

Effect of Surfactants on Clay – Water Slurry Rheology

*Thesis submitted
by*

HIMANSHU DESAI (10500002)

In partial fulfillment for the award of the Degree of

**BACHELOR OF TECHNOLOGY
IN
CHEMICAL ENGINEERING**

Under the guidance of
Dr. SANTANU PARIA



**Department of Chemical Engineering
National Institute of Technology, Rourkela
Rourkela-769008, Orissa, India**

May, 2009

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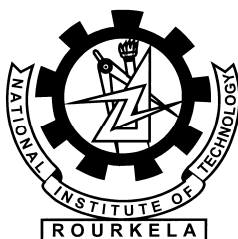
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CERTIFICATE

This is to certify that the thesis entitled, “**EFFECT OF SURFACTANTS ON CLAY – WATER SLURRY RHEOLOGY**” submitted by Shri Himanshu Desai 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.

Date: 07/05/2009

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Date: 07/05/2009

Himanshu Desai

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Abstract

The rheological behavior of clay-water slurry has been studied in presence of different surfactants. The effects of solid concentration as well as the effect of three synthetic surfactants, nonionic Triton X-100 (TX-100), anionic sodium dodecyl benzene sulfonate (SDBS) and cationic cetyl pyridinium bromide (CPB) surfactant on the rheological behaviors of pyrophyllite-water slurry were experimented by using a rotational cone and plate BOHLIN VISCO-88 viscometer. It was found that the cationic surfactant addition to pyrophyllite slurry causes first an increase in viscosity and later a decrease in viscosity due to charge reversal where as for nonionic surfactant; viscosity increases and after a certain concentration remains constant. The zeta-potential values of pyrophyllite-water slurry at different pH and in presence surfactants were also correlated with the adsorption and rheological behavior. It was found that at lower pH the viscosity of clay water slurry is more and with increase in pH it decreases and after a certain pH it remain constant. These experiments were conducted under both constant and variable shear stresses at a temperature of 30°C.

Keywords: Viscosity, Surfactants, Clay, Rheology, Zeta potential

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Chapter 1

Introduction

INTRODUCTION

Rheometry refers to a set of standard techniques that are used to experimentally determine rheological properties of materials (fluid or solid). The idea underpinning rheometry is to realize flows, where the stress and/or strain fields are known in advance, which make it possible to deduce rheological properties from measurements of flow properties. A rheometer is usually an instrument, which can exert a torque/force on a material and accurately measures its response with time (or conversely, it can impose a strain and measures the resulting torque). (Ancy C, 2005)

1.1 Shear

Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move relatively to another layer. The greater the friction the greater the amount of force required to cause this movement which is called shear. Shearing occurs whenever the fluid is physically moved by pouring, spreading, spraying, mixing, etc. High viscous liquids require more force to move than less viscous liquids (McCabe et al, 2001).

If we have two parallel planes of fluid of equal area A and they are separated by a distance dx and are moving in the same direction at different velocities v_1 and v_2 . The force required to maintain this difference in velocities is proportional to the difference in speed through the liquid, or the velocity gradient:

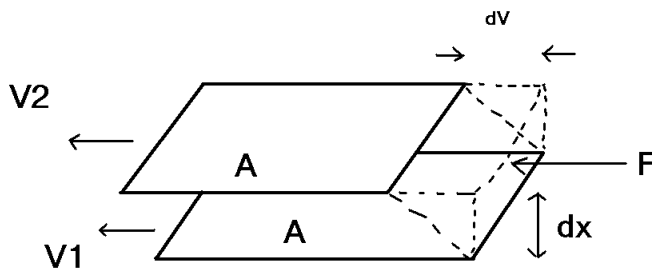


Fig.1.1 sliding of two plates over each other

1.2. Shear Rate

The velocity gradient, dv/dx , is a measure of the speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and is called shear rate – R and its unit of measure is called reciprocal second (sec^{-1}).

1.3. Shear Stress

The term F/A indicates the force per unit area required to produce the shearing action and it is called shear stress – S and its unit is N/m^2 . So viscosity can be defined as: viscosity = shear stress S / shear rate R .

The fundamental unit of viscosity is the poise. A material requiring a shear stress of one dyne per square centimeter to produce a shear rate of s^{-1} has a viscosity of 1 poise or 100 centipoise. One Pascal-second (Pa-sec) is equal 10 poise.

1.4. Newtonian Fluids

Below graphs show the relationship between shear stress S and shear rate R and the fluid's viscosity at a varying shear rate R . Typical Newtonian fluids include water and thin motor oils.

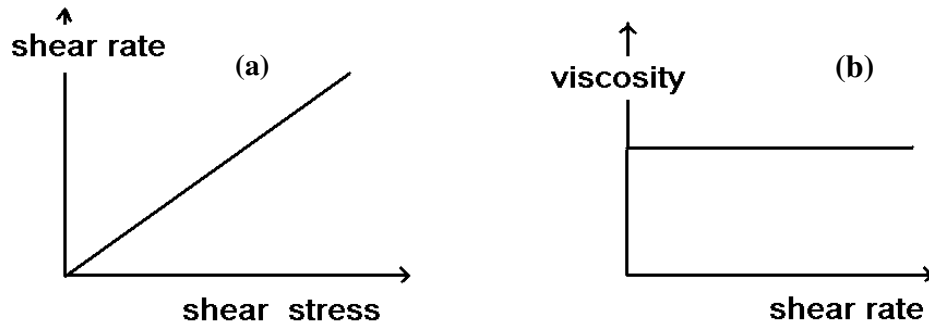


Fig.1.2: Plot of (a) shear rate vs. shear stress (b) shear rate vs. viscosity for Newtonian fluids.

So, at a given temperature the viscosity of a Newtonian fluid remains constant regardless of which viscometer model, spindle or speed is used to measure it.

The behavior of Newtonian liquids in experiments conducted at constant temperature and pressure has the following features:

1. The only stress generated in simple shear flow is the shear stress S , the two normal stress differences are zero.
2. The shear viscosity doesn't vary with shear rate.
3. The viscosity is constant with respect to the time of shearing and the stress in liquid falls to zero immediately the shearing is stopped

The viscosities measured in different types of deformation are always in simple proportion to one another.

A fluid showing any deviation from the above features is called non-Newtonian.

1.5. Non-Newtonian Fluids

A non-Newtonian fluid is defined as one for which the relationship S/R is not constant. The viscosity of non-Newtonian fluids changes as the shear rate is varied. Thus, the parameters of viscometer model, spindle and rotational speed have an effect on the measured viscosity. This measured viscosity is called apparent viscosity and is accurate when explicit experimental parameters are adhered to. There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate.

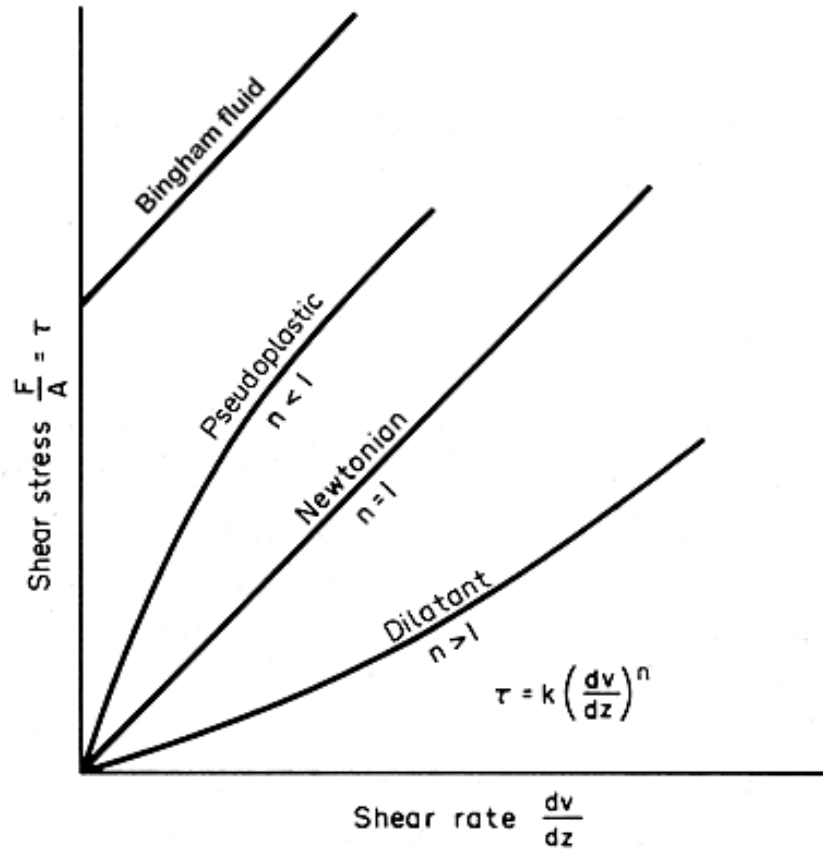


Fig.1.3 Shear Stress vs. Shear Rate for different fluids

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.

1.6 Determination of parameters of time dependent non-Newtonian fluids

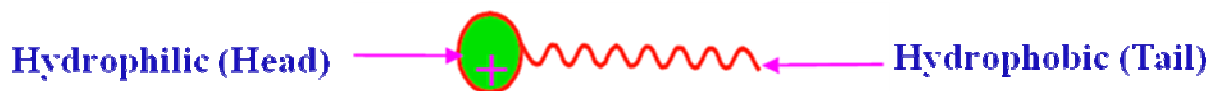
Usually, the analysis of thixotropic and rheopectic fluids involves plotting changes in viscosity as a function of time. The simplest method is to select a spindle and speed and leave the viscometer running for an extended period, noting the readings at regular intervals. It is essential to have the sample in the same temperature throughout the experiment. A change in fluid's viscosity over time indicates time-dependent behavior: a decrease means thixotropy, an increase rheopexy.

Another method is to graph the viscometer reading vs. speed, using a single spindle. Starting at a low speed, note the reading at each successively higher speed until the reading goes off the scale. A graph of such readings is an upward curve. Without stopping the viscometer, reduce the speed incrementally to the starting point, again taking readings at each speed. This is a downward curve. It is good to allow some time before each speed change. If the fluid is time independent the curves will overlap. If they don't, the fluid is time dependent. If the upward curve indicates a higher viscosity than the downward curve, the fluid is thixotropic; if the upward curve indicates lower viscosity than the downward curve, the fluid is rheopectic.

1.7 Surfactants

The term surface-active agent or “surfactant” represents a heterogeneous and long chain molecule containing both hydrophilic and hydrophobic moieties.

Surface-Active Agent or Surfactant



1.8 Types of Surfactants

There is a broad range of different surfactant types, each having unique properties and characteristics. Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic or amphoteric/zwitterionic family.

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

1.8.2 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.

1.8.3 Non-ionic surfactants

These surfactants do not have any 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.

1.8.4 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.

Chapter 2

Literature Review

2.1 Introduction

The rheology of slurries and their characterization has received widespread attention in recent years because of its wide range of industrial applications and academic interest. The reduction of slurry viscosity can be of use in slurry transportation. Viscosity or rheological properties of slurry, emulsion, or paste is also important in modifying the physical properties of cosmetics, creams, gels, foods, biofluids etc. These fluids can be subjected to surfactant treatment to alter the viscosity or rheological properties or these systems are containing surfactants as one of the essential components that may cause the change in rheological properties. Interactions between the suspended particles in the slurry are very important in the rheological behavior of the system. In general, the properties depend on different parameters like the solid/water ratio, size, shape, pH (Lagaly, 1989), surface charge of the particles (Luckham and Rossi, 1999), exchangeable ions of clay particles (Lagaly, 1989; Luckham and Rossi, 1999), additive types like surfactants (Günister et al, 2006) and polymers (Voisin and Vincent, 2003), temperature etc.

Clays are natural products and used in many industrial applications like catalysts, engineering and construction, agricultural, environmental remediation etc. (Murray, 2007). Like the other suspension rheological properties of clay – water slurry also greatly influenced in presence of surfactants and polymers (Isci et al., 2004; Gunister et al., 2006a, b). Gunister et al. (2006 a, b) have studied the effect of cationic surfactants (benzyltrimethyltetradecyl ammonium chloride (BDTAC) and dodecyltrimethyl ammonium bromide (DTAB)) on bentonite clay. They found that at low solid concentration (1 or 2 %) the exhibit Newtonian but at high solid concentration flow becomes pseudoplastic. Addition of cationic surfactants at low concentration there was no change in rheological parameters significantly but at higher concentration there was increase in viscosity and hysteresis area. Between two cationic surfactants change was sharp for DTAB that BDTAC. Isci et al. (2004) have studied the rheological properties of Ca – bentonite (CaE), Na – bentonite (NaE), and hectorite (HC) in presence of a nonionic hydrophilic polymer (poly vinyl acid, PVA). When the PVA concentration was increased the viscosity of CaE and HC increased with a sharp and significant change for CaE but

that was decreased for NaE. They showed by XRD analysis that the more increase in viscosity was due to increase in interlayer clay spacing in CaE.

2.2 Studies on rheology of bentonite clay in presence of additives

The rheological behavior of clay particles in presence of additives have been studied in the past. Oztekin et al (2002) have studied the adsorption of CPB on the rheology of bentonite dispersions. They determined the effects of clay composition on adsorption capacity of clays (CaE and NaE) and correlated the adsorption isotherms with the rheological behavior of clay dispersions. CPBr surfactant is strongly adsorbed on bentonite clay particles. High affinity type of interactions between CPBr and bentonite samples is attributed to electrostatic interaction between the clay particles in suspensions and the positively charged cationic surfactant. The adsorbed polyelectrolyte affects the rheological properties of bentonite suspensions. Adsorption capacity and the influence of the polyelectrolyte on the rheological behavior change with the exchangeable ions, i.e. Na and Ca ions of the bentonite samples.

They found out that the swelling of the clays did not affect the adsorption rates. They plotted shear stress vs. shear rates for neutral CaE dispersion. The shear rate was first increased between 0 and 350 sec^{-1} and then decreased to its starting point at the same rate, and a hysteresis loop was obtained. The plot indicated that the sample follows the Bingham plastic flow model.

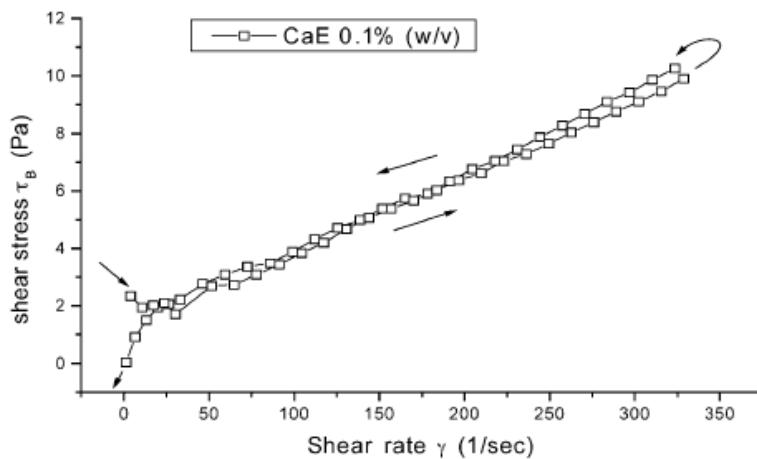


Fig. 2.1 Shear stress- shear rate rheogram for CaE (Oztekin et al, 2002)

Ece et al (2002) studied the influence of polyethylene glycol (PEG) on rheological properties of bentonite suspensions. They have shown the variations in plastic viscosities and the zeta potential as a function of concentration of PEG. The viscosity of the bentonite – water slurry increased with increase in the montmorillonite (dominant clay mineral in the bentonite sample) content. XRD studies showed that there was an expansion in the layer spacing which indicated introduction of PEG molecules into the interlayer structures.

The effect of MEG and different molecular weights of PEG solutions on bentonite was studied by Tunc and Duman (2007). They found out that the bentonite concentration did not affect the zeta potential values of Na-bentonite – water suspensions in the concentration range of 0.1–0.5%. Na-bentonite did not have an isoelectric point value in the pH ranges of 1.75–11.56 and it had a negative surface charge in studied pH ranges. High concentrations of large molecular weights PEGs in the Na-bentonite–polymer suspensions led to less negative values of zeta potential. Shear stress and shear rate values of Na-bentonite–polymer suspensions were fitted well the Bingham model. Na-bentonite–polymer suspensions showed a thixotropic behavior with a hysteresis loop. Some displacements in the peak positions were observed when FTIR spectra of purified Na-bentonite and pure polymer were compared with the spectra of Na-bentonite interacted with PEG molecules.

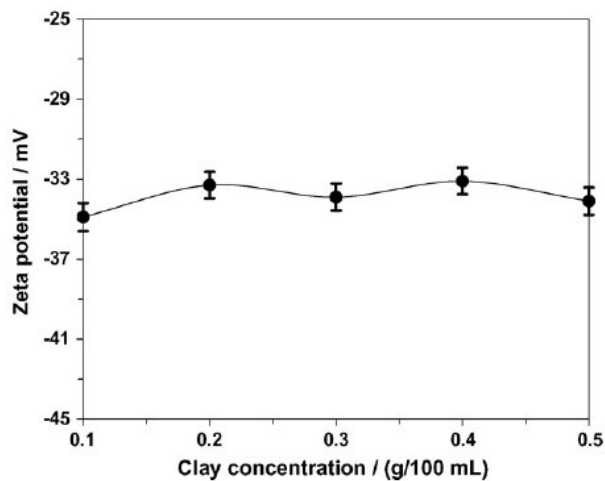


Fig. 2.2 Zeta potential vs. clay concentration (Tunc and Duman, 2007).

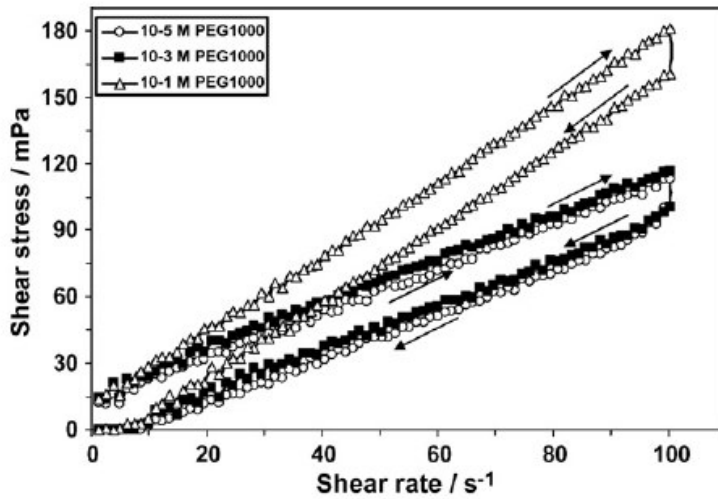


Fig. 2.3 Shear stress vs. shear rate graph of 0.2% Na-bentonite with different concentration of PEG1000 (Tunc and Duman, 2007).

Gungor (1997) studied the effect of the adsorption of surfactants on the rheology of Na-Bentonite slurries. He found out that the distearyl dimethyl ammonium ion was adsorbed on the negative faces of bentonite only at low pH values, (pH ~ 2.4) and reduced the charge, thereby decreasing the heteropolar (face-edge) interaction and so lowering the value of yield stress.

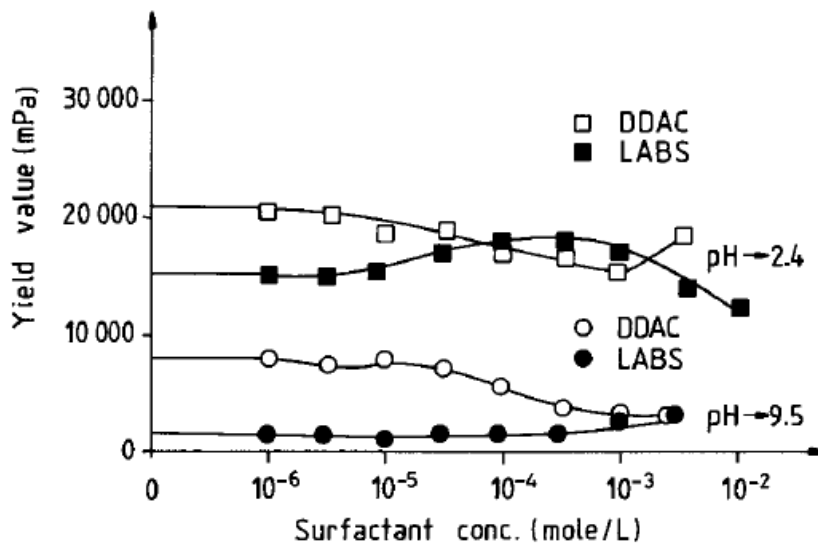


Fig. 2.4 Yield value of the sodium bentonite slurries (6% w/w) vs. the amount of DDAC and LABS (Gungor, 1997).

At pH ~ 9.5, the flow values changed with the DDAC concentration. He found that the behavior is governed by the electroviscous effect. At DDAC concentrations $> 10^{-4}$ the particles settled as flocs because the exchange of the counterions by DDA^+ cations made the particles less hydrophilic. When DDAC and LABS surfactants were added in a ratio of between 10^{-6} to 10^{-2} mol/L of the Na-bentonite, variation of shear stress with shear rate was obtained as in figure 2.6 (at pH ~9.5). After addition of DDAC surfactant, flow properties of Na-bentonite still followed the Bingham plastic model. However, an increase at yield point value was observed after addition, because viscosity increases together with increasing gel strength. It was observed that upon the addition of LABS (for 10^{-3} mol/L) Newtonian flow was obtained (at pH ~9.5).

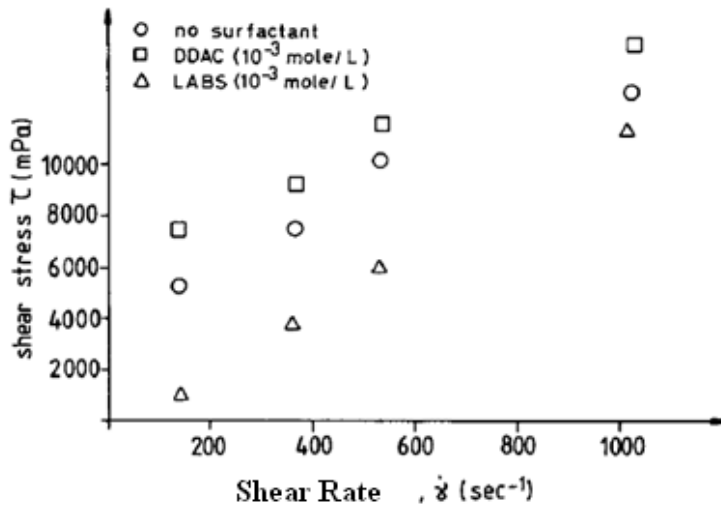


Fig. 2.5 Shear stress vs. shear rate rheogram (Gungor, 1997).

Gunister et al (2006b) studied effect of cationic surfactant on rheology of bentonite slurry. In this study, the adsorption, bridging, and intercalation effects of a cationic surfactant, benzyldimethyltetradecyl ammonium chloride (BDTDACl), on bentonite clay suspensions was investigated. The adsorption, rheological behaviors, and colloidal properties of the clay dispersions were determined as a function surfactant concentration. The degree of interaction between BDTDACl and the montmorillonite particles depends on the BDTDACl concentration in the suspension. Addition of the surfactant results in firstly flocculant and then deflocculant effect on 2% w/w of clay dispersion.

The studies on zeta potential measurements indicate that BDTDACl cationic surfactant attached onto the surface of clay particles. From the XRD studies, the increase in $d_{(001)}$ spacing is the indication of intercalation of the surfactant into the interlayers.

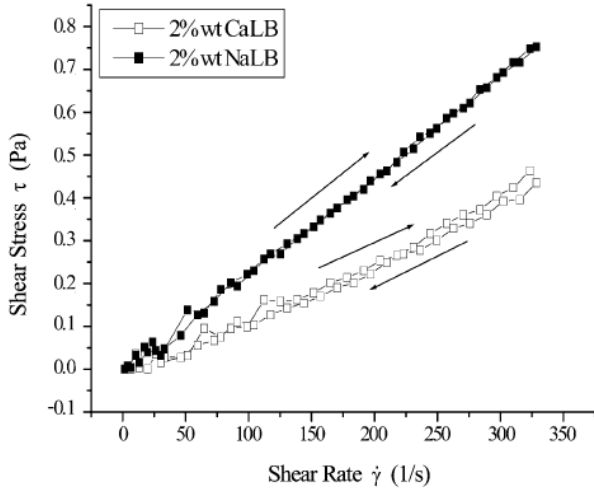


Fig. 2.6 The shear stress (τ) versus shear rate ($\dot{\gamma}$) rheogram of CaLB and NaLB dispersions (Gunister et al, 2006b).

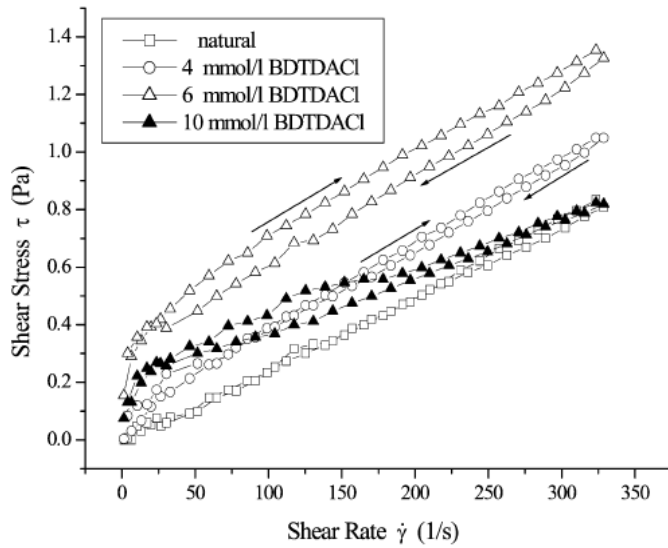


Fig. 2.7 The changes of flow curves of NaLB dispersions with BDTDACl surfactants added to dispersions (Gunister et al, 2006b).

In the figure 2.8, Gunister et al (2006b) showed the flow curves of 2% bentonite and the organoclay dispersions modified with 4, 6, and 10 mM/L BDTDACl. The figure shows a

steady increase in gelation until the 6 mM/L surfactant addition. However, at 10 mM/L surfactant addition a clear decrease is observed. The degree of thixotropic or antithixotropic behavior was measured by the area of the hysteresis loop (Figure 2.9).

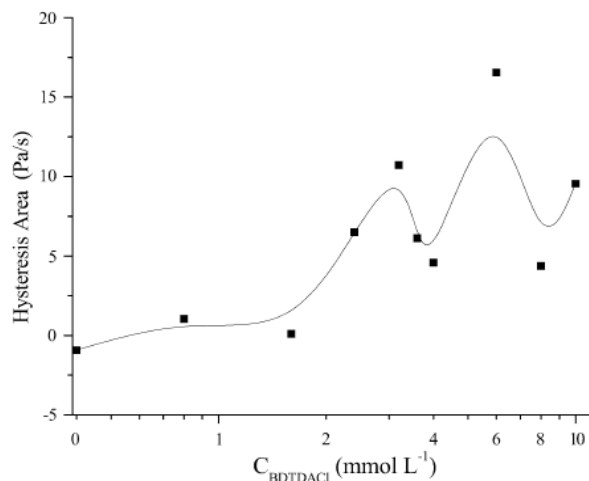


Fig. 2.8 The hysteresis loop area of 2% w/w bentonite dispersion with BDTDACl concentration.

In presence of anionic surfactants, the viscosity of bentonite dispersions were also studied (Yalcin et al, 2002). They studied the effect of sodium dodecyl sulfate (SDS) and ammonium lauryl sulfate (ALS) on the flow properties of bentonite–water systems. It was found that zeta potential values decrease in absolute values (becomes less negative), while the viscosity of bentonite suspensions increases for both surfactants above 10^{-3} mol/l or higher concentrations.

2.3 Studies on rheology of kaolin clay in presence of polymers/additives

Some studies have also been made on Kaolinite suspensions. Nasser and James (2007) have studied the effect of PAM on rheology of kaolin. The effect of polymer charge-type, density and molecular weight in the flocculation and rheological behaviour for kaolinite suspensions was investigated by them. The floc size showed a strong dependence on polymer structure. In general, larger flocs were produced using anionic polyacrylamides than using cationic polyacrylamides. On the other hand, increasing the cationic and anionic surface charge from 10 to 35% reduced the floc size and increasing the anionic and catatonic molecular weight increased the floc size. The difference in the compression

or shearing sensitivity of the flocculated slurries was attributed to floc structure-related adsorption. Cationic polymer chains adsorb via hydrogen bonding interactions between the silanol and aluminol OH⁻ groups at the particle surface and polymer's primary amide functional groups, these electrostatic attractions produces strong and less compressible floc structures. For anionic PAM, however, although the adsorption is still via hydrogen bonding between the silanol and aluminol OH⁻ groups at the particle surface and polymer's primary amide functional groups. The repulsive forces between the polymer and kaolinite surface allows the polymer molecules to be extended and produces loops and tails, which leads to the formation of large open structure flocs of less resistance to the compression load, subsequently produces compact sediment by applying some compression load.

Sjoberg et al, 1999 investigated the effect of different water-soluble polymers and surfactants, commonly used as additives in paper coating formulations, on the rheology and the colloidal stability of concentrated kaolin dispersions. They found out that highly negatively charged polymers, such as- NaPAA and NaCMC, adsorb in low amounts on kaolin at pH 8.5. The negative zeta-potential of the particles increases in magnitude at low additions, which indicated that the polymers adsorb flat on the particle surface. The corresponding kaolin dispersions are colloidally stable and have a low relative viscosity. The polymer with zero charge, PVA, displayed a higher adsorbed amount and the magnitude of the zeta-potential decreased slowly upon addition. This indicated that the polymer adsorbs in thick layers on the kaolin surface. The colloidal stability of these dispersions is poor and relative viscosity is high.

2.4 Concluding Remark

Much of the work has been done on study of rheology of bentonite dispersions. Rare studies are available on the rheological behaviour of pyrophyllite – water dispersions. The effects of cationic and anionic surfactants as well as polymers on the rheology of clays were seen in the various studies. It was seen that for most of the studies the bentonite concentration was taken less than 5%. The viscosity and zeta potential data was obtained

for the clays and analysis had been done on the variations of the surface charge of the bentonite and kaolin clays.

In the present project the effect of surfactants on the viscosity of clay-water slurry was studied. Pyrophyllite, a clay mineral, has also a broad variety of applications in industry. For example, pyrophyllite is used in ceramics, cosmetics, paint, plastics, rubber, sealant, adhesive and chemical industries. It is one of the very common low cost natural clay adsorbent with ionic crystalline structure. Pyrophyllite has a 2:1 aluminosilicate structure with two layers of silica to one of alumina. The absence of hydroxyl group at the surfaces of the triple layer prevents hydrogen bonding. In this case, the layered structure is held together by Van der Waals interaction between the plates. These are weak, so that the crystals can readily be cleaved along the basal planes (Hamley I W.)

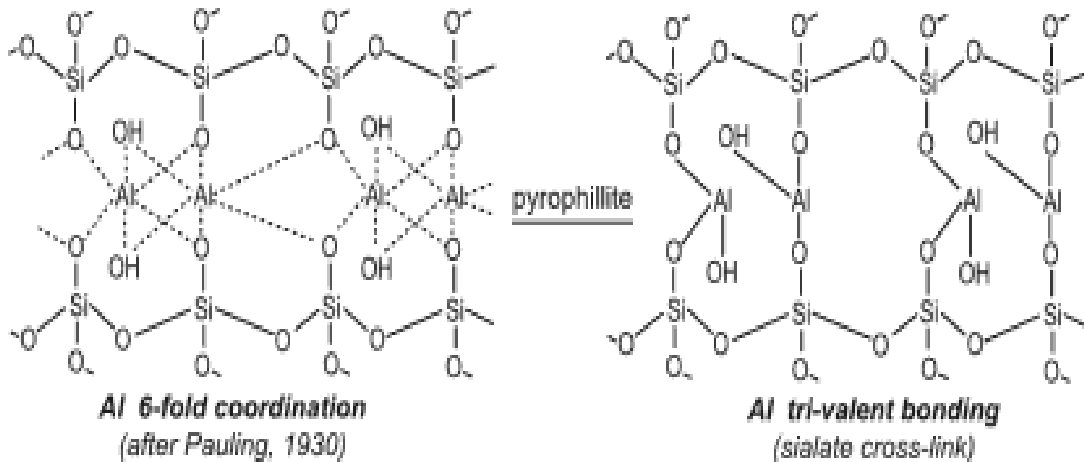


Fig. 2.9 Pyrophyllite structure

2.5 Research Objectives

In this project we have studied the rheological behavior of pyrophyllite clay. Our main objective in this study is to investigate the effect of solid concentration of slurry, pH, and finally surfactants (anionic, cationic, and nonionic) on the viscosity of pyrophyllite-water slurry. Also we have attempted to correlate the zeta potential and adsorption behavior with the rheological properties.

2.6 Organization of the thesis

In the thesis we have started with a brief introduction to rheology and the surfactant systems. Then we have given some literature review and the basis and motivation of the project work. The materials and method section comes next where all the materials and their relevant properties have been specified in detail. The experimental methods adopted are explained clearly. The results and discussion part is done later and finally the conclusion of the project work.

Chapter 3

Experimental Procedure

3.1 Materials: Pyrophyllite was obtained from Loba Chemie Pvt. Ltd., India. The surfactant Triton X-100 (TX-100) was purchased from Loba Chemie Pvt. Ltd., India of 99% purity, Cetyl pyridinium bromide (CPB) and Sodium dodecylbenzene sulfonate (SDBS) of 99% purity were purchased from Sigma Aldrich chemicals, Germany. For measurements ultra pure water (Sartorius, Germany) of 18.2 MΩ cm resistivity, 71.5mN/m surface tension and 6.5-7 pH at 27 °C were used.

3.2 Methods: The surface tension of aqueous solution of surfactants were measured at 27 °C by the Wilhelmy plate technique with a surface tensiometer DCAT 11EC (Data physics GmbH, Germany).

Surfactants	Critical Micellar Concentration CMC (mM)
SDBS	1.5
CPB	0.9
TX-100	0.15

The average particle size was measured by Malvern particle size analyzer (Mastersizer 2000, Malvern, U.K.) and found average diameter 8.092 μm. Zeta potential was measured using a zeta potential analyzer (Zeta sizer Nano ZS, Malvern, U. K.). The specific surface (BET) area of the pyrophyllite powder was measured by N₂ adsorption–desorption studies at liquid nitrogen temperature (–195.8°C) using Autosorb-1 (Quantachrome, USA). The specific surface area is found out to be 11.38m²/g (fig. 3.1). Prior to the analysis, samples were degassed at 200°C. For all the experiments, a single surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

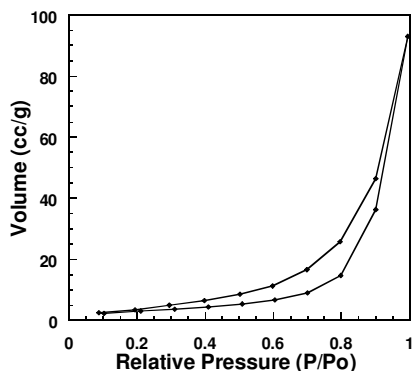


Fig. 3.1 Specific surface area of pyrophyllite

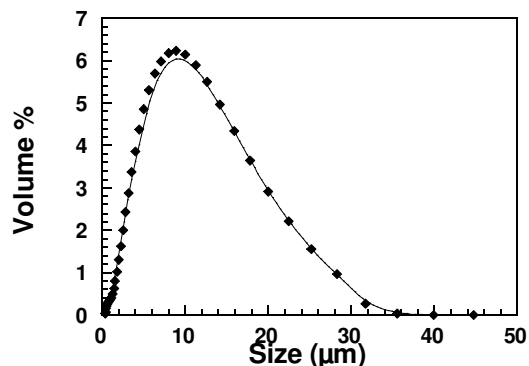


Fig. 3.2 Particle size distribution

The low nitrogen adsorption at relative pressure values <0.2 shows the absence of microporosity, a fact that is confirmed by the low value of the BET surface area, $11.38 \text{ m}^2 \text{ g}^{-1}$. The isotherm presents a narrow hysteresis loop that is associated with the presence of mesoporosity. Furthermore, the adsorption limit is not well defined at relative pressures close to one, which is an indication of the presence of macroporosity in the material.

For the viscosity measurement a cone and plate viscometer (BOHLIN VISCO-88, Malvern, U.K.) was used. The angle of the conical section is 5.4° and diameter 30 mm. A gap of 0.15 mm was maintained between the cone and plate for all the measurements. A cover was used with a wetted layer of sponge inside to reduce the moisture loss from the slurry during the measurement. All the measurements were carried out at constant temperature 30°C maintained using an external water circulator. The viscosity of the slurry without surfactants containing 40%, 45%, 50%, 55%, 60% (% by wt.) were measured at variable shear rates from 12 sec^{-1} to 99 sec^{-1} . The slurry in presence of surfactants TX-100, SDBS, CPB were prepared by adding desired surfactant solution and kept for a period of 20-25 mins for complete adsorption. All the experiments were performed at 60 sec^{-1} shear rate and at 30°C .

SEM imaging was done with JEOL JSM – 6480LB to study the structure. Fine pyrophyllite clay was dispersed in water and dropped on the glass slide. Platinum coating was done for a period of 15minutes. XRD (Phillips PW 1830HT) was done to study the changes in layer spacing upon surfactant adsorption. Five samples were taken –

pyrophyllite (without washing), pyrophyllite – CPB, pyrophyllite – TX-100, pyrophyllite – SDBS and pyrophyllite washed with ultrapure water. The surfactant solutions were prepared in proper concentrations such that the left out solution (after adsorption on the clay) was above CMC. This was checked by UV spectroscopy.

Chapter 4

Results & Discussion

4.1 Zeta potential of pyrophyllite particle

4.1.1. Aqueous medium: Zeta potential of pyrophyllite at different pH was measured to know the variation of surface charge with pH and point of zero charge pH_{PZC} . Figure 4.1 shows the zeta potential of pyrophyllite in aqueous medium become more negative with increasing pH of the medium. The Figure also shows the pH_{PZC} of pyrophyllite particle is 3.

4.1.2. Surfactant medium: Figure 4.2 zetapotential of pyrophyllite in presence of CPB and SDBS. Pyrophyllite is originally negatively charged in neutral aqueous medium ~ -15 mV, in presence of CPB first the cationic surfactant will be adsorbed through the headgroups and the surface become more hydrophobic due to orientation of the tail groups towards aqueous medium. From the Figure it is clear that about 0.01 mM CPB concentration pyrophyllite shows zero surface potential, that indicates the monolayer of surfactant is formed at that concentration. Above that concentration the surface become positive due to formation of bilayer of surfactant molecules. In presence of SDBS the zeta potential is more negative than in presence of pure water due to adsorption of anionic surfactant molecules at the pyrophyllite surface through tailgroups.

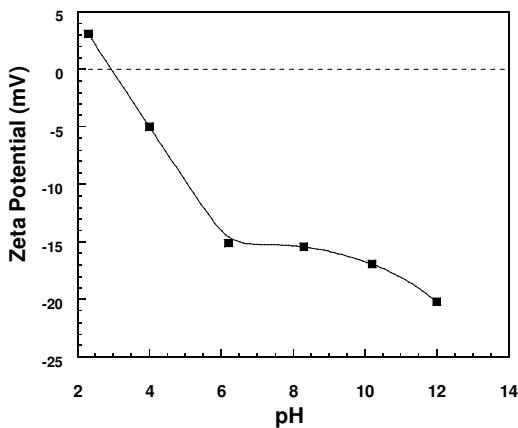


Figure -4.1: Zeta potential pyrophyllite with pH.

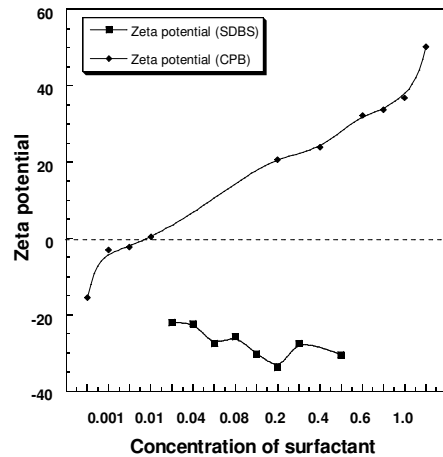


Figure -4.2: Zeta potential of pyrophyllite in presence of SDBS and CPB.

4.2. Effect of solid concentration: Experiments were performed for five different concentrations (40 %, 45 %, 50 %, 55 %, and 60 %) of pyrophyllite-water slurry and the hysteresis curve was obtained by varying the shear rate from 12 sec^{-1} to 99 sec^{-1} . It is observed that the shear stress increases with increasing the shear rate and that the viscosity decreases at higher values of shear. Also the upward curve cycle indicates a higher viscosity than the downward curve so the slurry is thixotropic in nature.

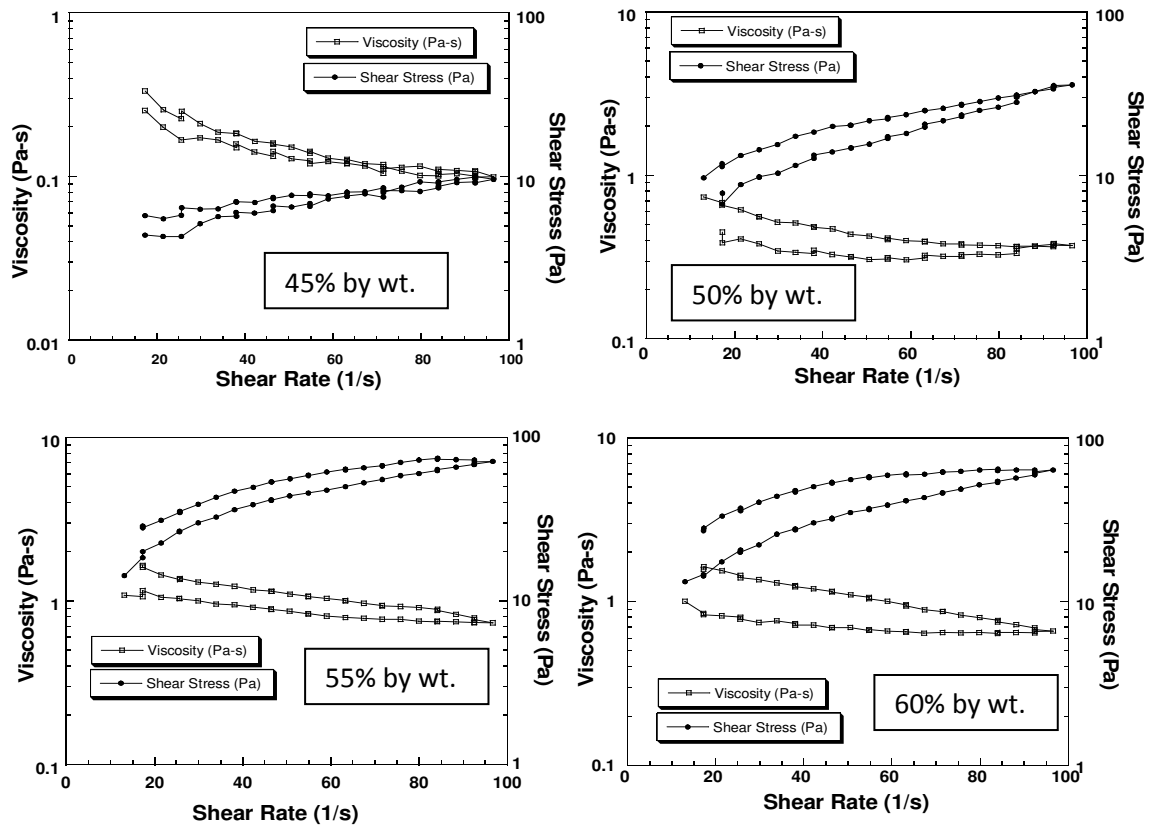


Fig.4.3 Shear rate vs. Shear stress & Viscosity

The viscosities of different concentrations were plotted in Figure 4.4 at 60 sec^{-1} shear rate. It is observed that the viscosity increases nonlinearly with increasing the concentration. The Figure obtained is “S” shaped, up to 50 % concentration the rate of change is slow but above 50% there is a sudden increase in viscosity.

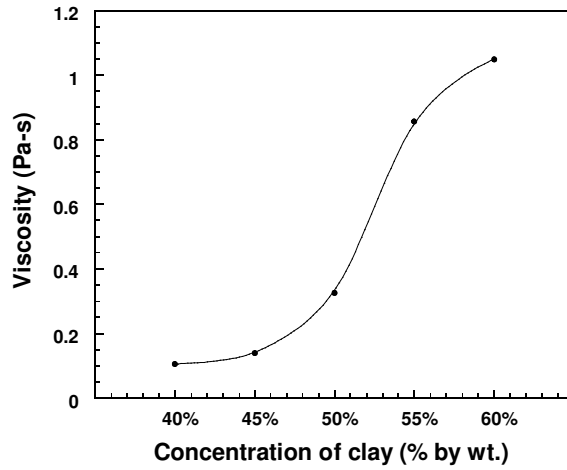


Fig.4.4 Concentration vs. Viscosity

Figure 4.5 shows, the viscosities obtained when operating at a constant shear rate of 30 sec^{-1} , 60 sec^{-1} and 90 sec^{-1} and those obtained from the hysteresis curve (taken as the average of the viscosity obtained at the above shear rates from up and down curves) are compared.

Slight variations are there in the two values which can be accounted for hysteresis losses and the varying shear rate for a long period of time.

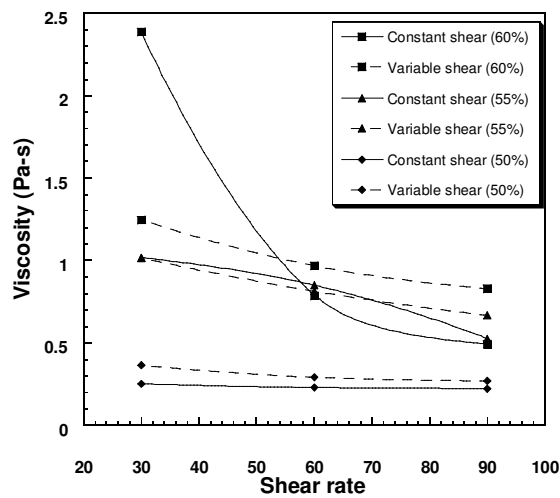


Fig. 4.5 Viscosity vs. Shear rate

4.3. Effect of pH: A solution of 55% by wt. of pyrophyllite and water was made in different pH and the viscosities were compared (fig. 4.6). The viscosity was found to be dropping with increasing pH and at a later stage became constant. The zeta potential was also measured and it was found that first it was positive, at pH = 3 it became zero and then negative. After pH = 6, the value is almost constant (Fig. 4.2). This phenomenon can be explained by the adsorption of H^+ ions on the surface of negatively charged pyrophyllite thus reducing the inter-particle repulsion which increases the viscosity at low pH. At high pH, more OH^- ions are present which will adsorb on the particle surface thereby increasing the net negative charge and hence more repulsion between the particles. As a result the viscosity of the solution decreases (Herrington et al, 1992).

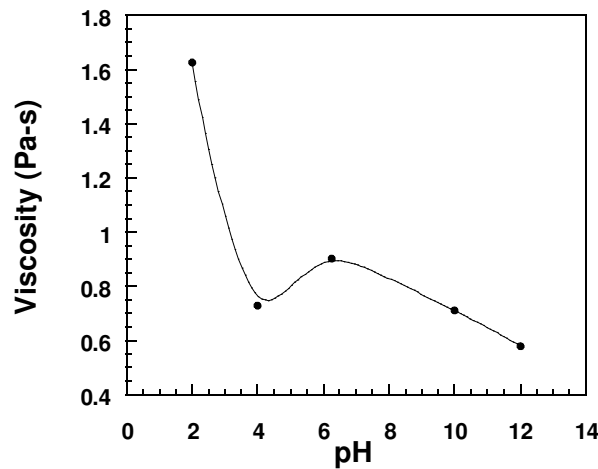


Fig.4.6 Pyrophyllite-water slurry (55% by wt.) vs. pH

4.4. Effect of surfactants: Various concentrations of TX-100 were taken and the viscosity was measured at 60sec^{-1} shear rate. These viscosities obtained were then plotted against concentration in Figure 4.7 (a). It was observed that with the increasing concentration of the surfactant in the mixture the viscosity increases. The behavior also can be attributed in terms of surface charge. Since TX -100 is a nonionic surfactant, after adsorption on the pyrophyllite surface, the surface charge is reduced, so, viscosity also increases. After 1 mM of TX -100 concentration viscosity reached to a plateau, since adsorption is also expected to reach the plateau.

Similarly, various concentrations of CPB were taken and the viscosity was measured at 60sec^{-1} shear rate. These viscosities obtained were then plotted against concentration. It

was observed that with the increasing concentration of the surfactant in the mixture the viscosity increases very rapidly up to 1.5mM concentration and then starts decreasing. This behavior may be explained in terms of surfactant adsorption behavior. Since the clay is negatively charged, cationic CPB adsorbed initially on the surface using the headgroups towards the solid surface and the surface becomes hydrophobic. The hydrophobicity of the pyrophyllite particle increases the coagulation tendency and ultimately shows higher viscosity.

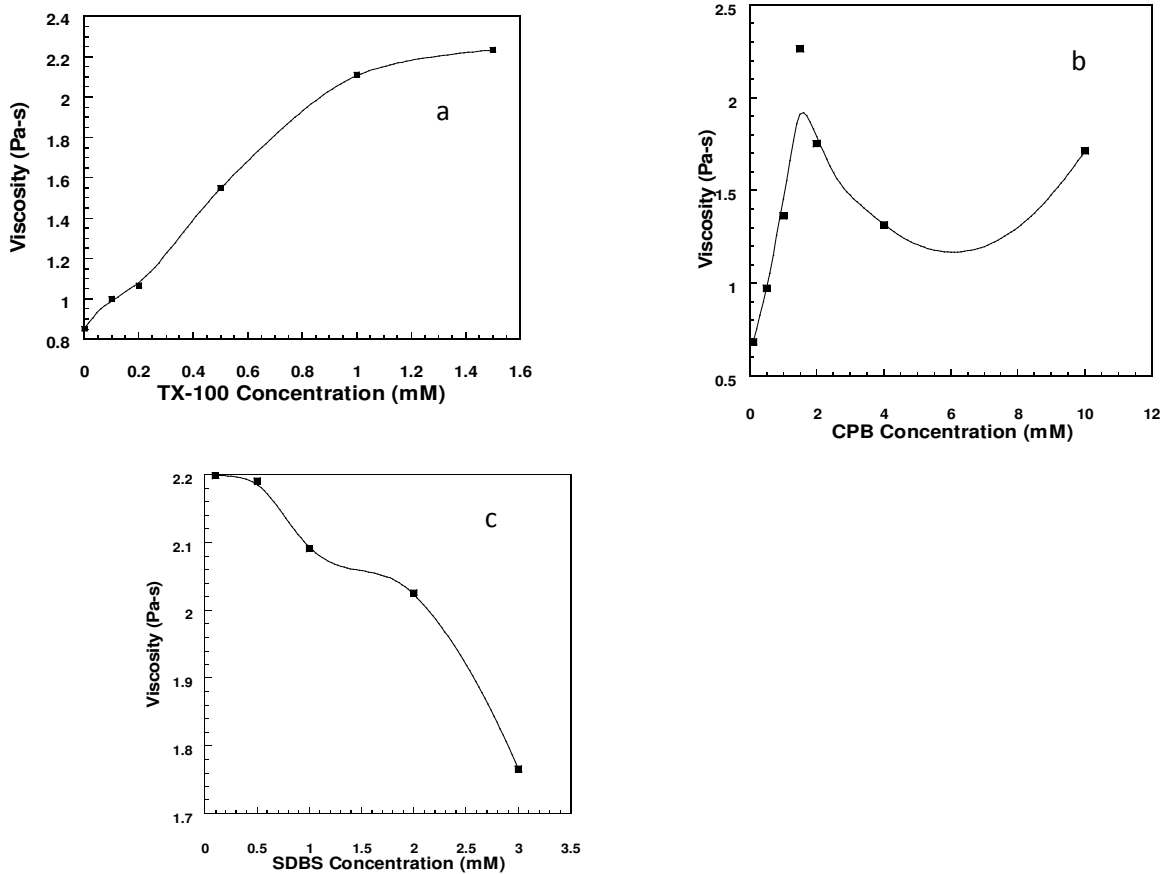


Figure – 4.7: Viscosity of 55 % pyrophyllite - water slurry at 60 sec^{-1} shear rate in presence of (a) TX-100, (b) CPB, and (c) SDBS.

With the increase in surfactant concentration, surfactant form a bi-layer by attaching the tail groups towards the solid surface and surface become more hydrophilic (positively charged). The zeta potentials values shown in Figure – 4.2 also support this behavior.

This may also explain the decreasing behavior of viscosity at higher surfactant concentration.

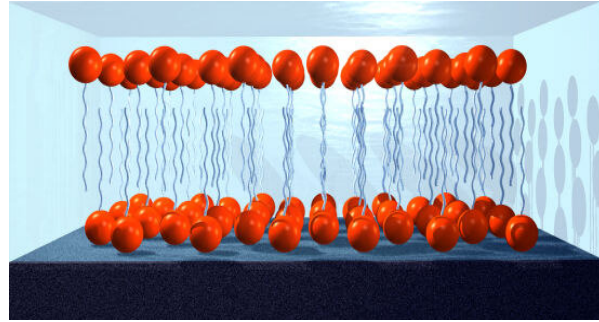


Fig. 4.8 Formation of bi-layer of surfactants

Various concentrations of SDBS were taken and the viscosity was measured at 60sec^{-1} shear rate. These viscosities obtained were then plotted against concentration. The rheogram obtained for anionic surfactant showed that the viscosity is much shear dependant, i.e., when a constant shear rate is applied over a period of time the viscosity decreases. So in order to obtain viscosities at constant shear rates, we devised a method. The first 75 seconds of the experimental run was omitted and the average of the viscosities was taken thereafter.

The change in viscosity in presence of SDBS as presented in Figure 4.7 (c) shows there is a constant decrease with increasing the surfactant concentration. This also can be correlated with the zeta potential results. When the pyrophyllite particles are more negative more reduction in viscosity is there.

4.5 Effect of surfactant adsorption on pyrophyllite layer spacing

The image of fine pyrophyllite dispersed in water was taken in scanning electron microscope (SEM). It can be clearly seen in the figure that pyrophyllite has a layer structure with plate type particles. The surfactants absorb between the layers and change the layer spacing.

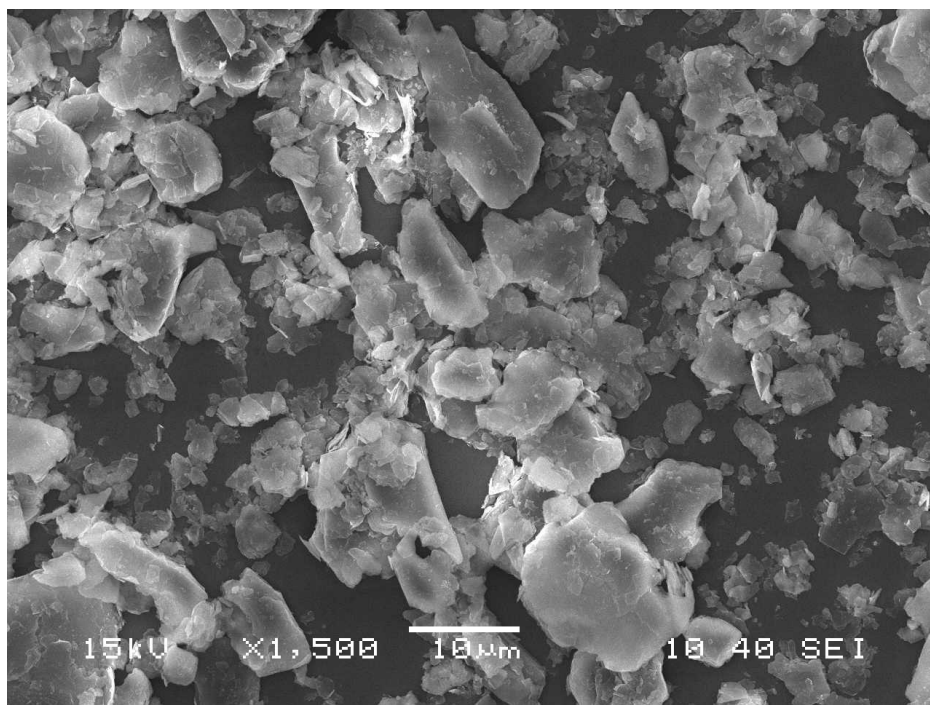


Fig. 4.9 SEM micrograph of pyrophyllite

The layer spacing obtained by the XRD data is as follows:

Pyrophyllite	d₀₀₁ spacing (Å)
Without washing	9.27
After washing	9.12
With SDBS	8.99
With TX - 100	9.16
With CPB	9.21

It can be seen from the above data that the spacing of the pyrophyllite clay decreases upon washing. This is because water dissolves some salts into it as a result of which the layers come closer. Upon adsorption of nonionic TX-100 there is a slight increase in layer spacing confirming that the TX-100 particles are adsorbed in between the spaces. As affinity for cationic CPB is more for pyrophyllite, the increase in layer spacing is much more. In case of SDBS there is a decrease in the spacing. This may be due to some cation exchange as Ca^{2+} ions are also present in the clay which may come out when SDBS is treated with the clay.

Chapter 5

Conclusion

Conclusion

It is observed that the viscosity of solid-liquid slurry increased with increasing solid content. The change in pH and the adsorption of surfactants change the surface charge of pyrophyllite. When the surface charge is less (either negative or positive) the slurry shows higher viscosity. The slurry viscosity can be reduced or increased by changing pH of the system or by adding surfactants. Anionic surfactants are more effective in reducing the viscosity of pyrophyllite-water slurry. TX-100 and CPB increased the viscosity of the clay – water slurry. It was also observed that the spacing of the pyrophyllite clay decreases upon washing. For nonionic TX-100 there is a slight increase in layer spacing. The increase in layer spacing is much more in case of CPB. In case of SDBS there is a decrease in the spacing.

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