STUDIES ON ADSORPTION OF SURFACTANTS ON SOLID-LIQUID INTERFACE AND ITS IMPORTANCE IN SLURRY-RHEOLOGY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
in
Chemical Engineering

By
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Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "STUDIES ON ADSORPTION OF SURFACTANTS ON SOLID-LIQUID INTERFACE AND ITS IMPORTANCE IN SLURRY-RHEOLOGY" submitted by Sri Suvra Das & Sri Bikash Ranjan Sahoo in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Suvra Das

2.5.2007 **Bikash Ranjan Sahoo**

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ABSTRACT

The knowledge of rheological properties for different materials for slurry preparation is of great importance. These topics are studied and severely important for several technical applications e.g. process control in chemical engineering, casting of ceramics, storage, transport of solids in pipelines and atomization. A literature on the change in rheological properties of coal water slurry is reviewed. The adsorption effect of surfactants like cationic, anionic and non-ionic on the solid liquid interface is investigated. The rheological behaviors of kaolin-water slurry are experimented by using a rotational viscometer (Brookfield syncrolacto viscometer) with different solid concentrations. These experiments are conducted under a particular speed (in rpm) of the spindle, temperature and ph condition. The adsorption kinetics for the three different surfactants at their CMC values is studied for different amount of kaolin (in wt %) using a UV spectrophotometer. The cause of change in viscosity is investigated with the out coming results of the experiments and found that cationic and anionic surfactants affect the kaolin-water slurry rheology severely.

Keywords: adsorption; kaolin-water slurry; rheology; surfactants.

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Chapter 1

GENERAL INTRODUCTION

1.1 Introduction

Adsorption is a technique that is used in many different fields. It involves the accumulation of solute molecules at an interface. The surface characteristics of coal may be altered significantly by the adsorption of a surface active agent on the coal surface. Reagent usage and type of coal are important factors in coal cleaning processes, coal-liquid mixtures and the dewatering characteristics of slurries.

The separation performance and rheological behavior of coal-liquid mixtures are affected by reagent adsorption on the fine coal particles as well as the nature of solid particles. The degree and extent of adsorption may significantly affect the performance of the process. The adsorption of chemical reagents on coal surfaces is markedly affected by the functionality of the solid surface, the molecular structure of the surfactant (the nature of the head group and tail part) being adsorbed and the properties of the aqueous phase. Much research has been conducted on the adsorption of chemical reagents on solid-liquid interface. Anionic, cationic and non-ionic surfactants were used to show their adsorption behaviour. The effects of various parameters on the adsorption process such as the pH, the presence of electrolytes, the rank of coal and temperature were studied.

Coal particles that have been rendered mutually repulsive through the adsorption of ionic or nonionic surfactant form a well-dispersed suspension characterized by low viscosity. The thicker the adsorption layer, the more the coal particles are prevented from interaction which favors the dispersion of coal particles resulting in the reduction of the viscosity of CWS. Therefore, an understanding of the mechanism of adsorption of surfactants on coal is essential for the preparation of highly concentrated coal–water slurry (HCCWS) of the desired viscosity with good sedimentation stability.

Desirable rheological properties can be obtained by suitable selection of the coal and mixing of coarsely and finely ground particles in an appropriate ratio. Previous work has revealed that the CWS viscosity is closely related to a number of physical and chemical variables such as parent coal properties, particle size and distribution, type of dispersing agent, solids volume fraction and slurry temperature. The present report describes an investigation of the effect of the addition of anionic, cationic and non-ionic surfactants on kaolin water slurry.

1.2 Surfactant Adsorption

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:

- 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.
- 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.

1.3 General Structural Features and Behavior 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 physicochemical properties have been observed in aqueous solution of surfactants. These changes are illustrated schematically in Figure-1.1 [1]. 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.

A characteristic of the micelle is the relative sharpness of concentration above which it appears. Measurement of the size and shape of micelles has carried out remarkably by light-scattering techniques. Micellar sizes have been reported over a range of from 10 to 20 monomers to many thousands. With a given surfactant the size of the micelle depends on:

- The temperature
- The concentration of surfactant to a very limited extent
- The concentration and nature of added electrolytes and non-electrolytes

1.4 Types of Surfactants

There is a broad range of different surfactant types, each with unique properties and characteristics: the type of dirt and fabric on which they work best, how they can cope with water hardness. Detergents use a combination of various surfactants to provide the best possible cleaning results. There are four main types of surfactants used in laundry and cleaning products. Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic or amphoteric/zwitterionic family.

1.4.1 Anionic surfactants

In solution, the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. Still, they can react in the wash water with the positively charged water hardness ions (calcium and magnesium) , which can lead to partial deactivation. The more calcium and magnesium Molecules in the water, the more the anionic surfactant system suffers from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrants) and more detergent should be dosed in hard water.

The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps.

1.4.2 Cationic surfactants

In solution, the head is positively charged. There are 3 different categories of cationics each with their specific application:

In fabric softeners and in detergents with built-in fabric softener, cationic surfactants provide softness. Their main use in laundry products is in rinse added fabric softeners, such as esterquats, one of the most widely used cationic surfactants in rinse added fabric softeners. An example of cationic surfactants is the esterquat. In laundry detergents, cationic surfactants (positive charge) improve the packing of anionic surfactant molecules (negative charge) at the stain/water interface.

This helps to reduce the dirt/water interfacial tension in a very efficient way, leading to a more robust dirt removal system.They are especially efficient at removing greasy stains. An example of a cationic surfactant used in this category is the mono alkyl quaternary system. In household and bathroom cleaners, cationic surfactants contribute to the disinfecting/sanitizing properties.

1.4.3 Non-ionic surfactants

These surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dishwashing liquids.

Most laundry detergents contain both non-ionic and anionic surfactants as they complement each other's cleaning action. Non-ionic surfactants contribute to making the surfactant system less hardness sensitive. The most commonly used non-ionic surfactants are ethers of fatty alcohols.

1.4.4 Amphoteric/zwitterionic surfactants

These surfactants are very mild, making them particularly suited for use in personal care and household cleaning products. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis.

These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties. An example of an amphoteric/zwitterionic surfactant is alkyl betaine.

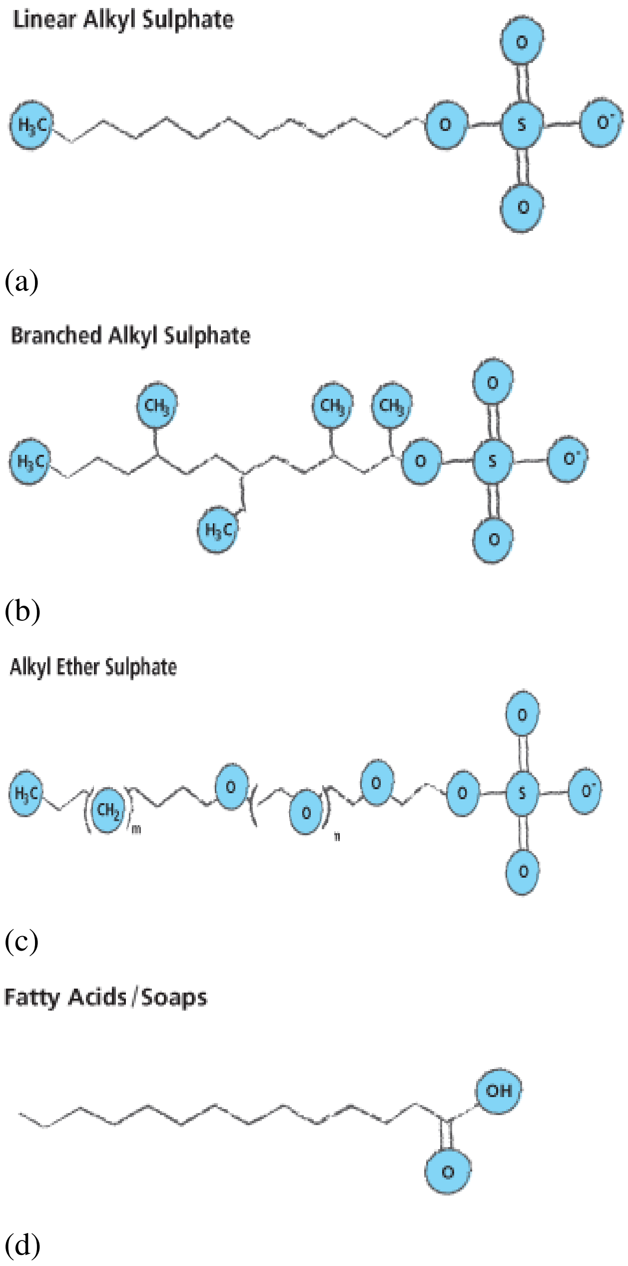


FIG1.1: Chemical Structures of different types of surfactants: (a) Linear Alkyl Sulphate, (b) Branched Alkyl Sulphate,(c)Alkyl Ether Sulphate,(d)Fatty Acids/Soaps

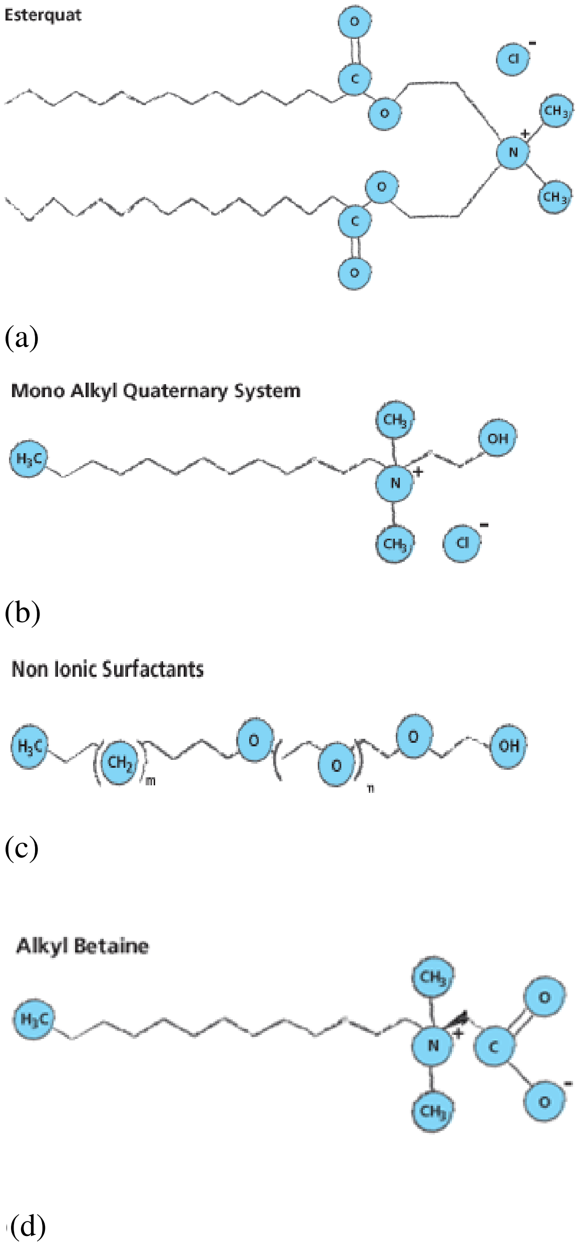
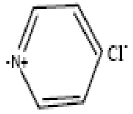


FIG 1.2:Chemical Structures of different types of surfactants:(a)Esterquat,(b)Mono Alkyl Quaternary System,(c)Non Ionic Surfactants,(d)Alkyl Betaine

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

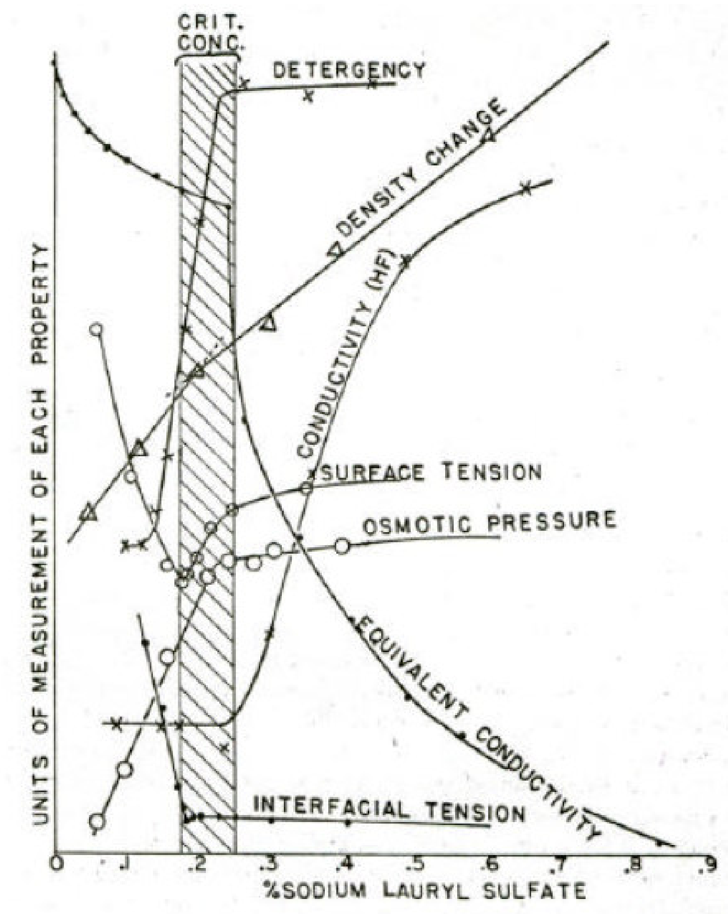


FIG1.3: Physical properties for Sodium Dodecyl Sulfate at 25-28^{0}C (Preston 1948)

The onset of micellization was originally inferred from the marked changes in the thermodynamic properties by which it is accompanied. Below the CMC deviations from ideality in the solutions are relatively small: osmotic pressure, density change etc. Above CMC, however, the increase in such properties with increased surfactant concentration is much smaller than below the CMC that in the thermodynamic view it is markedly non-ideal.

1.5 Applications of Surfactant Adsorption at Solid-Liquid Interface:

1.5.1 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.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.

1.5.2 Mineral/particulate flotations

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 [3] 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.

1.5.3 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 breakthrough 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 [3].

1.5.4 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 adjutants, 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) [4] 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.

1.5.5 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 [5].

1.5.6 Modifications of kaolin through chemical treatment with surfactants

Wetting, dispersion, flow properties, and general physical-chemical behavior are most important in the organic medium into which the kaolin is to be utilized. Thorough wetting of kaolin by the vehicle is essential in order to derive maximum utility and functionality. Wetting breaks down the attractive forces between kaolin particles and facilitates the coating of each particle with the wetting medium. Even though wetting is complete, dispersion will not necessarily be the ultimate, because the attractive forces between kaolin particles may still be effective across interfaces causing loose agglomeration of the particles. Flow properties are closely related to wetting and dispersion. Inter particle attraction produced by unlike surface charges causes the formation of an internal structure which inhibits flow and gives rise to thixotropy. Uniform wetting and good dispersion tend to give flow properties which approach Newtonian and dilatant systems. Improvements in functionality of kaolin fillers after surface modifications have been noted in the ink, paint, rubber, and plastics industries.

1.5.7 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 especially when the system has high ionic strength [7].

1.6 Organization of project report

Preliminary introduction about surfactant adsorption, general behaviour of surfactants, types of surfactants, application of surfactants and organization of project report is discussed in chapter 1. Chapter 2 provides a detailed discussion of literature on mechanism & techniques of adsorption, effects of surfactants on solid-liquid interface, adsorption isotherm and adsorption of ionic & non-ionic surfactants. The main objective of the present work, which is based on the literature survey on kaolin and its general properties, is presented towards the end of chapter 2. In chapter 3, the various techniques used in the present work such as materials used, surfactant analysis, adsorption & rheological experiments are described in detail. Chapter 4 describes the results of adsorption of surfactants in kaolin-water slurry. Finally, conclusions of project work are given in Chapter 5.

Chapter 2

LITERATURE REVIEW

2.1 Adsorption of surfactants at solid-liquid interface

The adsorption of surfactants at the solid/liquid interface is strongly influenced by the number of factors:

- The nature of structural groups on the solid surface, i.e. highly charged sites or non-polar sites.
- The nature of surfactant molecule i.e. the nature of hydrophilic (ionic or nonionic) or hydrophobic groups.
- The environment of the aqueous phase i.e. presence of electrolyte, pH and presence of other additives.

2.2 Mechanisms of adsorption

There are several mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution. According to Griffith and Alexander [8], adsorption of surfactants involves single ions rather than micelles. These involve:

(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. 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 [9],

$$C_S = \frac{C_{SM} C_b}{k + C_b} \qquad 2.1$$

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.

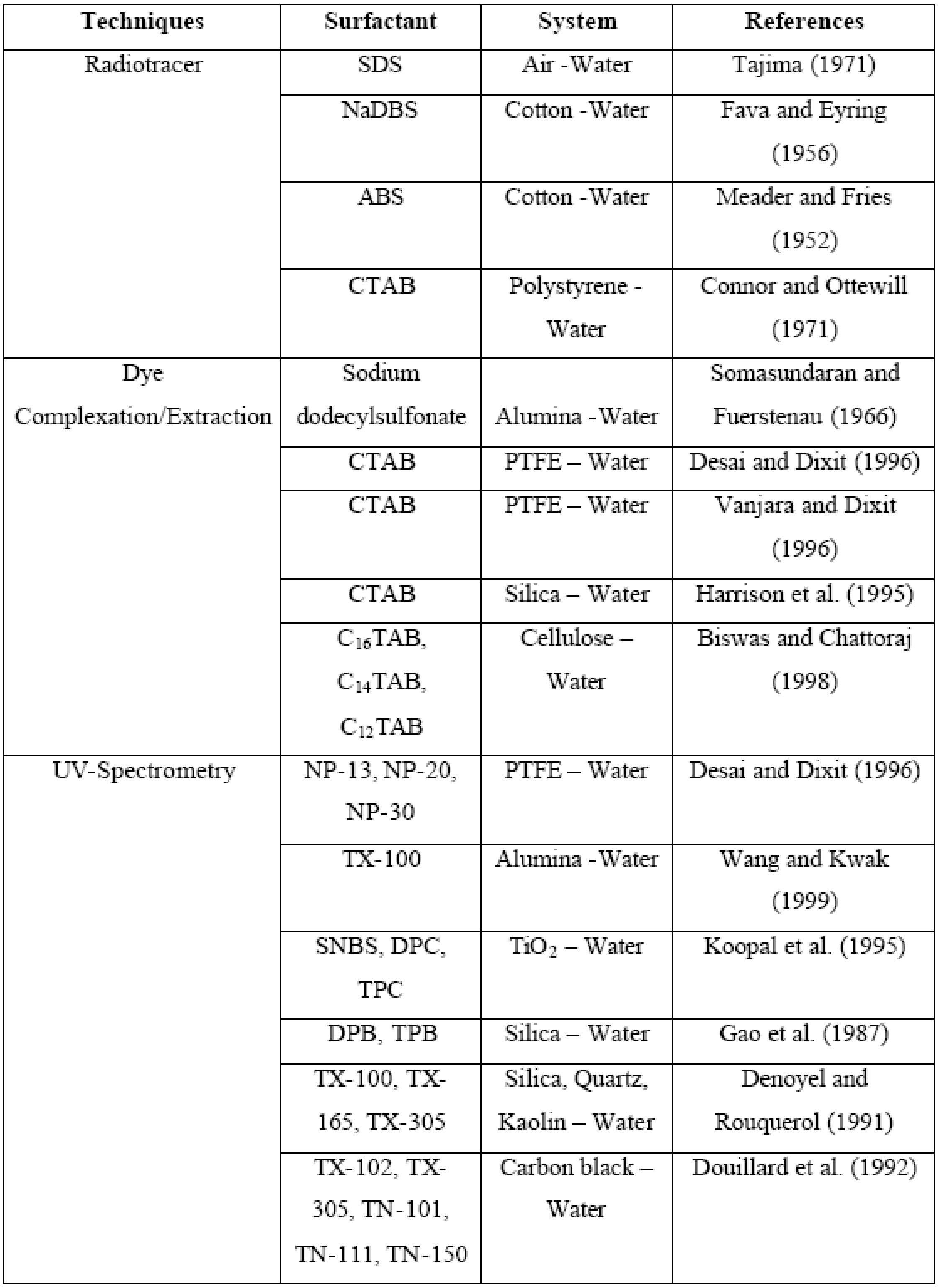
2.3 Techniques of Surfactant Analysis in Adsorption Process

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 involve the stability of colloid dispersions. An understanding of the mechanisms of adsorption is essential for improving the efficiency of such 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-1.2 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.

Table2.1 Different techniques of surfactant analysis in different adsorption process:



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)

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)

2.4 Effects of surfactants on 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.

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. 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 sub layer 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 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 [10] 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 [11] 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 first order rate process with two different process rate constants.

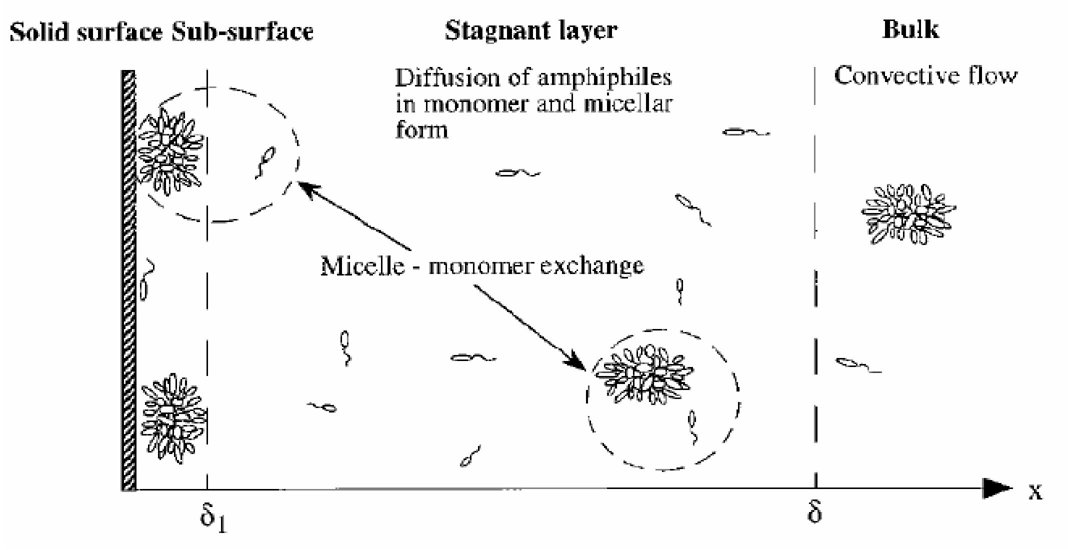


Figure 2.1 schematic representation of solution profile outside the silica surface

2.5 Equilibrium Adsorption of Surfactant

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.

2.6 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. 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.

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.

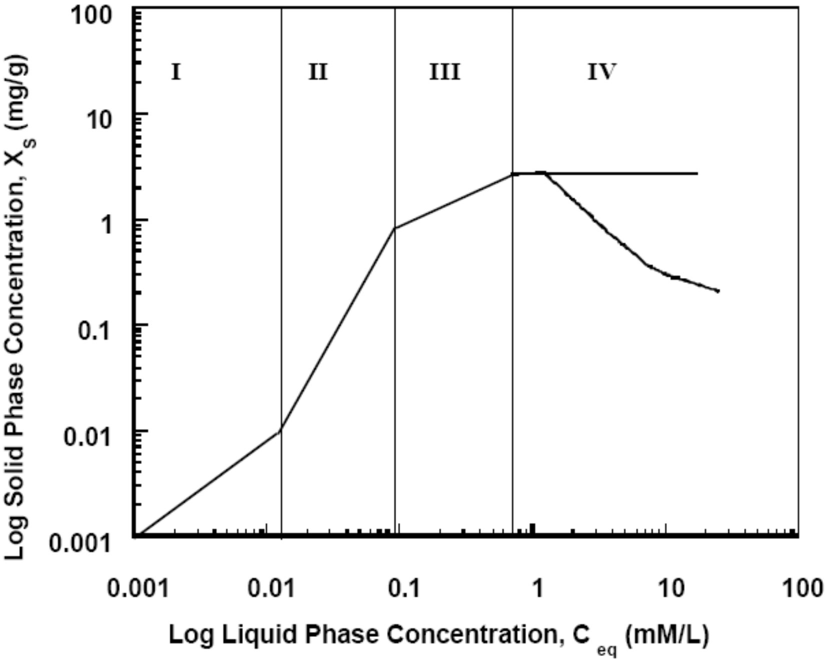


Figure-2.2: schematic presentation of typical four-regime adsorption isotherm depicts the typical isotherm of adsorption of surfactants on the solid-liquid interface in a rather wide range of concentration of surfactants going beyond the CMC.

In general, a typical isotherm can be subdivided into four regions when plotted on a log-log scale [12-19]. 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.

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' [20] which form beyond a critical concentration below the CMC, and is known as critical hemimicellar concentration (HMC).

In region III, there occurs a slowdown of surface cluster formation and hence there is a reduction in slope of isotherm. Gao[13] have proposed an empirical equation to calculate the average aggregation number of the hemimicelle, nhm, which is determined by the given formula below.

$$n_{hm} = \frac{\Gamma_\infty}{\Gamma_{hm}} \qquad 2.2$$

Hemimicellar equilibrium constant and free energy also can be calculated using following equations -

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

$$-\Delta G^0_{hm} = RT \ln K_{hm} \qquad 2.3$$

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[10] . The observation of a maximum in region IV has drawn attention of some researchers and attempts have been made to explain this occurrence.

2.7 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 surfactant

2.8 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 [21]. 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 [21].

$$\frac{1}{\kappa} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{e^2 \sum C_i z_i} \right)^{\frac{1}{2}} \qquad 2.4$$

where,

ε, ε0 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.

2.9 Adsorption of Non- ionic surfactant

The adsorption of non- ionic surfactants on the solid- liquid interface has not been studied as extensively as the ionic surfactants. The adsorption isotherms of non-ionic surfactants are generally Langmurian or L_2 [22] like those of most other highly surface-active solutes adsorbing from the dilute solution. However, the isotherms are often the stepped L_4 types of Langmuir isotherm.

Nonionic surfactants are physically adsorbed rather than electrostatically or chemisorbed. However, they differ from many other surfactants 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.

2.10 Charge of kaolin and general properties

Electrophoresis studies have shown that kaolin has an overall negative charge. The exchange capacity of kaolin results from broken bonds and isomorphous substitution of A_1 for Si in the tetrahedral sheet in the structure. The choice of surface treatment or chemical modification depends upon the polarity, structure, and composition of the organic system into which the kaolin is to be utilized and the physical and chemical properties desired in the end product. Wetting, dispersion, flow properties, and general physical-chemical behavior are most important in the organic medium into which the kaolin is to be utilized. Thorough wetting of kaolin by the vehicle is essential in order to derive maximum utility and functionality. Wetting breaks down the attractive forces between kaolin particles.

2.11 Effect of temperature

The adsorption of nonionic surfactant on solid surface in general, increases with increasing temperature [23-25]. Corkill and Partyka have studied the effect of temperature on adsorption of C_8E_3 and C8E6 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.

2.12 Objectives of the project

The overall objective of the project is to understand the adsorption of surfactants onto the kaolin-water interface under a wide range of conditions such as types of surfactants like anionic, cationic, non-ionic, different concentrations of these surfactants with various amount of kaolin solids and the effect of surfactants on rheological properties.

The specific objectives of this study are:

- To study the nature of samples of kaolin water slurry with the preparation of these test samples of various concentrations.
- To study the equilibrium of adsorption on these samples using a UV-spectrophotometer. To develop a standard graph between absorbency Vs concentrations of these test samples.

- To study the degree of adsorption of surfactants on kaolin slurry by plotting adsorption kinetics curves.
- To study the effects of surfactants on the rheological properties of kaolin water slurry by using a viscometer (Brookfield analog type rotational viscometer)

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 Materials

Non-ionic surfactant-Triton X-100 [$C_{14}H_{22}O$ $(C_2H_4O)_{10}$] (chemical name-Glycol Tertoctylphenyl ether) of scintillation grade was obtained. Cationic Surfactant-C_{16}PB and Anionic surfactant- Sodium Lauryl Sulphate ($C_{12}H_{25}$ NaO_4S) was used for the adsorption kinetics and rheological experiments. In all the experiments performed ultra fine water (pH=7.00) is used along with kaolin (plastic clay) of particle size in the range of few nanometers.

3.2 Surfactant Analysis

The concentrations of non-ionic surfactant Triton X-100 and cationic surfactant C_{16}PB were determined using an UV spectrophotometer. The calibration plot (Absorbance vs Concentration) was obtained by measuring UV absorbance of surfactant at 223 nm wavelength (for Triton X-100) & 258 nm wavelength (for C_{16}PB). The calibration plot is drawn by measuring absorbance of surfactant of solution of known concentration at 223 nm wavelength.

Unfortunately the calibration curve for anionic surfactant could not be plotted as this surfactant is not UV spectra sensitive & is not responded by the instrument.

For the rheological behaviour of (kaolin + surfactant), 3 slurries of known concentration of kaolin (30.07%w/w, 28.57% w/w, 31.03% w/w) were prepared in ultra fine water.

3.3 Adsorption Experiments

In the adsorption study, three surfactants (TX-100, C_{16}PB, and SDS) were prepared by diluting the concentration stock solution. For the calibration curve of TX-100 & C_{16}PB different surfactant solution of known concentration within the range of their CMC value (from the literature survey) were taken. The corresponding values of Absorbency were collected from the spectra analysis experiments. These spectra analysis was conducted in an UV spectrophotometer (computer aided). The absorbency was taken at 223 nm λ for TX-100 & 258 nm λ for C_{16}PB upto the concentration of 0.2 mM & 0.5 mM respectively. In all these experiments the slurry is centrifuged at 1500 rpm.

For rheological study kaolin was taken and weighed to get the best possible value for viscosity measurement with a specific spindle. The speed of the spindle is kept constant throughout all the experiments at 30 rpm. The temperature was almost constant during each set of experiment with the 3 surfactants. The kaolin water slurry was prepared with different amount of kaolin (20%, 30.04%w/w). The effect of surfactants on the rheological behaviour of the kaolin water slurry was recorded with the help of analog type Brookfield rotational viscometer.

Adsorption kinetics of two surfactants TX-100, C_{16}PB was studied on the solid liquid interface (kaolin-water slurry). Graphically present the kinetics of adsorption of TX-100 & C_{16}PB respectively at two different initial concentrations. The curve is plotted between amounts of surfactant adsorbed on the solid (kaolin) taken in mg of surfactant per gm of kaolin vs time (in min). For these experiments the amount of solid taken is 2 gm in 10 ml of surfactant of 0.2 mM concentration for TX-100 and 0.5 for C_{16}PB. Cationic surfactants adsorption is very high as compared to non-ionic which are discussed in chapter 4.

3.4 Rheological Experiments

For the studies of rheological properties kaolin was taken as a sample. The effect of surfactants on kaolin is the primary objective here. At first kaolin water slurry was prepared in which 300ml water and 129 gms of kaolin (30.07%by wt) were mixed. Then the viscosity of the slurry was measured using the Brookfield Analog type Viscometer at constant rate of 30 rpm. First the viscosity of the mixture is measured without surfactant. Later on different concentrations of a non-ionic surfactant was added in the kaolin-water slurry to obtain the effects of the surfactant with time. For non-ionic surfactant, 0.05, 0.1, 0.5, 1, 5, 10 & 15 mM concentrations of surfactant were added in the kaolin-water slurry. Here TX-100 was used as a non-ionic surfactant.

Similarly for cationic and anionic surfactants also the viscosity measurements were taken. For Cationic surfactant in 300 ml water 120 Gms of kaolin (28.57% by wt) was added. Here also at first the mixture of kaolin & water was measured without the surfactant. Then at 0.5, 0.75, 1, 3, 5, 10, 15&20 mM concentrations of cationic surfactant, the viscosity of the kaolin water slurry were measured with respect to time. C_{16}PB was used as a cationic surfactant.

Sodium Lauryl Sulphate was used as the anionic surfactant. 123 Gms of kaolin was added in 300 ml distilled water (29.08%by wt). As like as the previous two surfactants, the kaolin water slurry without surfactant was analyzed by using the viscometer with respect to time. Then different concentrations of surfactant, 0.5, 0.75, 1, 3, 5 & 10 mM were added in the kaolin water slurry respectively and the change in viscosity with time was noted down.

Chapter 4

RESULTS AND DISCUSSION

4.1 Adsorption Kinetics

For the calibration curve of TX-100 & C_{16}PB different surfactant solution of known concentration within the range of the limited value of the instrument were taken. These spectra analysis was conducted in an UV spectrophotometer (computer aided). The corresponding values of Absorbence were noted from the spectra analysis experiments. The absorbency was taken at 223 nm λ_{max} for TX-100 & 258 nm λ_{max} for C_{16}PB upto the concentration of 0.2 mM & 0.5 mM respectively. Calibration curve is given in the fig 4.1 and 4.2 for TX-100 & C_{16}PB respectively. It is seen that the calibration curve for TX-100 & C_{16}PB is almost a straight line. The equation of the straight line is derived. The values of the unknown concentration of surfactant adsorbed can be known by the data of absorbency from the UV spectrophotometer by using the equation of the straight line.

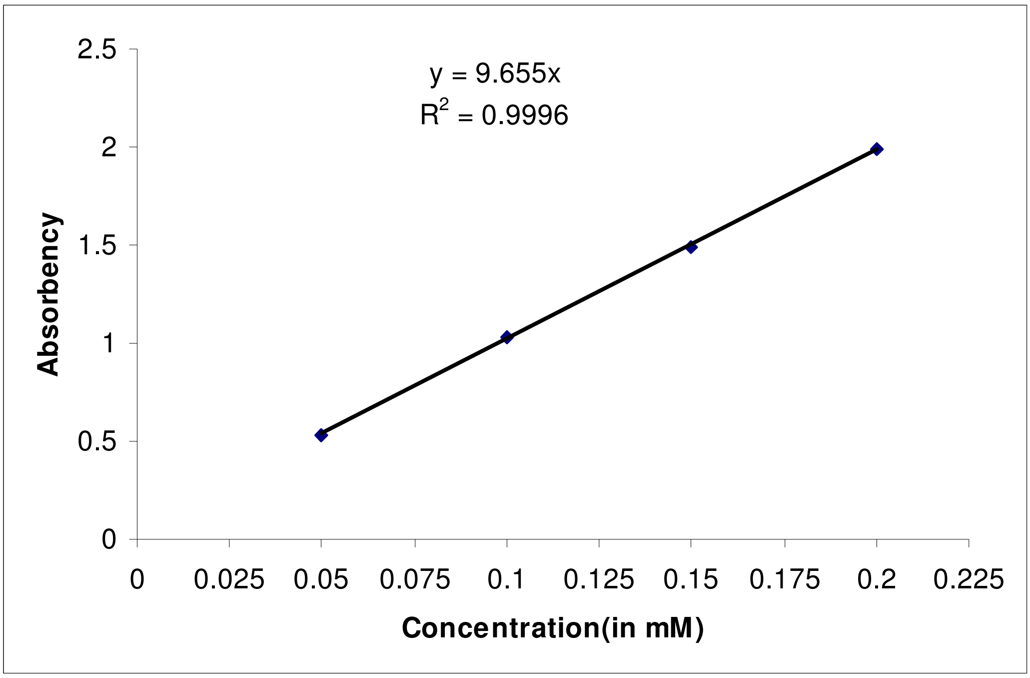


Fig4.1: Calibration curve of TX-100 plotting absorbency vs. concentration (λ_{max}=223)

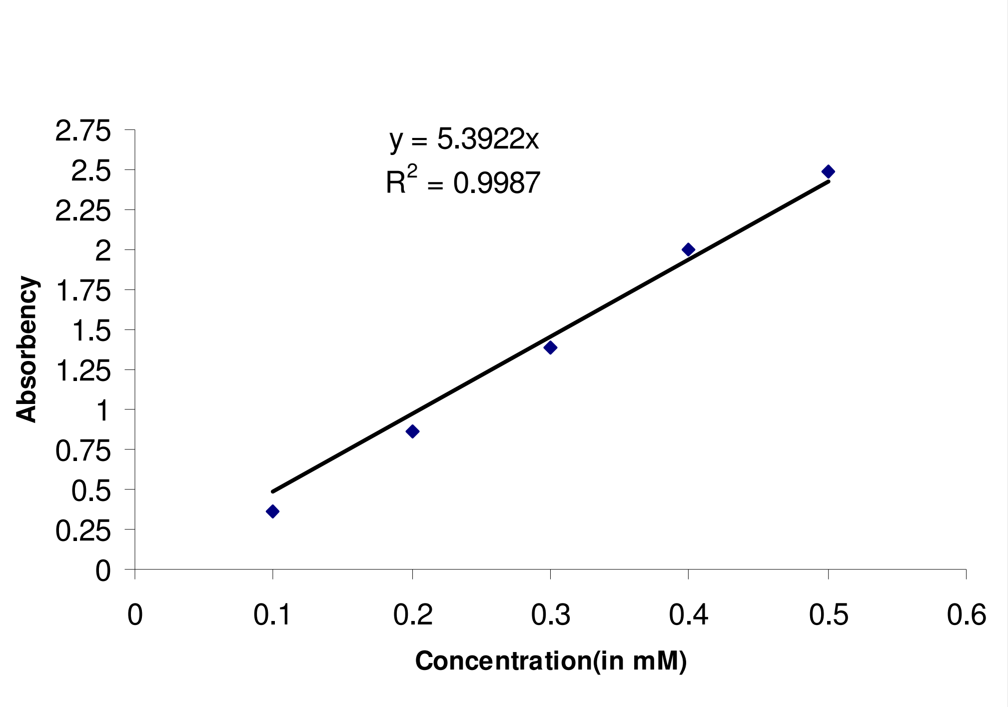


Fig 4.2: Calibration curve of $C_{16}PB$ plotting absorbency vs. concentration (λ_{max} = 258)

Fig 4.3 & 4.4 shows the amount of surfactant absorbed per gm of solid (kaolin) in case of non-ionic surfactant TX -100 and cationic surfactant $C_{16}PB$.The nature of the plot for TX-100 is non-linear. There is a sharp increase in the amount of surfactant adsorbed in the first 5 minutes. Then the amount of surfactant adsorption decreases and remains almost constant after 20 minutes. This shows equilibrium value is reached which indicates saturation in adsorption of surfactant after 20 minutes. But in case of cationic surfactant the amount adsorbed on the solid- liquid interface is more and shows a little variation with increase in adsorption time. . The adsorption of non-ionic surfactant on kaolin-water interface is less than the cationic surfactant. This shows that kaolin is more sensitive to cationic surfactant as compared to non-ionic surfactant. The reason of these different amounts adsorbed for both the surfactants is due to the difference in chemical structure in alkyl group (tail) and ionic group (head).

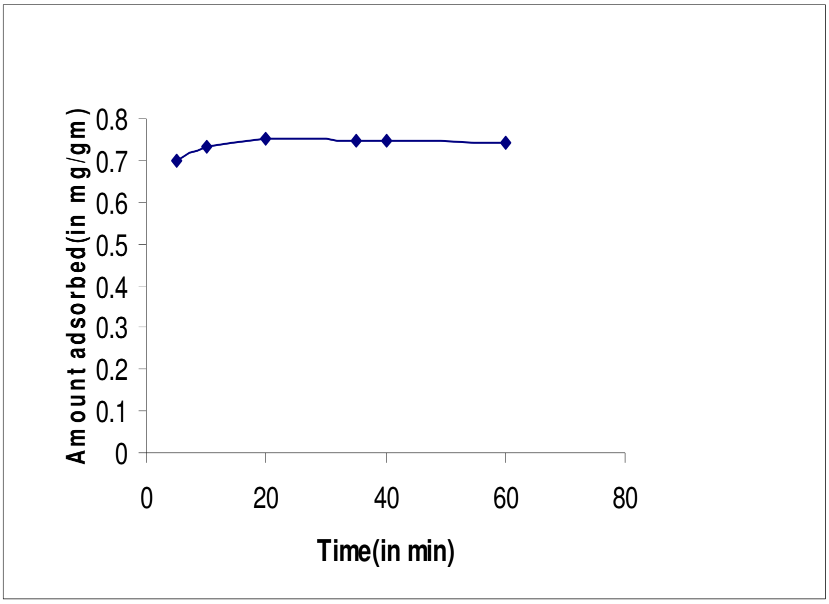


Fig 4.3: Adsorption kinetics for TX-100 (0.2 mM)

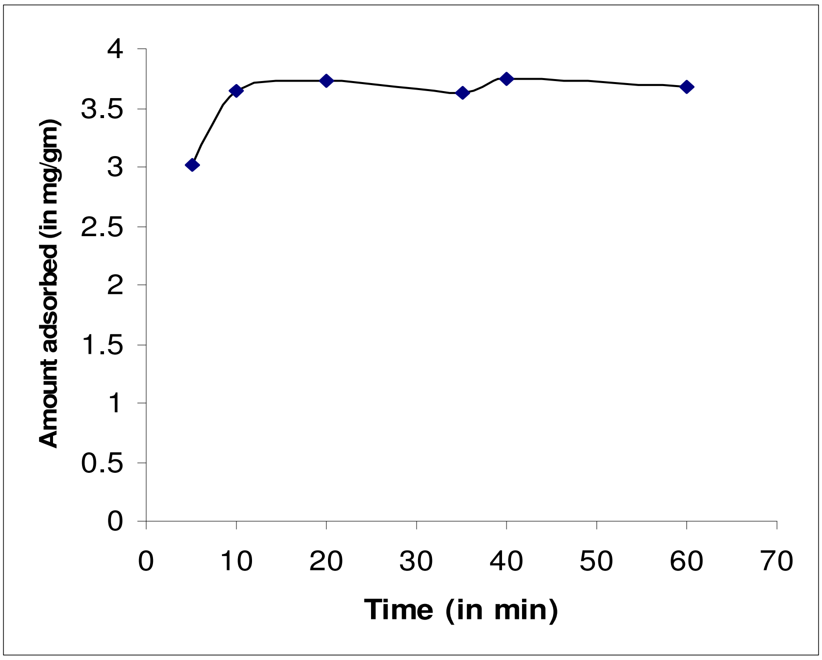


Fig 4.4: Adsorption kinetics for $C_{16}PB$ (0.5 mM)

4.2 Rheological behaviors

For the rheological properties of the kaolin-water slurry three different slurries with 30.07 % by wt., 28.57% by wt. & 31.03 % by wt. were taken for non-ionic surfactant (TX-100), cationic surfactant ($C_{16}PB$) & anionic surfactant (SLS) respectively. The change in viscosity with respect to time is given in fig 4.5 for 30.07% by wt. of kaolin in water without addition of surfactant. The change in viscosity without surfactant is due to the swelling of kaolin in water. The effect of pH of ultra fine water also influences slightly on the solubilisation of kaolin in water [23].

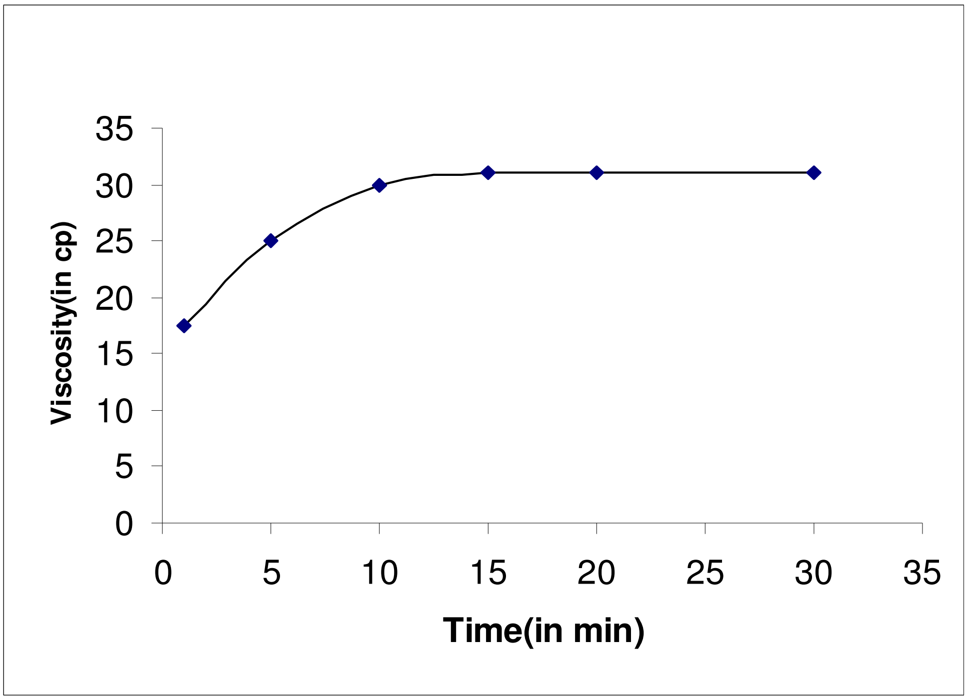
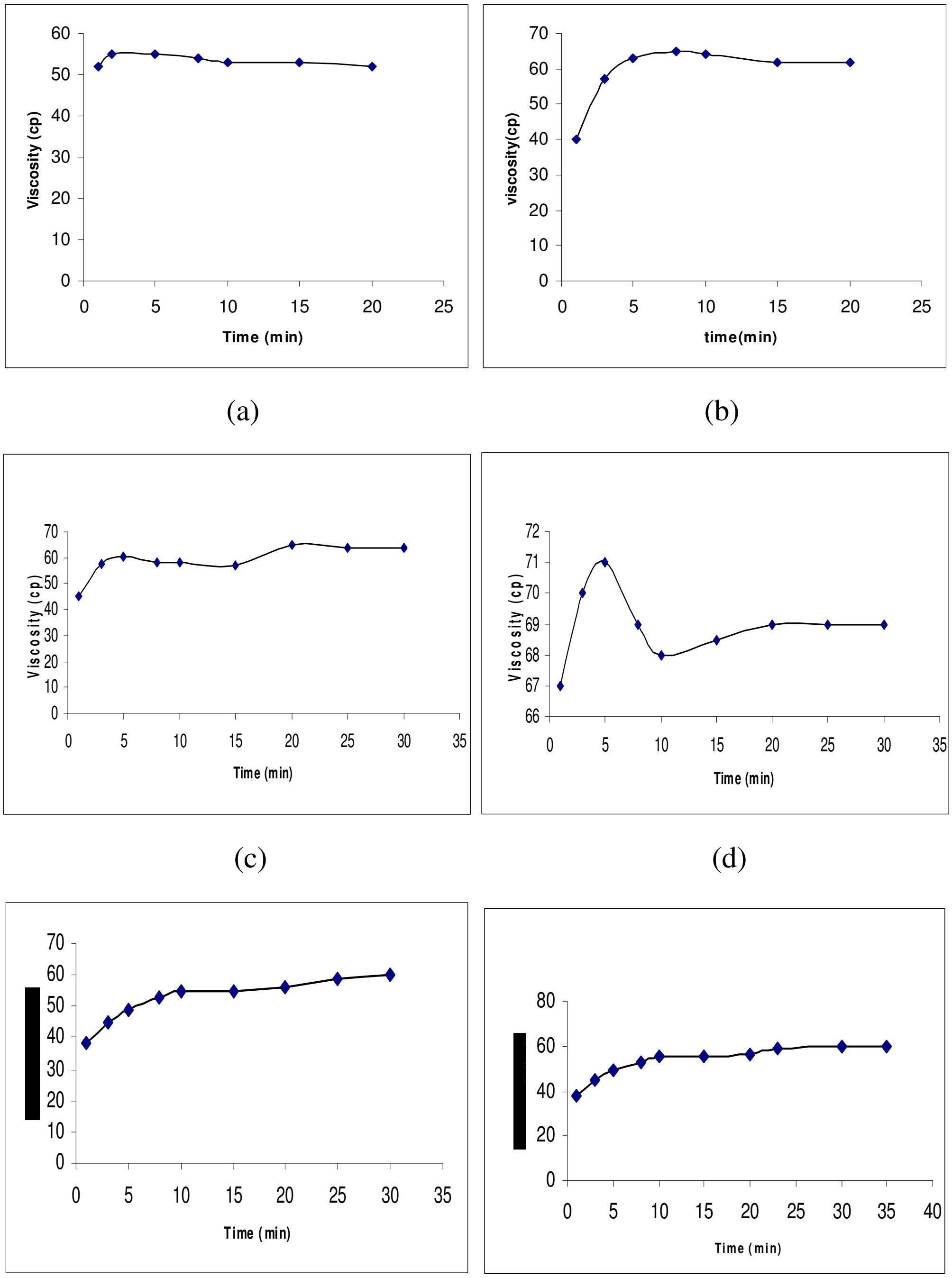


Fig 4.5: Viscosity vs. Time curve without TX-100 (30.07% by w/w)

Figures 4.6 (a), (b), (c), (d), (e), (f) shows viscosity variations with time for 0.05 mM, 0.1 mM, 0.5 mM, 1 mM, 10 mM concentrations of TX-100 surfactant respectively. The graph plotted shows that the change of viscosity w.r.t time & concentration is not significant. The viscosity changes remarkably up to the CMC value of TX-100 i.e. 0.2 mM then the viscosity remains almost constant due to equilibrium adsorption. This may be due to less adsorption of alkyl group of the non-ionic surfactant which induces no charge on kaolin particles. Due to chemical structure also the adsorption is not so high on kaolin water interface and the change in viscosity is not noticeable.



(a) (b)

(c) (d)

(e) (f)

Fig 4.6: Viscosity vs. Time curve with TX-100 of different concentrations- (a) 0.05Mm, (b) 0.1Mm, (c) 0.5Mm, (d) 1Mm, (e) 10Mm, (f) 15mM.

The plot for viscosity vs. time for kaolin (28.57 % by wt.) in the case of cationic surfactant ($C_{16}PB$) without surfactant is given in fig 4.7.

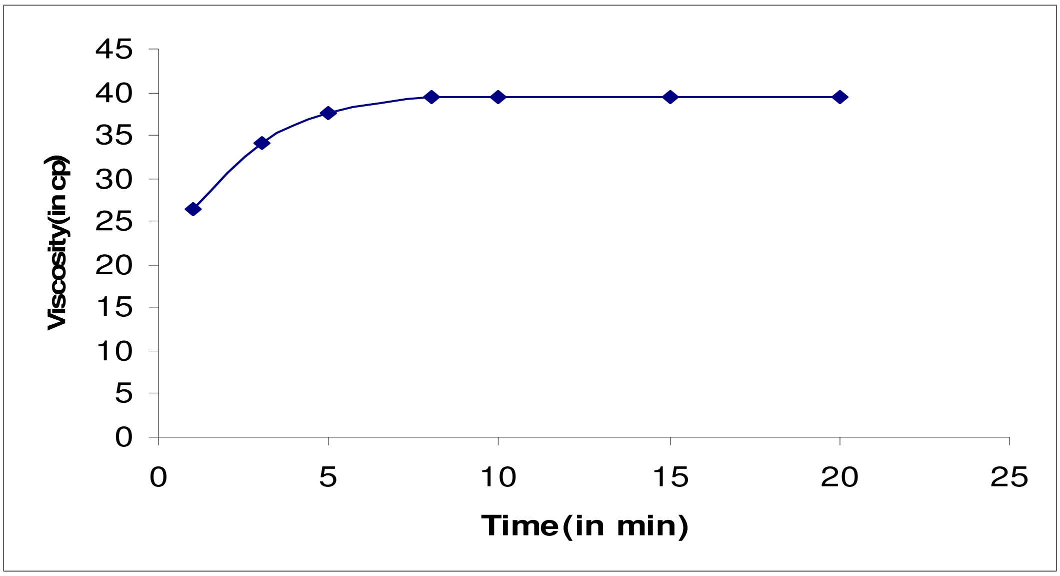
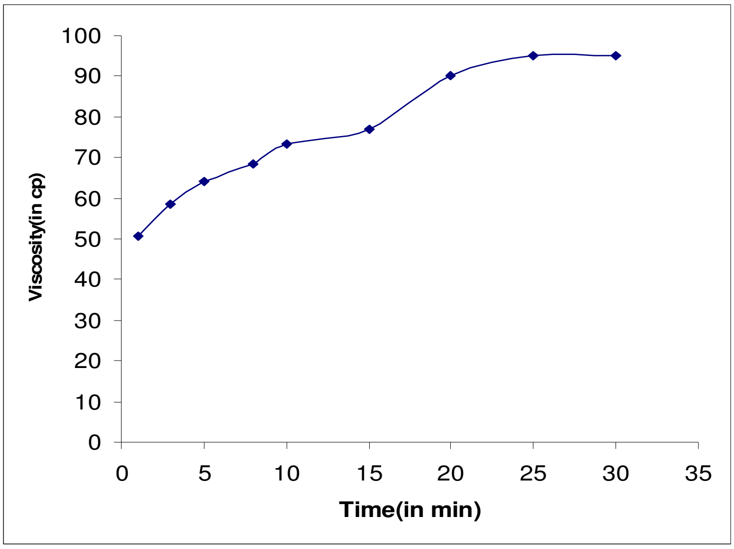
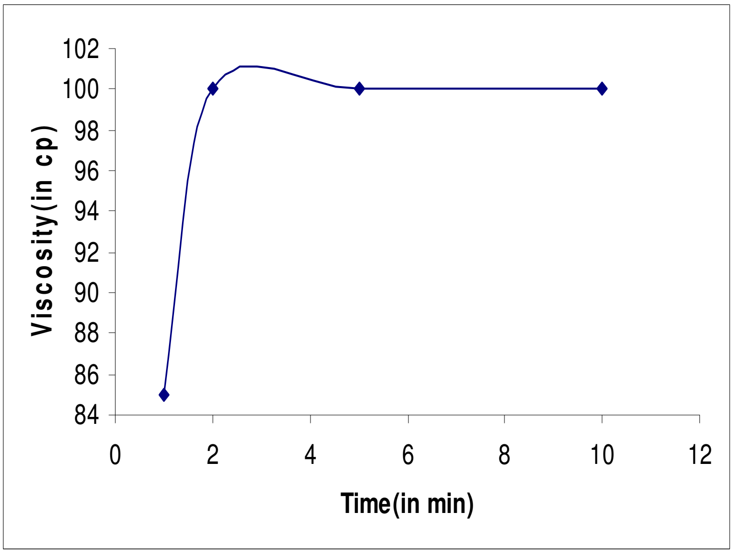


Fig 4.7: Viscosity vs. time curve for kaolin (30.07 % by wt.) without cationic surfactant

The effect of adding cationic surfactant in the slurry with the concentrations 0.5 mM & 0.75 mM on viscosity is shown in fig. 4.8 (a) & (b) respectively. Cationic surfactant increases the viscosity of kaolin water slurry to a great extent. There is a sharp increase in viscosity after 0.75 mM concentration as this concentration is just above the CMC value of 0.5 mM.



(a)



(b)

Fig 4.8: Viscosity vs. Time curve with C_{16}PB of concentrations-(a) 0.5mM, (b) 0.75mM

In fig. 4.9 viscosity is plotted against the increasing concentrations of surfactant. There is a sharp increase in viscosity beyond 2 mM but the data could not be produced due to the limitation of the rotational viscometer as the values are crossing the maximum or cut-off value i.e. 100 for that spindle. Many cationic surfactants with appropriate counter ions are effective drag reducing additives. However, drag reduction effectiveness is determined by many factors such as temperature, pH and chemical structure of the cationic surfactant alkyl group (tail) and ionic group (head) and its concentration.

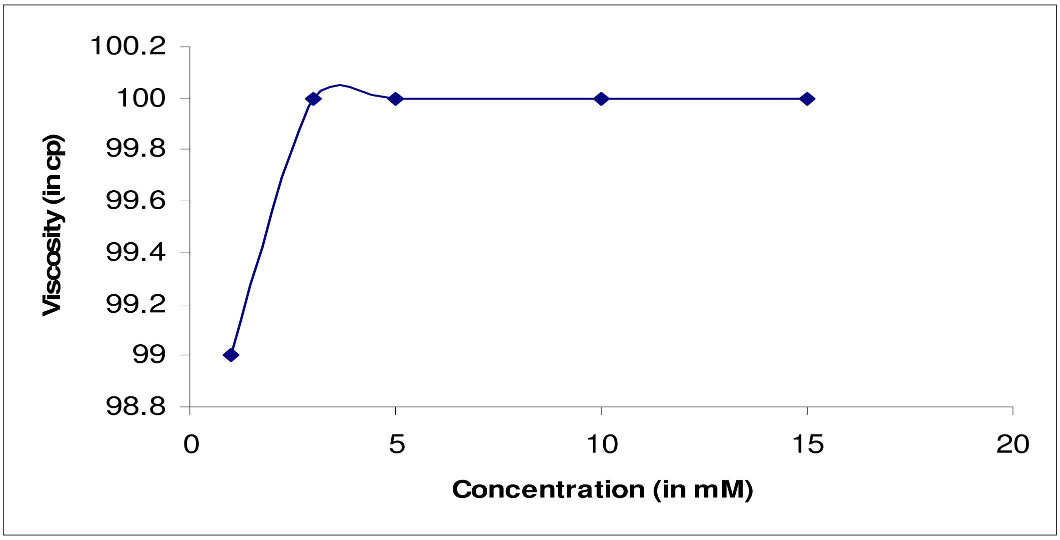


Fig 4.9: Viscosity vs. concentrations of cationic surfactant ($C_{16}PB$)

In the figure 4.10, a graph is plotted between viscosity vs. time for kaolin (31.03% w/w) without anionic surfactant (SLS). The curve is non-linear. The variation in viscosity may be due to swelling of kaolin particles & instrumental error. The viscosity becomes almost constant after 25 minutes.

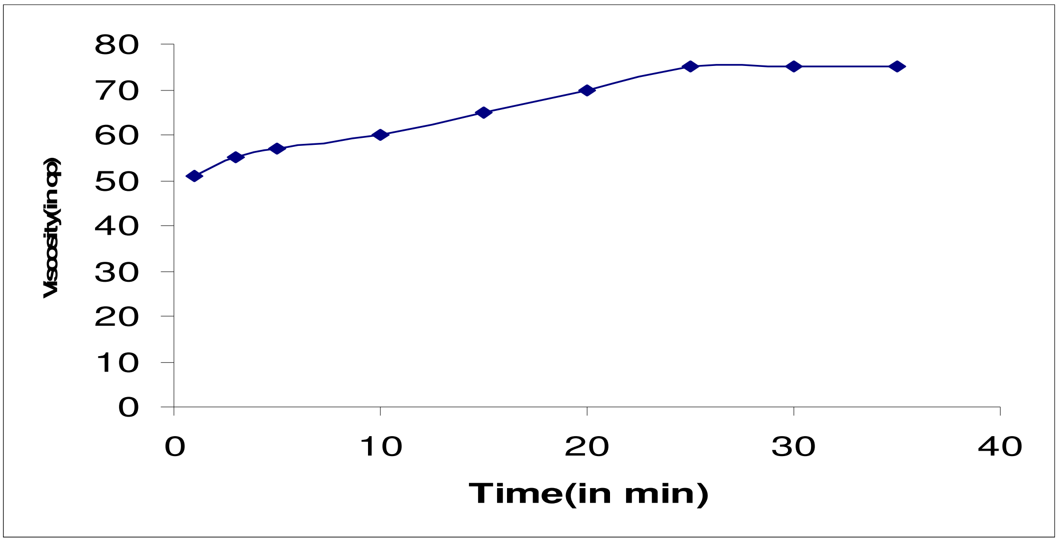
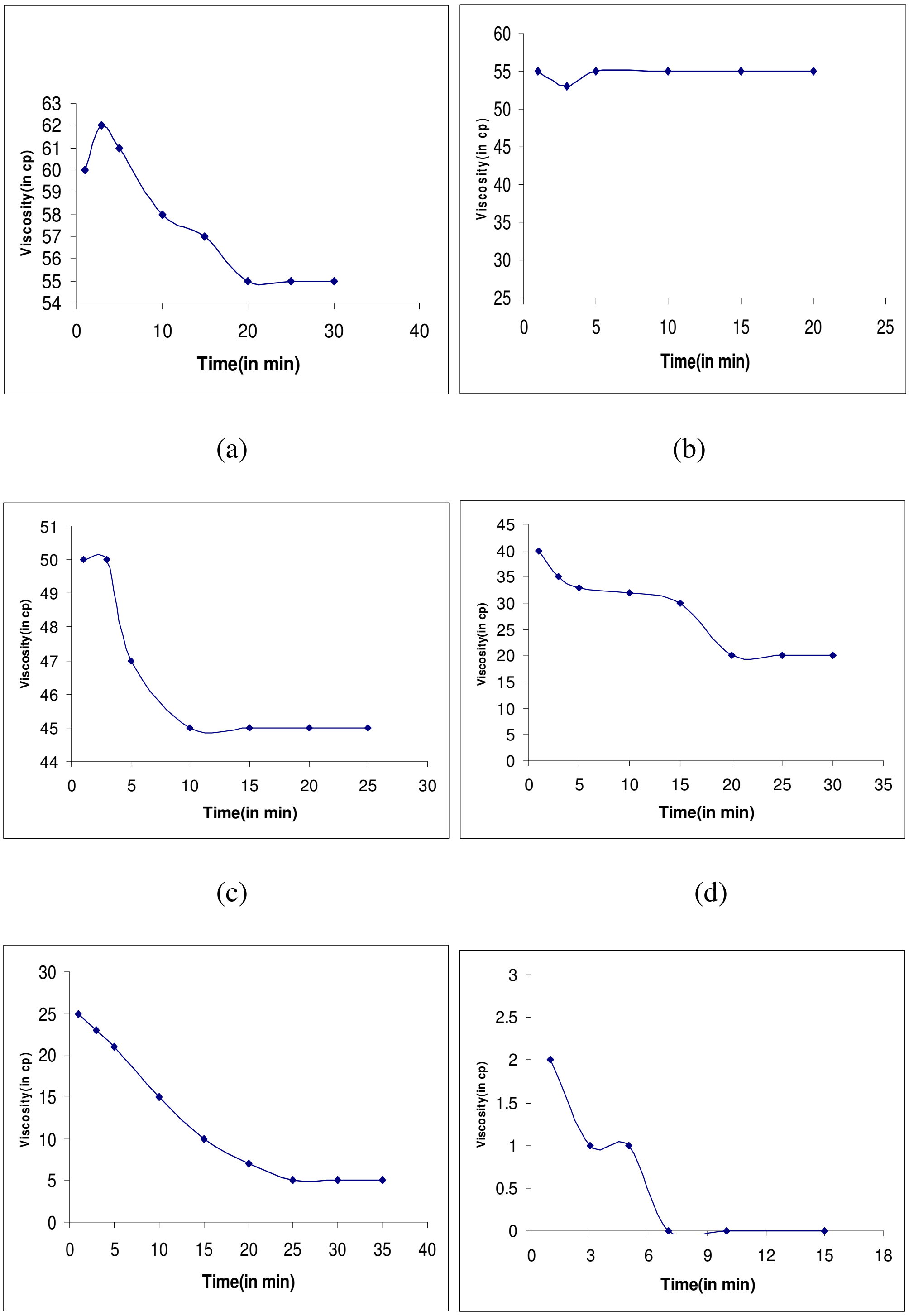


Fig 4.10: Viscosity vs. Time for kaolin (31.03% w/w) without anionic surfactant (SLS)

Figures 4.11 shows viscosity variations with time for (a) 0.5 mM, (b) 0.75 mM, (c) 1 mM, (d)3 mM, (e) 5 mM & (f) 10 mM concentrations of anionic surfactant- Sodium Lauryl Sulphate surfactant respectively. In case of addition of anionic surfactant, the viscosity of the slurry always decreases. But in 1 Mm concentration, the viscosity remains constant. It may be due to the instrumental error.



(a) (b)

(c) (d)

(e) (f)

Fig 4.11: Viscosity vs Time curve with anionic surfactant (SLS) of concentrations (a) 0.5 mM, (b) 0.75 mM, (c) 1 mM, (d) 3 mM, (e) 5 mM & (f) 10 mM

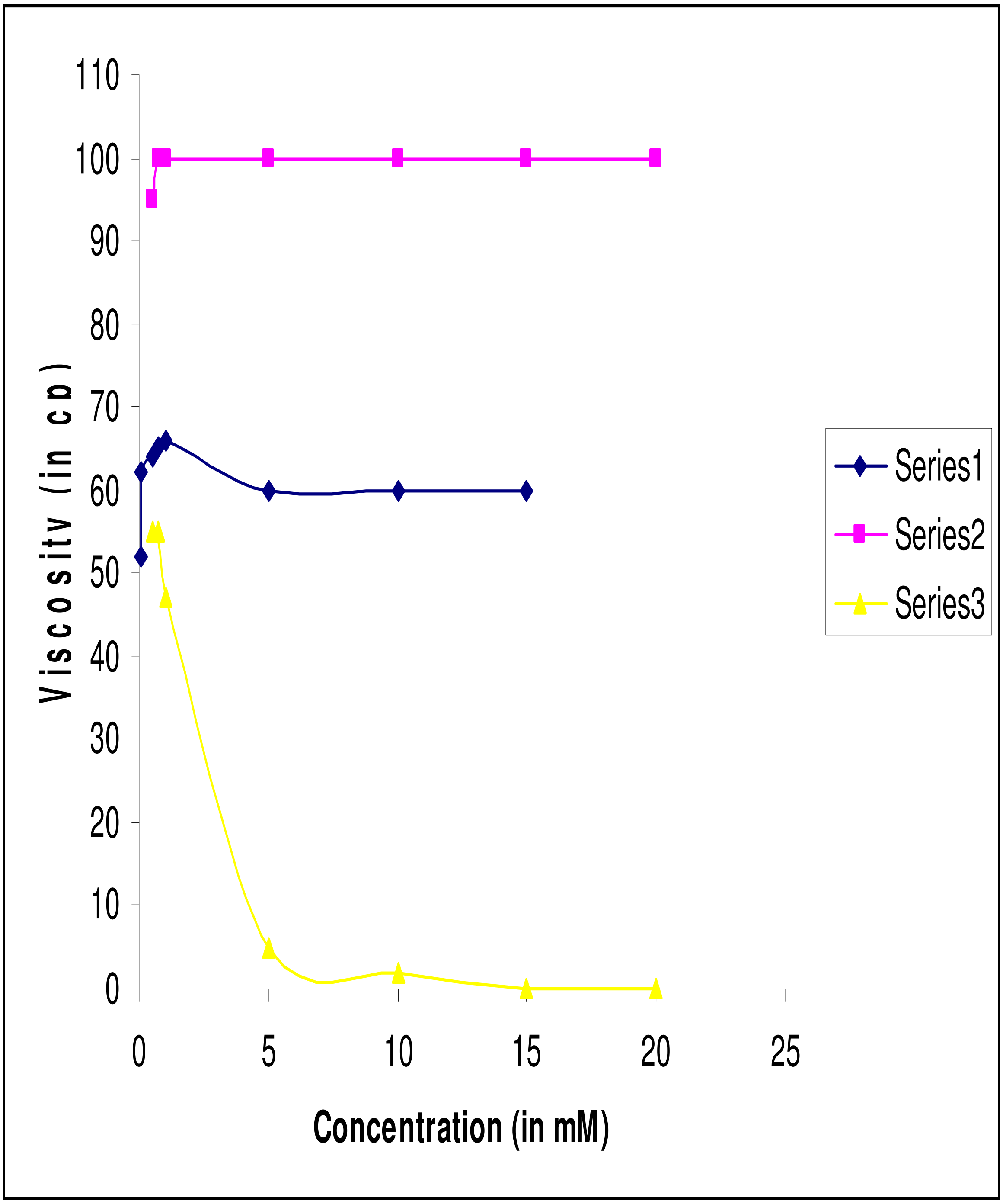


Fig 4.12: Comparison of viscosity change with respect to concentrations for 3 surfactants Series1-(non-ionic surfactant TX-100), Series2-(cationic surfactant C_{16}PB) & Series-3(anionic surfactant SLS).

As from the figure 5.1 it can be shown that viscosity values for cationic mixed surfactant is more than non-ionic & anionic mixed surfactant. So viscosity for kaolin water slurry increases in the order of cationic > non-ionic > anionic surfactants respectively. From the literature review, we know that kaolin posses a deficiency in positive charges rather the particles are negatively charged. So, when cationic surfactant is mixed with kaolin-water slurry, then the negatively charged particles of kaolin are highly attracted by the positive hydrophobic part of cationic surfactants and forms an agglomerate of surfactant adsorbed kaolin particles. These agglomerates formed are quite stable in nature and is more compact may be due to the bonding and influence of surfactant concentrations. This reduces drag force on these agglomerates and hence strain is more required to release the surfactant particles or fragmentize the agglomerates into still further smaller ones. Hence the viscosity increases to a greater extent by the surface chemistry and adsorption of cationic surfactant on the kaolin-water interface.

But in case of anionic surfactant the hydrophobic part of the surfactant get repulsion from the positively charged part of the kaolin. Hence the adsorption of the surfactant on the inter face is less. The hydrophobic part of the surfactant and negatively charged part of the kaolin are far away from each other without any attraction. That’s why there is a less amount of agglomerates formation and the particles are free to move or scatter here & there freely in the slurry. As a result the surface tension is less and there is always gap in between kaolin and surfactant particles. So the viscosity is less due to no bond formation as compared to cationic surfactant. But in case of non-ionic surfactant the behavior is somewhat in between these two surfactants. As non-ionic surfactant posses negligible charge the hydrophobic part does not get more attraction or repulsion by the charged kaolin particles. So the viscosity change is quite not severe in case of non-ionic surfactant. The exchange sites are the locations on the surface where polar molecules can be adsorbed and oriented. The choice of surface treatment or chemical modification depends upon the polarity, structure, and composition of the organic system into which the kaolin is to be utilized and the physical and chemical properties desired in the end product.

Chapter 5

CONCLUSION

From the project work, it can be concluded that

1. The rheological properties kaolin water slurry changes by the addition of cationic and anionic surfactants to a greater extent than the non-ionic surfactant.
2. For cationic surfactant the viscosity increases to a high value due to the attraction between the negatively charged kaolin particles and positively charged hydrophobic part of surfactant.
3. In case of anionic surfactant the viscosity values decreases sharply due to repulsion between kaolin and surfactant particles.
4. And in case of non-ionic surfactant there is no significant effect on the rheological properties of kaolin water slurry.
5. So anionic surfactants are the best for industrial applications like transportations of kaolin slurry, their atomization.
6. Cationic surfactants are the best for increasing the viscosity of the kaolin slurry which can be used as filler in paper industries, rubber industries & for thickening purposes.

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