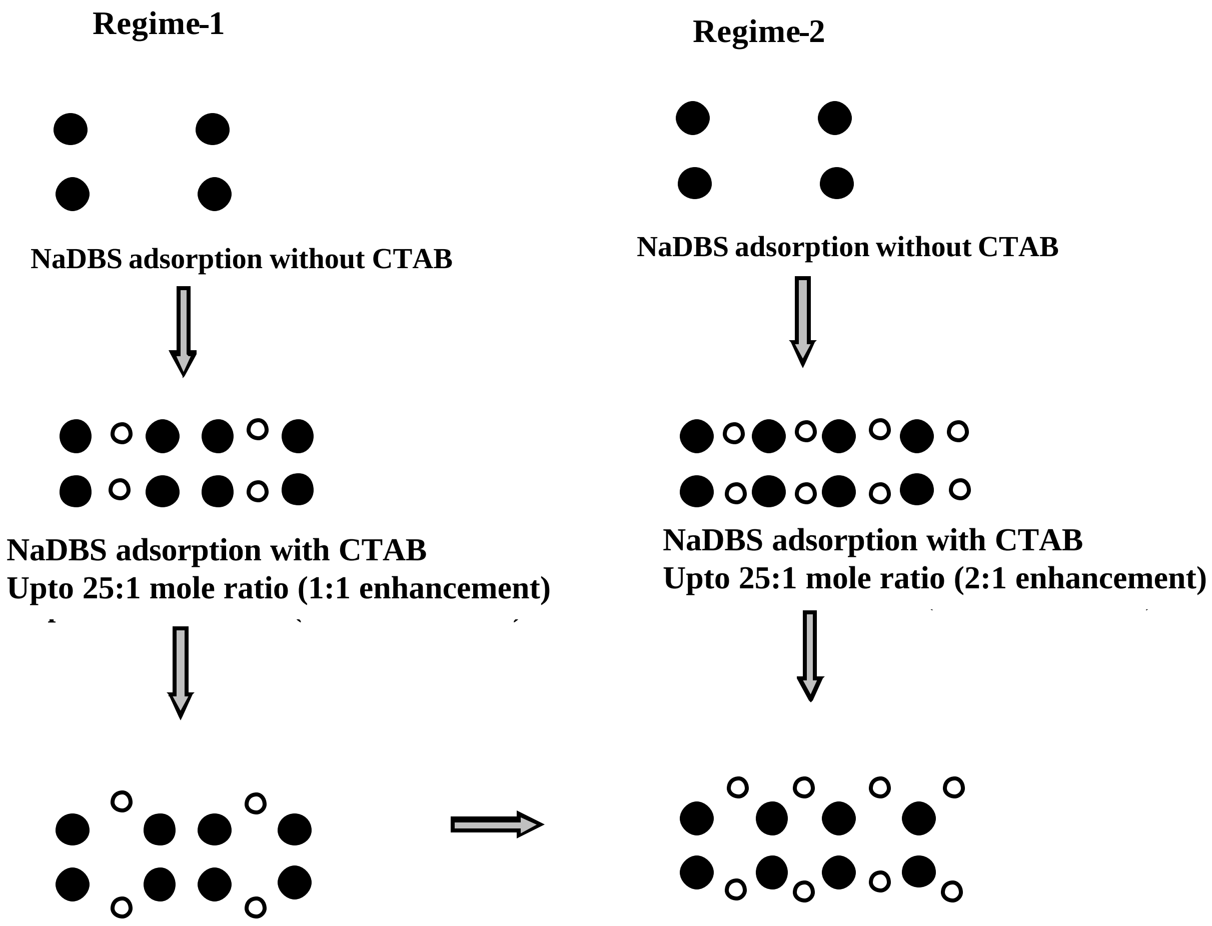


Figure-5.5: Proposed two-dimensional hexagonal honeycomb or graphite like arrangement with anionic and cationic surfactant on solid-liquid interface at two different enhancement regimes. (●),Anionic surfactant; (O), Cationic surfactant.

To support our hypothesis of 2-D lattice formation at the surface, we have carried out other measurements, which also indicate some kind of change at the interface at 25:1 mole ratio of NaDBS/CTAB.

The rate of evaporation of water per hour in percentage at different mixing ratio of NaDBS/CTAB is plotted in Figure-5.6. At 25:1 mixing ratio the rate of evaporation is minimum. Such reduced evaporation can occur if the vapor-liquid interface experience enhanced adsorption of surfactant that interferes with evaporation. The potential for enhanced adsorption can be attributed to the tendency of the organized structure formation at the interface.

Figure-5.6 shows the plot of conductivity of NaDBS/CTAB mixture at different NaDBS/CTAB mixing ratio and the sum of the conductivities of NaDBS and CTAB in the same concentration. The sum of the conductivity shows a linear plot. Significantly, the conductivity of the mixed solution shows a minimum in conductivity at 25:1 mixing ratio indicating that the maximum hydrophobicity has been generated at this mixing ratio arising out of coupling of anionic-cationic surfactant in the mixture.

Surface tension data presented in Figure-5.7 show that a minimum in surface tension at 25:1 mixing ratio arising out of maximum surfactant adsorption at the air-liquid interface.

To further probe into the possible coupling of anionic and cationic surfactant molecules the ^{1}H NMR spectra of CTAB and CTAB-NaDBS mixture were taken at room temperature in D_2O, operated at 600 MHz. We have taken 0.5 mM CTAB and added NaDBS at different mixing ratio. Figure-5.8 (a) shows the different peaks present in the CTAB molecule (Rao et al., 1987). The peak C and B corresponding to $(CH_2)_2$ and $(CH_2)_{11}$ of the $(CH_2)_{13}$ hydrocarbon chain with chemical shift (δ) of 1.4 and 1.3 respectively. The peak C occurs at higher δ due to the presence of charged head group $[N(CH_3)_3]$ of the CTAB. With increasing concentration of NaDBS progressively chemical shift (δ) of peak C shifts to lower δ (higher field), and ultimately gets merged with B, indicating some favorable interactions between the CTAB and NaDBS molecules, as shown in Figure-5.8 (b).

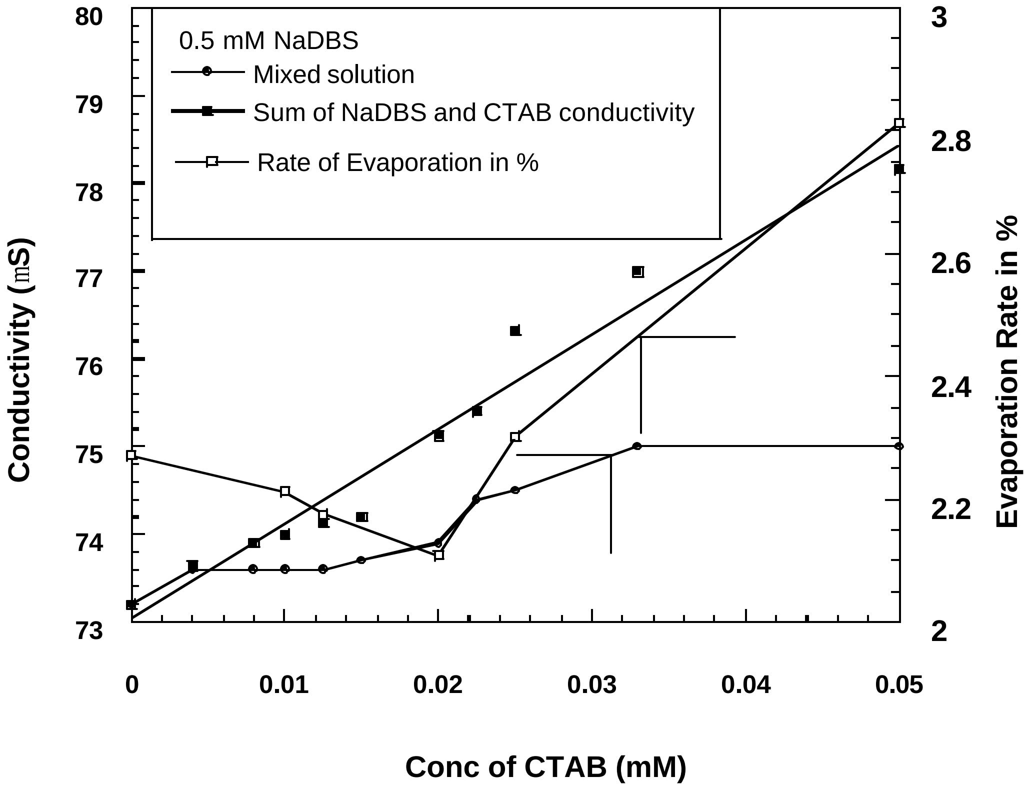


Figure-5.6: Plot of rate of evaporation of water in % per hour and conductivity from NaDBS/CTAB mixture at different NaDBS/CTAB mixing ratio.

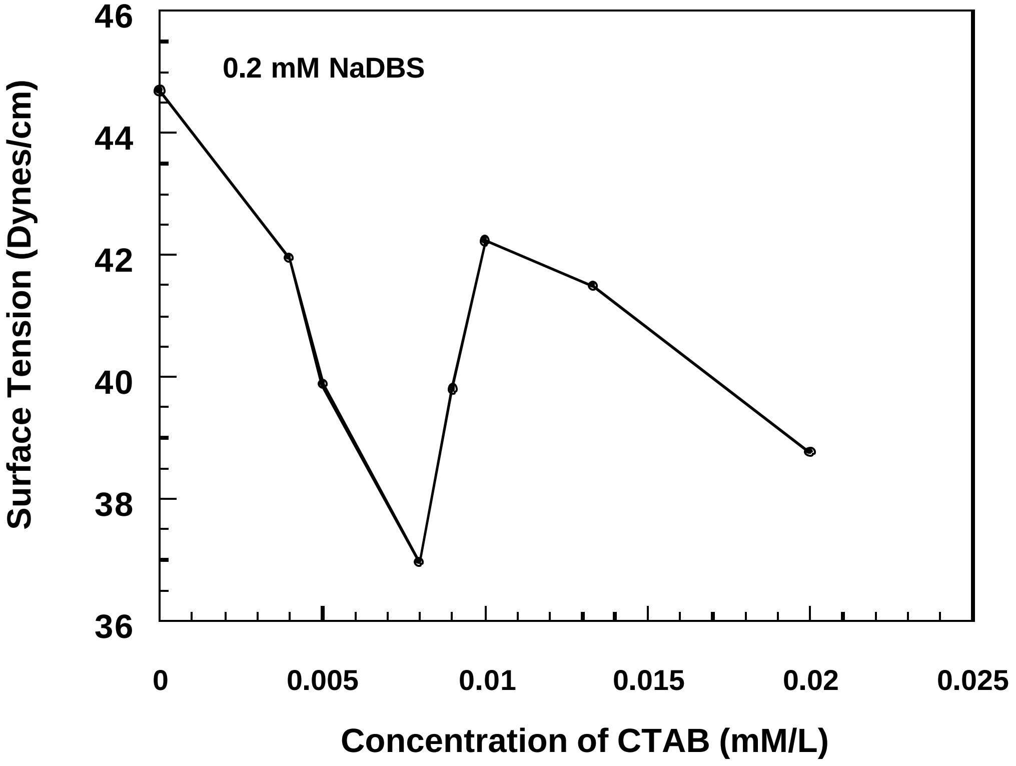


Figure-5.7: Plot of surface tension of NaDBS/CTAB mixture at different NaDBS/CTAB mixing ratio.

$\overset{F}{(CH3)_3}\text{-N-}\overset{E}{CH_2}\text{-}\overset{D}{CH_2}\text{-}\overset{C}{(CH_2)_2}\text{-}\overset{B}{(CH_2)_{11}}\text{-}\overset{A}{CH_3}$

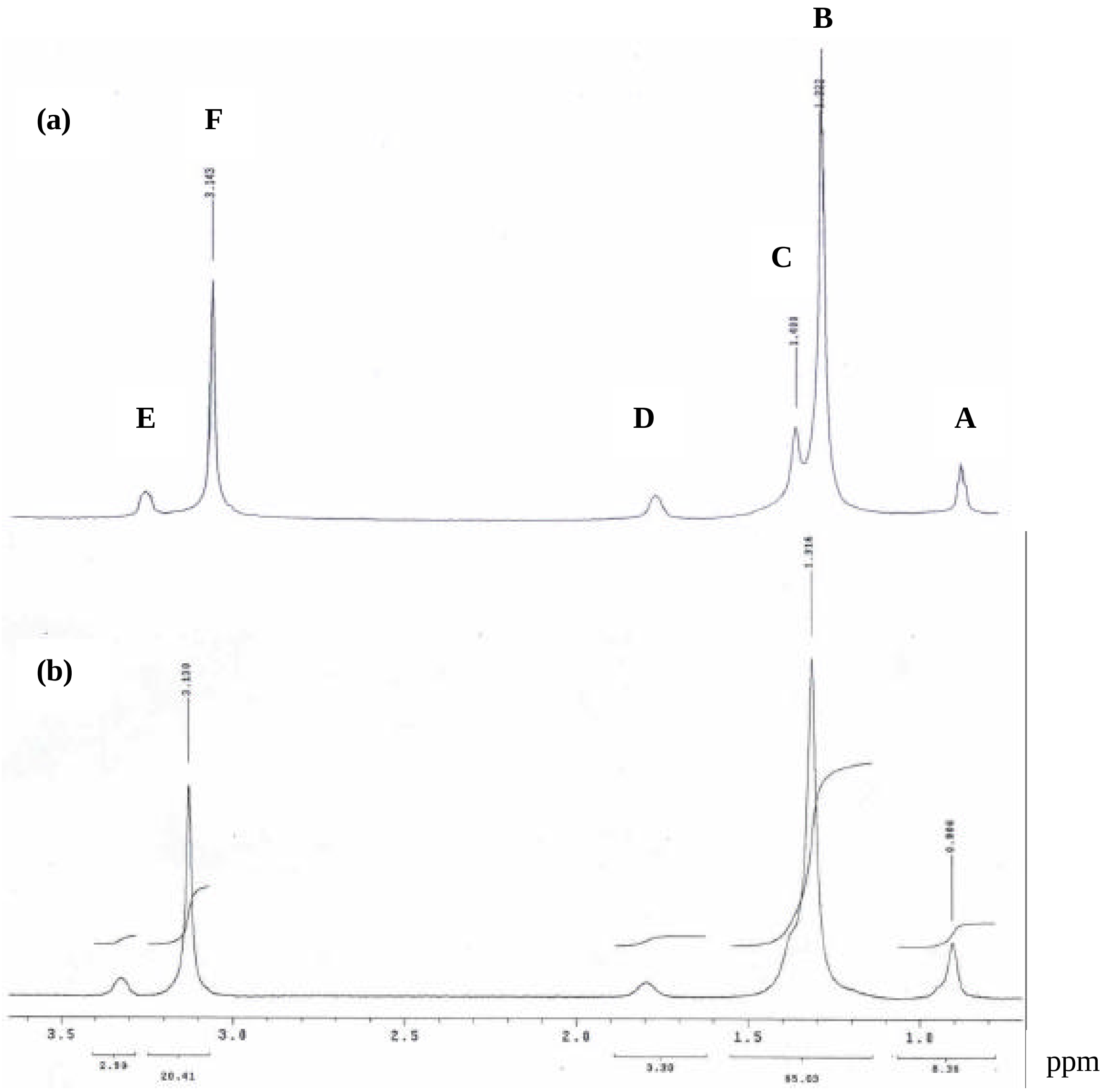


Figure-5.8: (a) ^{1}H NMR spectrum of CTAB. (b) CTAB-NaDBS mixture at 5:1 mixing ratio; CTAB concentration = 0.5mM.

5.4 Conclusions

The adsorption enhancements of anionic surfactant below the CMC, from a mixture of cationic and anionic surfactants goes through two regimes. In the first regime of the anionic-cationic enhancement, it is hypothesized that anionic and cationic surfactants from a two-dimensional hexagonal honeycomb or graphite like arrangement, which shows 1:1 enhancement. In the second regime of the enhancement it is hypothesized that anionic and cationic surfactants form a more dense hexagonal arrangement, which shows 2:1 enhancement.

Chapter-6

Role of Surfactant Adsorption in Detergency

6.1 Introduction

Detergency can be defined as removal of unwanted substance (soil) from a solid surface brought into contact with a liquid (Kissa, 1987). It is indeed a complex process due to the complex nature of textile, variety of soils present in the textile, and variety of components in detergent. A detergent contains one or more surfactants with majority of anionic surfactant and other components to enhance detergency and reduce soil re-deposition. Surfactant adsorption on both fiber and soil is the most important step in detergency. The main force responsible for removing the particulate soils from the fabric by non-mechanical means is the electrical force, as substrate (fiber) and particulate soil both are usually negatively charged in the aqueous medium. The adsorption of the anionic surfactant in the washing system further increases the negative potentials on both substrate and particulate soils and hence the removal of particulate soils enhanced. Another important role of surfactant adsorption is to provide good wetting, displacement of soil, suspension of soil etc. The combination of all these effects will show good detergency. Anionic and nonionic surfactants alone can show better performance in some specific cases but combination of two can show better detergency. Apart from the surfactant adsorption, extent of surface charge increases with increasing pH. This is one of the reasons for enhancement of wash performance by the introduction of alkali. However, repulsive forces between soil and fibers alone are insufficient to produce satisfactory washing even at high pH. Surfactant adsorption is essential for wetting of particulate agglomerate and substrate. This effect is particularly important for hydrophobic particulate soils where little wetting occur in the absence of a suitable surfactant.

In practice, in addition to electrical force, some mechanical forces also influence the soil removal. During laundering, increasing temperature (Morris and Prato, 1982) and mechanical action (Bacon and Smith, 1948) increases the particulate and oily soil removal. Hydrodynamic force during laundering also facilitates the soil removal. The effect of hydrodynamic forces is dependent on the particle size. Their significance in the removal of particulate soil from fibers increases as particle size increases.

In the previous three chapters adsorption of surfactants on cellulose water interface has been studied under different conditions. In this chapter an attempt has been made to study the relation between detergency and surfactant adsorption under different conditions.

6.2 Experimental Section

6.2.1 Materials

Anionic surfactant, Sodium dodecylbenzenesulfonate (NaDBS) was obtained from Fluka Chemicals. Calcium chloride di-hydrate was obtained from E. Merk (India) Ltd., Potassium chloride, Sodium carbonate and Sodium hydroxide was obtained from S. D. Fine-Chem Ltd, India. Deionized water was used for the detergency test.

6.2.2 Methods

Two types of artificially soiled cotton, terrace (soiled with carbon black particulate) and

WFK-10D (mixed oily and particulate soil) were used for the detergency experiments. The WFK-10D contains kaolin + lampblack + black and yellow iron oxide as particulate soil and wool fat oily soil (Schott, 1975). Each swatch was cut into 8×8 cm small pieces. A reflectometer (Gretagmacbeth, Model- 7000A) was used to measure reflectance before and after the detergency tests. Reflectance was taken at 460 nm wavelength excluding UV absorbance. The instrument was standardized using standard white ceramic plate. The swatches were make four fold and reflectance were taken as the average of four places of each swatch before and after detergency. Detergency experiments were done in an Atlas Launder-Ometer. The Launder-Ometer has eight steel jars including nine steel balls in each jar. Launder-Ometer was run at 45 r.p.m and 28 ^{o}C for 40 minute. For the detergency experiment, five swatches of each sample were taken in the jar, then the swatches were soaked for 30 minute in the surfactant solution. After completing the laundering for 40 minute each swatch was rinsed for four times with fresh deionized water. The swatch was then dried in a rotary drier and final reflectance was measured. The change in reflectance before and after detergency, ΔR, were used to measure detergency.

6.3 Results and Discussion

6.3.1 Influence of surfactant adsorption in detergency

Figure-6.1 shows the plot of ΔR with varying NaDBS concentration using two different types of soiled cotton, terrace and WFK-10D. Figure-6.1 also presents the adsorption isotherms of NaDBS onto filter with and without Na_2CO_3. Adsorbent concentration was used 100 g/l and 9.5 mM Na_2CO_3 was used to maintain alkaline pH (pH = 10-11). From the Figure-6.1 we observe that in both the cases of soiled cottons the maximum in detergency occur virtually at the same concentration at which the maximum in adsorption occur with increasing the concentration of surfactant. It also can be concluded that if other parameters are kept constant, the extent of detergency increases with the increase in surfactant adsorption. It can be noted here that, in general, a maximum in detergency may occur, in a binary mixture of surfactants of different CMC. The commercial detergents

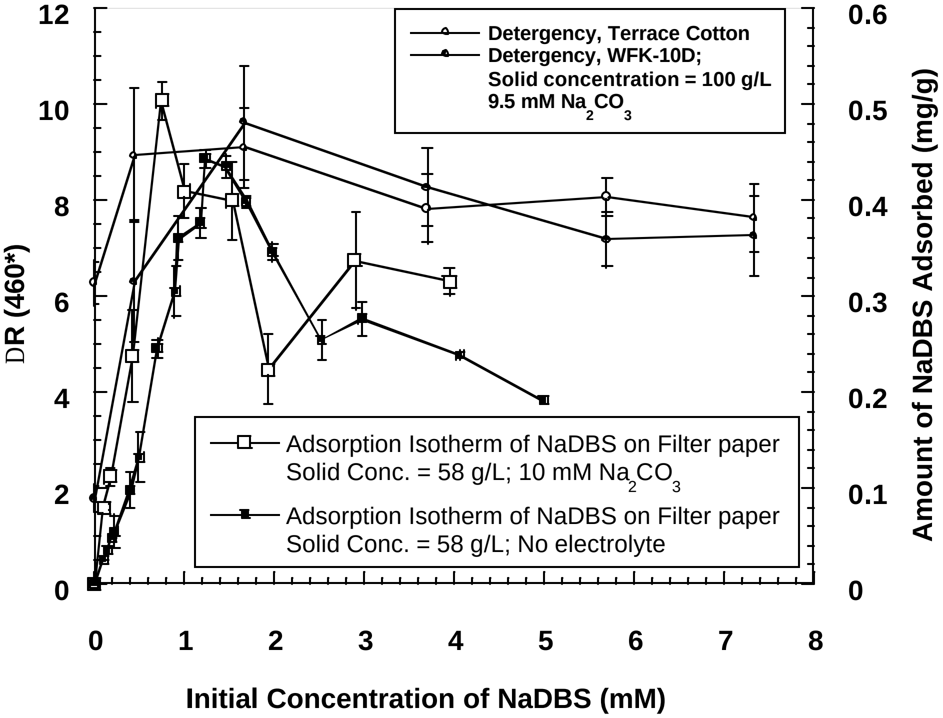


Figure-6.1: Relation between adsorption isotherm of NaDBS on cellulose-water interface and detergency of terrace and WFK-10D.

in general, contain mixture of different surfactants to improve the efficiency of the detergent. Improvement of detergency may result from the enhancement in adsorption. It should be further noted that maximum adsorption occurs at a particular concentration and this concentration is the optimum concentration of surfactant in detergent mixture.

Another correlation between detergency and surfactant adsorption is presented in Figure-6.2. From this figure we observe that with increasing solid content to 200 mg/lit, the maximum in detergency disappears. This observation is consistent with the effects of solid-liquid ratio on the adsorption isotherm of NaDBS. Thus, it appears that the maximum in adsorption gives rise to the maximum in detergency.

6.3.2 Influence of electrolyte in detergency

Figures-6.3 (a) & (b) show the detergency of terrace and WFK-10D cotton with and without the presence of 100 mM KCl respectively at pH 10 – 11. The pH was maintained by adding 9.5 mM Na_2CO_3. Figure-6.3 presents an interesting observation. From the figures we observe that the detergency of terrace cotton decreases in presence of KCl. The detergency, however, increases for WFK-10D cotton. Figure-4.12 shows the adsorption isotherm of NaDBS in presence of KCl. Figure-4.12 shows the extent of adsorption of NaDBS enhanced 275 % in presence of 100 mM KCl. The reason for enhancement is the negative charge of the surfactant molecules is shielded by the Na^+ ions. In addition, the compressed electric double layer at the cellulosic surface shields the charge. Consequent to this charge shielding, the adsorption of surfactant molecules on to cellulosic surface does not experience any inhibition arising out of electrical repulsion. The explanation of decreasing detergency in terrace cotton can be attributed to the decrease of electrical double layer force. The addition of neutral electrolyte causes a decrease of the repulsive force between the soil and substrate, and as a result removal of particulate soil becomes difficult, although adsorption of surfactant is enhanced on both the soil and fabric surface. In addition, it is reported that deposition of particle, suspended in a moving phase, onto a surface increases dramatically with ionic strength (Marshall

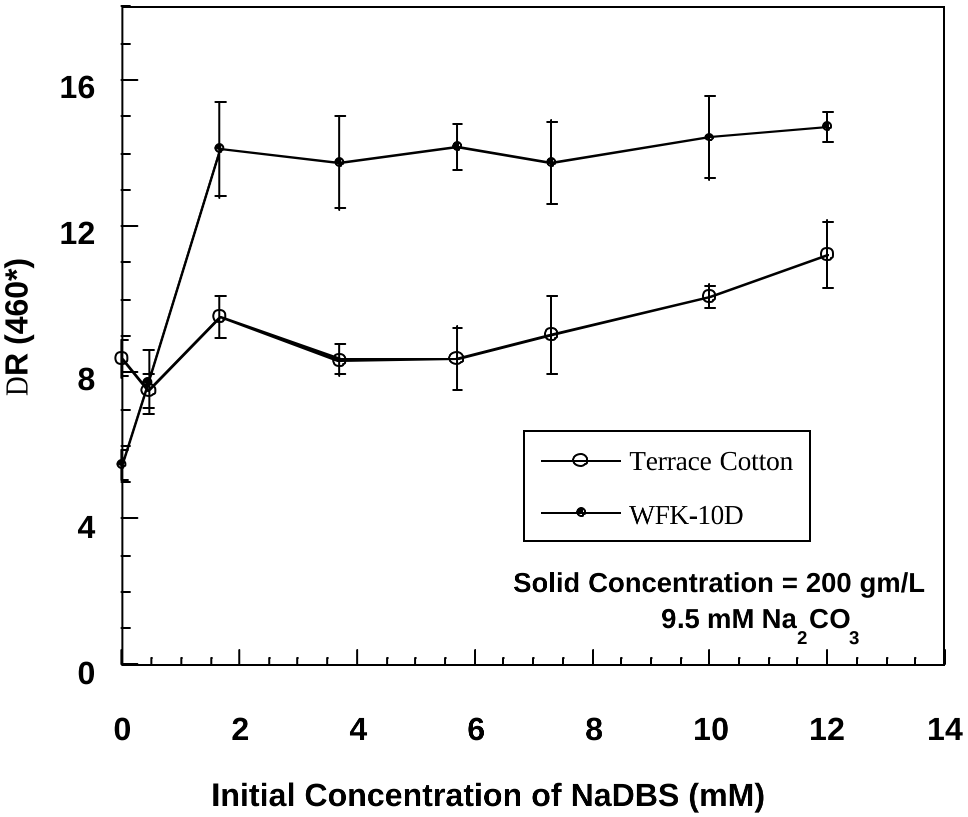


Figure-6.2: Effect of solid-liquid ratio in detergency.

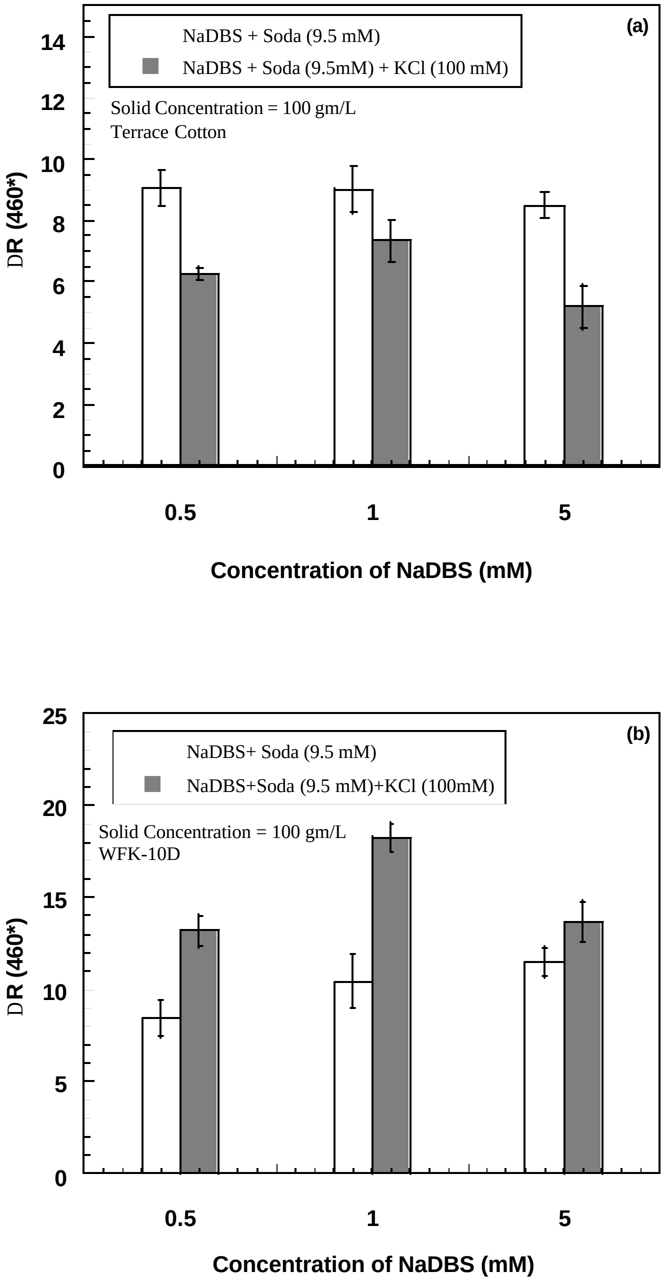


Figure-6.3: (a) Effect of ionic strength in detergency of NaDBS, terrace cotton. (b) Effect of ionic strength in detergency of NaDBS, WFK-10D cotton.

and Kitchener, 1966; Hull and Kitchner, 1969; Clint et al., 1973) and the removal of particle decreases (Sharma et al., 1992).

Detergency with WFK-10D cotton is found to increase with increasing electrolyte concentration. The reason is as follows. For the case of composite soil not only electrical double layer but also surfactant adsorption plays an important role. In the composite soil, particulate is hydrophobic in nature and contains oil. Hence, for the removal of composite soil, enhancement of surfactant adsorption plays an important role in wetting of fiber and soil leading enhancement in detergency. Therefore, detergency of composite soil increases in presence of electrolyte since adsorption of surfactant is also enhanced on both the soil and fabric surface.

6.3.3 Influence of pH in detergency

Figures-6.4 (a) and (b) show the effects of pH on detergency of terrace and WFK-10D cotton respectively. We observe from the figures that for both the samples, detergency increases in alkaline pH. In presence of alkaline pH negative surface charge of soil and fiber increases than the neutral pH (Schott, 1972). So, it is expected that the adsorption of anionic surfactant decrease with increasing pH at the negatively charged surface. Effect of pH on adsorption of NaDBS on cellulose water interface has been discussed in Chapter-4 (Figure-4.15). With increasing pH, removal of particulate soil is facilitated due to the increase in repulsive force between fiber and soil. There is a balance between decrease in electrical repulsive force due to less adsorption of anionic surfactant and increase in electrical repulsive force due to increase in pH. This result is consistent with DLVO theory. Sharma et al. (1992) have found that removal of negatively charged glass particle from the negatively charged surface gets enhanced at higher pH, which is consistent with our observation. Essentially similar results are obtained for all major particulate soils. This is one of the reasons for enhancement of wash performance by simple introduction of alkali (Jakobi and Löhr, 1987). However, repulsive forces between soil and fibers alone are insufficient to produce satisfactory washing even at high pH.

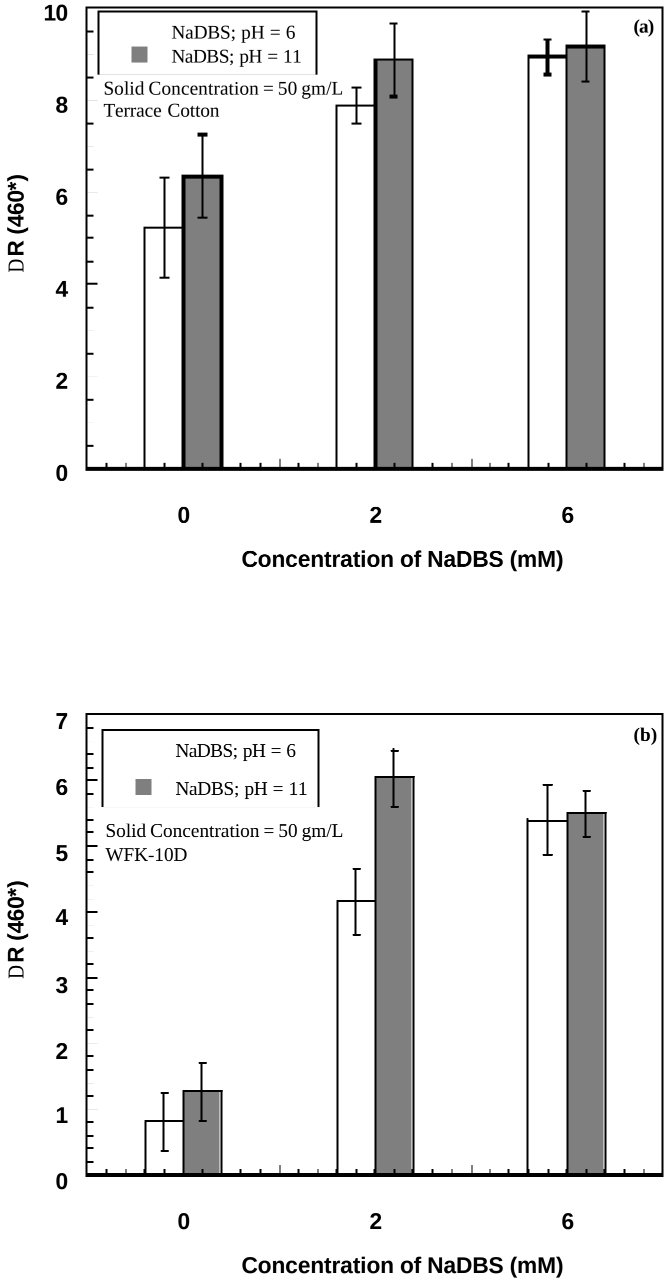


Figure-6.4: (a) Effect of pH in detergency of NaDBS, terrace cotton. (b) Effect of pH in detergency of NaDBS, WFK-10D cotton.

6.3.4 Influence of calcium ion in detergency

Figure-6.5 (a) & (b) presents the effect of calcium ion in detergency in neutral pH medium using terrace and WFK-10D cotton. Detergency experiments were done at two different calcium ion concentration, NaDBS:Ca^{++} = 1: 0.12 and 1:0.18 similar to that of adsorption experiments. We observe from Figure-6.5 (a) that for detergency of terrace cotton, presence of Ca^{++} ions has virtually no effect. If at all, there seems to a small decrease at higher concentration of surfactant. Interestingly, the presence of Ca^{++} ions considerably enhances the detergency in case of WFK-10D, at higher concentration of surfactant.

The role of Ca^{++} ions in detergency seems to be two fold: one is related to the adsorption of surfactant and the other is related to the adherence of particle to the fiber. Ca^{++} ions enhance the adsorption and thereby increase the detergency. However, it also forms bridge between particulate soil and fiber, thus enhancing the force of adherence, resulting in decrease in detergency.

The effect of calcium ion at alkaline pH for terrace and WFK-10D are presented in Figures-6.6 (a) & (b). Terrace cotton shows there is no change in detergency at alkaline pH with and without calcium ion. WFK-10D shows small decrease in detergency at lower surfactant concentration but at higher surfactant concentration the effect is negligible. Overall, the presence of Ca^{++} ions has weak effects, if at all, on the detergency.

6.4 Conclusions

1. Terrace and WFK-10D show maximum in detergency with NaDBS at alkaline pH nearer to CMC. This maximum in detergency is very similar to maximum in adsorption on cellulose-water interface due to presence of short chain surfactant impurity. At higher solid-liquid ratio, maximum in detergency disappears which is consistent with the effect of solid-liquid ratio on the adsorption.

2. The effects of electrolyte influences both on double layer force and adsorption are different for the two types of soil. It adversely affects the detergency of terrace

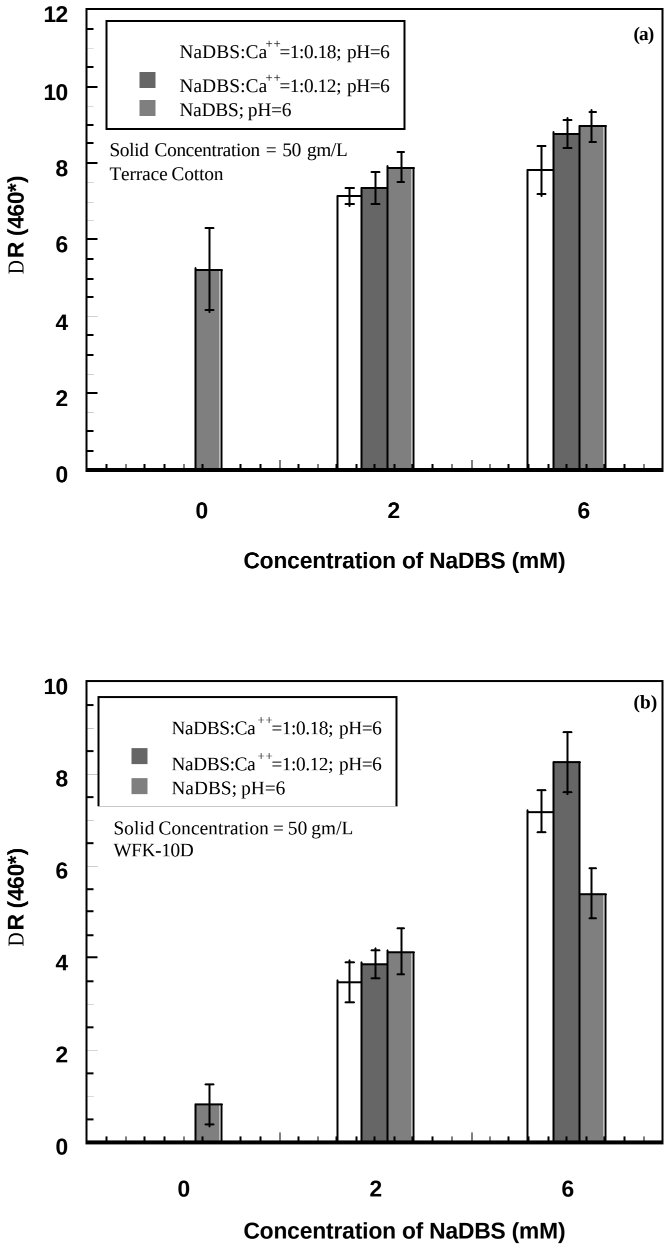


Figure-6.5: (a) Effect of calcium ion in detergency of NaDBS at neutral pH, terrace cotton. (b) Effect of calcium ion in detergency of NaDBS at neutral pH, WFK-10D cotton.

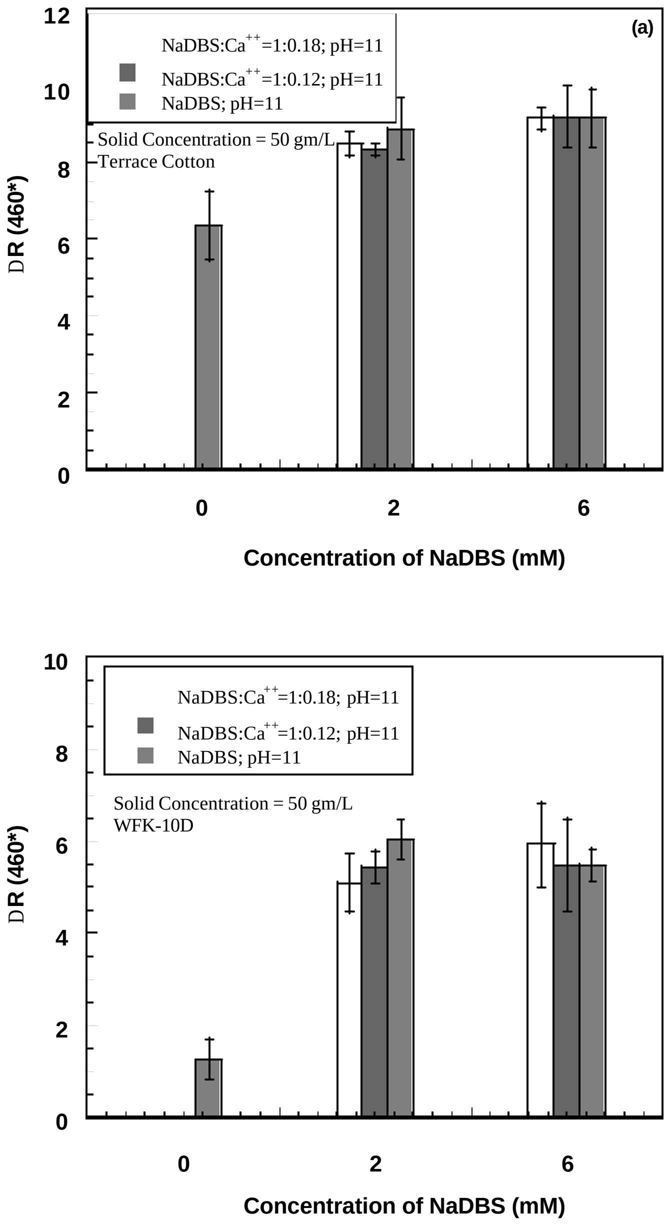


Figure-6.6: (a) Effect of calcium ion in detergency of NaDBS at pH = 11, terrace cotton. (b) Effect of calcium ion in detergency of NaDBS at pH = 11, WFK-10D cotton.

cotton, while it promotes the detergency of WFK-10D. Terrace cotton detergency is reduced due to the decrease in electrical double layer force. The enhancement in the detergency of WFK-10D can be attributed to the increase in adsorption that significantly influences the removal of this type of soil. In presence of alkaline pH detergency of both terrace and WFK-10D increases.

3. Presence of alkaline pH removal of particulate soil facilitate due to the increasing repulsive force between soil and fabric. The composite soil shows similar effect in presence of alkaline pH.
4. Effect of divalent calcium ion is very weak in detergency in presence of alkaline and neutral pH for both terrace and WFK-10D cotton, due to enhancement in the adhesion force of soil and fabric as the bivalent calcium ion acts as a bridging agent.

Chapter-7

Conclusions and Suggestions for Future Work

7.1 Conclusions

Studies have been conducted to gain understandings and generic knowledge on the kinetics and equilibrium aspects of adsorption of different surfactants onto the cellulose-water interface. The effects of various pertinent parameters on the adsorption of a number of surfactants have been measured and these measurements have been analyzed by means of modeling and hypotheses. The work has resulted in further understandings of this specific adsorption phenomenon. The findings are presented below.

In Chapter-3, adsorption kinetics of anionic surfactant, NaDBS, nonionic, TX-100, and cationic, CTAB, on cellulose water interface have been studied. CTAB is found to adsorb rapidly and to a higher extent than NaDBS and TX-100, with NaDBS showing the least adsorption. Adsorption of CTAB is rapid due to the favorable electrical interactions adsorption of cationic surfactant onto a negatively charged cellulose surface. It is hypothesized that cellulose surface contains two type of sites, negatively charged hydrophilic sites and electrically neutral hydrophobic sites. Cationic surfactants are preferably adsorbed on the hydrophilic site, where as anionic, and nonionic surfactants adsorb onto the hydrophobic site. Anionic surfactant in presence of salt adsorb onto the both sites. Adding of electrolytes such as KCl and $CaCl_2$, enhances the adsorption of NaDBS. At a particular concentration of surfactant with increasing concentration of electrolyte, the amount adsorbed increases and then levels off. The valency of co-ion does not have any effect on adsorption of NaDBS on cellulose-water interface. In presence of mixed salt at low concentration of KCl, addition of $CaCl_2$ enhances the rate of adsorption of NaDBS but at high concentrations of KCl addition of $CaCl_2$ decreases the rate of adsorption of NaDBS. A two-site model is developed to describe the experimental kinetics data successfully.

Chapter-4 deals with the equilibrium adsorption isotherms of NaDBS, CTAB and TX-100, which show that the isotherms cannot be described by simple Langmuir type isotherm. Rather, it shows a typical four-region isotherm. The presence of maximum in region IV can be attributed to the presence of shorter chain surfactant molecules for NaDBS. CTAB and TX-100 molecules show hemimicelle formation while NaDBS molecules do not form hemimicelles. Adsorption of cationic molecules, CTAB and methylene blue is strong, indicating that the charged sites on filter paper surface are negative and they dominate over the smaller number of hydrophobic sites. Detailed analysis indicates 25% that of sites are hydrophobic in nature and rest are negatively charged sites. Studies on the effect of salts, Ca^{++} and K^{+}, on NaDBS adsorption confirm the above conclusions. Ca^{++} ions may form 'bridges' between the head group of NaDBS and the charged sites of filter paper thus enhancing the extent of adsorption. Area per molecule estimated from the adsorption isotherm data indicate that methylene blue molecules adsorb densely on the anionic sites of filter paper. NaDBS molecules do so only in presence of Ca^{++} and K^{+}. NaDBS and TX-100 molecules adsorb on the hydrophobic sites and CTAB molecules adsorb on both sites.

Chapter-5 is concerned with the adsorption enhancements of anionic surfactant below the CMC, from a mixture of cationic and anionic surfactants, which show two distinct regimes. First regime of the anionic-cationic enhancement, anionic and cationic surfactants are forming two-dimensional hexagonal honeycomb or graphite like arrangement, which shows 1:1 enhancement. In the second regime of the enhancement it is hypothesized that anionic and cationic surfactants are forming more dense hexagonal arrangement, which shows 2:1 enhancement.

Chapter-6 presents the results on the application of surfactant adsorption to detergency. Detergency of two different soiled cotton, terrace and WFK-10D show maximum in detergency with NaDBS at alkaline pH nearer to CMC. This maximum in detergency is very similar to maximum in adsorption on cellulose-water interface due to presence of short chain surfactant impurity. At higher solid-liquid ratio maximum in detergency disappears, as does the maximum in adsorption. Increasing ionic strength of the laundering medium, detergency of terrace cotton is reduced but that of WFK-10D is enhanced. In presence of mono-valent electrolyte, detergency of terrace cotton is reduced due to decreasing repulsive energy barrier of the electrical double layer of soil and substrate. For WFK-10D detergency is enhanced as the adsorption of NaDBS increases. In presence of alkaline pH, detergency of both terrace and WFK-10D increases. Effect of divalent calcium ion is negligible in detergency for both terrace and WFK-10D cotton.

7.2 Suggestions for Future work

Following suggestions are made for the future work.

- Kinetics of adsorption of NaDBS and TX-100 above the CMC need to be studied in absence and presence of salt, to obtain a broader understanding of the phenomenon.
- In the two-site kinetic model diffusion term is neglected. More rigorous general model can be developed assuming two-sites present in the adsorbent and also diffusion term taking into account.
- Rate constants of anionic surfactant in presence of salt, cationic and nonionic surfactants need to be explained more quantitatively. Attempts should be made to develop theories for them.
- The HPLC analysis of NaDBS shows the NaDBS used is a mixture of different chain length or isomers. Different chain length compounds can be identified using the standard samples, and by means of other analysis.
- Formation of arranged adsorbed structure from the mixture of anionic-cationic surfactant could be studied using Atomic Force Microscopy and other techniques.

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