A Thesis

Entitled

The Evaluation of the Hindered Settling Behavior of the Never Dried Calcium Carbonate Suspension

by

Akshay Jain

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Pharmaceutical Sciences with Industrial Pharmacy option

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Abstract

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The aim of the study is to prepare and evaluate the hindered settling behavior of never dried calcium carbonate suspensions and the effect of various concentrations of Poloxamer 407® as a non-ionic surfactant. Never dried calcium carbonate suspensions have been prepared stoichiometrically by adding sodium bicarbonate to calcium chloride dihydrate. The various concentrations of Poloxamer 407® used for the hindered settling phenomenon were, 0.1%, 0.5%, 1% and 2% (w/v). Due to limitations, modifications of Stokes’ law were used namely Steinour’s equation, Richardson and Zaki’s equation and Dollimore-McBride’s equations. The determination of particle size was performed using a modified Stokes’ equations along with laser diffraction. SEM was used for the morphological studies. The conclusion was made that, upon increasing the concentration of surfactant, flocculation increased with a further increase in particle size. Laser diffraction studies were in agreement with the hindered settling results and showed an
increase in particle size with increasing poloxamer concentration. Kozeny and Carman permeability approach revealed that with increase in flocculation the permeability decreases. The reason concluded was that there was a reduction in the pore size. Zeta potential studies were crucial in explaining the DLVO theory and how it affected flocculation by a change in potential with a change in poloxamer concentration. Thermal analysis studies utilizing like Differential Scanning Calorimetry and Thermal Gravimetric Analysis were performed study the bound and unbound water content of the suspensions as well as the thermal decomposition with respect to weight against temperature. Powder X-Ray diffraction helped to establish the change in surface morphology of the particles as the peaks shift forward with increase in poloxamer concentration.
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Chapter 1

Introduction

The rate of sedimentation is a complex phenomenon where various factors influence the process of settling. Hindered settling is the most important factor of all. Hindered settling is studied using various laws proposed such as Stokes’ law. The primary focus of this project was to prepare and evaluate different concentrations of calcium carbonate suspension in the never dried state. A “never dried” suspension means that they are formulated as a stoichiometric product of a chemical reaction, in this case, between sodium bicarbonate and calcium chloride dihydrate. This method is employed in industry for the manufacture of calcium carbonate suspension. It is manufactured in never dried form instead of suspending the dried powder of calcium carbonate found in nature, as chalk, in dispersion media not just because of purity concerns but also its stability. The rate of sedimentation is slower in the case of a never dried suspension which provides higher accuracy in dosage. Moreover, upon sedimentation the particles do not form cake or heavy sediment and therefore it is easier to redisperse the suspension.

Hindered settling cannot occur at low concentrations. This is why higher concentrations are used. The rate of settling is modified with an increase in concentration since there are more particles to hinder the flow of particles above them. With higher concentrations the
larger aggregates are formed which eventually take the shape of flocs. The rate of hindered settling is utilized and implemented in stokes’ law modifications such as Richardson- Zaki’s equation, Steinour’s equation and Dollimore-McBride’s equations for particle size determination. The concept of permeability was explained and determined with the help of the Kozeny –Carman equation. The formulations prepared were dispersed in a variety of poloxamer concentrations. The effect of the poloxamer concentration on the flocculation was also observed and taken into consideration for particle size analysis. The surfactant used is basically anionic in nature and creates a polymer bridge to form floccules of calcium carbonate particles dispersed in the system. The electrostatic influence of the poloxamer on the suspension for flocculation can be measured using zeta potential. The thermal degradation of the suspension dispersed in various media gives the distinctive peaks for specific components of suspensions and their decomposed products. Thermo gravimetric analysis is performed to study the thermal degradation. On the other hand, Differential scanning calorimetry is used to measure the bound water and unbound water in the suspension. The endothermic and exothermic peaks, respectively, provide a thorough insight about the heat of crystallization, heat of fusion and heat of vaporization. The surface morphology can be evaluated using SEM and laser diffraction, the later gives the particle size distribution with precise results. Powder X-Ray diffraction is another approach to have better understanding of the crystal lattice of the formulation and effects of dispersion media on the surface.
Chapter 2

Calcium Carbonate Suspension

2.1 Origin of calcium carbonate:

Calcium carbonate is a basic constituent of limestone rock. It could be found with traces of alumina and silica. Limestone occurs in several crystal forms such as Calcite; it has a rhombohedral morphological structure and has molecular weight of 100.1. Another form is Dolomite which is a chemical ore consisting of Magnesium which is also rhombohedral as far as the morphology is concerned. Limestone also occurs in orthorhombic structure known as orthorhombic, having a higher specific gravity as compared to calcite. Among all the crystal forms, calcite is the most abundant.

For pharmaceutical suspension formulations, ground ore purified calcium carbonate is not appropriate. The never dried calcium carbonate is prepared with simple stoichiometrically calculated reaction. One mole of calcium chloride dihydrate is prepared and added in one mole of sodium bicarbonate to produce calcium carbonate with the release of water. After titration, the suspension prepared was shaken vigorously to attain complete reaction between sodium bicarbonate and calcium chloride dihydrate. The suspension was kept overnight and the supernatant liquid was decanted next day. The process of decanting the liquid media (water) was performed to wash the suspension until
the suspension is sodium chloride free. Silver nitrate can be used to detect the presence of
the chloride ion in the supernatant.

\[ 2\text{NaHCO}_3(\text{aq}) + \text{CaCl}_2.2\text{H}_2\text{O}(\text{aq}) \rightarrow \text{CaCO}_3\downarrow + 2\text{NaCl (aq)} + \text{H}_2\text{O (aq)} + 2\text{CO}_2 \]

2.1

2.2 Properties of Calcium carbonate

2.2.1 Physical and Chemical Properties:

The color of calcite is white, it might exhibit a certain color depending upon the
countituents or impurities. The structure of calcium carbonate is crystalline rhombohedra.
The porosity range of calcium carbonate lies between 0.3 to 12%. Calcium carbonate is
insoluble in nature but in some special cases of increased partial pressure of carbon
dioxide it might be considered as sparingly soluble. The solubility may be increased by
milling or pulverizing the limestone. The increase in temperature also increases the
solubility by a factor of 0.5 to 2 g /L at 100°C. It does not exhibit any flammable
characteristic. Water dispersions are slightly basic in nature and exhibit a pH of 9.4 when
saturated.

Calcium carbonate reacts with strong acids to form carbon dioxide. Upon thermal
degradation around 750 - 840°C it produces CaO and carbon dioxide. When reacted with
carbonated water, it produces soluble calcium bicarbonate.

2.2.2 Structure of Calcium carbonate

The crystal study for various forms of calcium carbonate provides useful information
about the shape, crystal pattern, and porosity. The structural studies help determine the
behavior of the various calcium carbonate types present. Grain size analysis is considered to be the most primary method of analysis. The types of grains collected can be differentiated as:

(1) Micro grained (extremely fine) - less than 4µ

(2) Fine grained – between 4 and 50µ

(3) Medium grained – between 50 and 250µ

(4) Course grained – over 250µ (up to about 1000µ)

2.2.3 Biomedical effects:

Calcium carbonate is an antacid used in the treatment of higher gastric acid levels known as hyperchlorhydria. It neutralizes the acids in the stomach leading to the formation of calcium chloride.

2.2.4 Uses

Calcium carbonate is used in the purification of iron from iron ore. It is also added in swimming pools to correct the pH of the water. Calcium carbonate is used as an extender in paints. It acts as inert filler in tablets and dietary supplements. Pharmaceutically, it is also used as an antacid and in the treatment of hyperphosphatemia. It also helps reducing diarrhea by binding water in the bowel.
Chapter 3

Hindered Settling and Compartment Theory

3.1 Introduction:

Suspensions are very exclusive dosage forms, designed to dispense poorly or insoluble drugs in liquid dispersion medium. The small powdered particles are suspended homogenously in the liquid media and exhibit hindered settling after attaining a certain concentration. However, with low concentrations the particles settle without exhibiting hindered settling and they could be analyzed using stokes law [1]. Hindered settling occurs due to the presence of several particles which hinder the motion of the particles above them. Inter-particle resistance is the reason for hindered settling, which can be seen as a clear interface between the liquid and settling particles. This process of settling is also known as “en bloc” with a well marked upper boundary of clear supernatant. Hence, Stokes law cannot be applied. Considering the high importance of the dosage form, analysis and study of its behavior is imperative. Several studies have been performed to optimize its efficacy. [2]
Free settling and hindered settling are concentration dependent phenomenon. In dilute suspensions particles fall freely without any hindrance. There are certain factors which affect the settling behavior such as the physical properties of the particles and tendency to exhibit flocculation, physical and chemical properties of the suspending agent and dispersion media, concentration of the suspension, time interval since settling began which would vary due to compression and increase in concentration in the lower levels.[3]

In general, pharmaceuticals are required to have high physical stability. Stability, in the case of liquid dosage forms, must be homogenous and should not aggregate. However in the case of suspensions, due to the presence of large sized particles, the settling occurs and no external agent can nullify the effect of gravity. Thus, it is necessary to analyze the factors affecting the stability and the particle size of the drug suspended in the suspension.

In the experiment set up for concentrated suspensions in graduated cylinders, the rate of fall of the interface is monitored. A plot is constructed between the height of the interface (mm.) and time (min.). The analysis of the curve provides three respective regions; (I) initial region, (II) subsequent “linear” region where the constant rate of fall is observed and (III) compressive region. Region (I) is observed in all flocculated systems, in which the system is adjusting itself to steady state. Due to agitation or shaking of the
suspension, flocs are broken and reflocculation is taking place. Region (II) is the major hindered settling region from where the particle size could be calculated. Region (III), where the sedimentation rate decreases due to saturation, which further moves toward final settled volume.

Figure 3-1 Height (mm) of the interface against Time (min.) demonstrating Segment I, II, III of hindered settling in a flocculated system.

3.2 Stokes Law

Low concentrations of solid particles suspended in a liquid dispersion follow gravitational pull and settle to the bottom without any hindrance. The law applied in this case is Stokes’ law:

\[ V_s = \frac{2gr^2(\rho_s - \rho_l)}{9\eta} \]  

Where, \( V_s \) is the stokes limiting velocity for a spherical particle;

\( r \) is the radius of the particle;
(g) is the acceleration due to gravity;

(\rho_s) is the density of the solid;

(\rho_l) is the density of the liquid medium; and

(\eta) is the coefficient of viscosity.

The particles suspended and undergoing sedimentation are not strictly spherical and thus they differ in their rate of settling. It is evident that, different particle shapes exhibit different rates of fall. Hence, there were difficulties in developing a common correlation for determining the settling of varied structured particles. Several modifications of stokes law have been tried but all results rely on dimensionless factor. In the case of smaller inter particle interactions the law is obeyed but, in case of higher interaction values for the “Constant” changes significantly. The transition state of low concentrations is free settling and for high concentrations hindered settling. This process includes an intermediate state know as “Haze”. Haze formation could be defined as the cloudy diffused system where the upper portion is settling into the lower sediment layer. The clear supernatant is certainly not observed and lower layer is somehow moving upward. The particles merge together to settle to a final settled volume, which indicates that the hindered settling did not occur. This haze could be the consequence of low concentration, high viscosity of the dispersion media or a high dielectric constant. Sedimentation is
function of particle size and concludes that the hindered settling occurs only at an optimum concentration. According to McKay[4] this occurs due to small particles escaping from the flocculating large particulate cloud.

The proper correction factor may be applied to floccules formation between large particles when the inter-particle distance is smaller than the distance from the container wall. The consequential effect is high settling velocity and a decrease in drag on the individual particles. Bhatty et al[3] explained the behavior for free settling and flocculated settling of a suspension at lower concentrations. Settling particles have different rates of fall since some have about spherical shape while some do not. [5] A temporary cluster is formed by small particles following the path of larger particles with higher settling velocity. If the settling velocities were different among particles then the force exerted by the large particles may not be able to gather the small particles into the cluster and it tends to break. Doublets were formed as compared to cluster formation, and quadruplets were rarely found by Bhatty and D. Dollimore[3]. The similar sized particles were settled in two horizontal planes. If they are not uniform, then they will fall in a different plane to form a tetrahedron structure.

The settling rate for a single particle in isolation is always less when compared to the sedimentation rate of the particle in the concentrated suspension. Downward movement of particles creates a volumetric flow rate of displaced fluid relative to which the particles
must move.[6] Mirza performed the study on binary mixture sedimentation of equal and unequal size. The binary mixture gives rise to four zones during the course of sedimentation. The four zones are distinguished according to their particle density and size. From top to bottom these layers can be seen as clear liquid, suspension of smaller particles, suspension of intermediate or mixed particle size and finally sediment at the bottom.[6] The hindrance effect due to high concentration was also explained by Zimmels.[7] He suggested that hindrance occurs due to increased fluid velocity, which occurs because of reduced available cross section for upward movement of the liquid. A decrease in the apparent difference in specific gravity between the particles and medium might decrease gravitational pull, hence decreasing the rate of flow. Another reason could be the variation in viscosity due to the addition of surfactant or other viscosity enhancers. Several factors govern the rate of sedimentation in concentrated suspensions and the equation could not legitimately be explained. A number of equations and investigations have been performed to examine the relationship between suspension concentration, sedimentation velocity, container dimensions, bulk volume and density.

3.2.1 Steinour’s equation.

Steinour modified Stokes law, to explain the distribution of spheres in an actual suspension under a fixed arrangement and a closely maintained constant sedimentation
velocity. The steady laminar flow is established by the fluid.[8] However, if the particles are well distributed throughout medium and are of uniform size, they will fall in accordance to Stokes law. The particles will settle to the bottom of the cylinder with a constant rate of fall, neglecting the effect of the wall of cylinder. Although, the particle size may not be strictly uniform, the settling velocity can be assumed constant. The steady laminar flow is maintained by the steady shape of the fluid space, where the flow rate rises from zero to maxima.

Under any given experimental conditions for various suspensions, the particle size and arrangement is considered identical. A further problem arises, namely, contrasting laminar flow of different particle systems in different suspensions having the same flow shapes. When the flow shape size is also similar, the mean velocities can be related to the function of the velocity gradient. Hence, velocity gradient and the dimension of laminar flow are the factors sufficient to solve the mean velocity of the spheres and fluid. It was concluded that mean velocity is directly proportional to the rate of shear on the surface of the particle having spherical shape.[8]

\[ V_l = \frac{2gr^2(\rho_s - \rho_f)e\sigma(\xi)}{g\eta} \] 3.2
Where, \((\varepsilon)\) = liquid volume fraction of the uniformly mixed suspension (the initial porosity of the suspension). At infinite dilution, \(\varepsilon \to 1\) (tends to 1) and \([\phi (\varepsilon)]\) also becomes one, when Eq. 3.2 reduces to Eq. 3.1.

\(V_1\) = The average relative velocity between the spherical particles and the liquid.

\((Q)\) = The measured velocity is that of the particle relative to a fixed horizontal plane.

The volumes of the solid and fluid that move in opposite directions in a unit time gives the relationship between \(Q\) and \(V\), i.e.

\[(1-\varepsilon)Q = \varepsilon(V_1-Q)\]  
\[Q = \varepsilon V_1\]

Substituting this into Eq. 3.2 gives:

\[Q = \frac{2gr^2(\rho_s - \rho_l)\varepsilon^2\phi(\varepsilon)}{9\eta}\]

The relationship between \((V_s)\) and \((Q)\) was derived by Steinour, with potential energy loss because of various resistances during the fall of a sphere:

\[\frac{4}{3}\pi r^3(\rho_s - \rho_l)gQ = \frac{4}{3}\pi r^3(\rho_s - \rho_b)gV_s\]

This can be reduced to:
\[ \frac{Q}{V_s} = \frac{(\rho_s - \rho_b)}{\rho_s - \rho_l} \quad 3.7 \]

Where, \((\rho_b)\) is the density for computing buoyancy

For the hydraulic radius of the suspension, Steinour deduced:

\[ \varphi(\varepsilon) = \left[ \frac{\varepsilon}{1 - \varepsilon} \right] \theta(\varepsilon) \quad 3.8 \]

Where, \(\theta(\varepsilon)\) represents those effects of shape that are not evaluated by using the hydraulic radius.

Substituting of Eq.3.8 in Eq 3.5 gives,

\[ Q = \frac{2gr^2(\rho_s - \rho_l)^2\varepsilon^{3}\theta(\varepsilon)}{9\eta(1 - \varepsilon)} \quad 3.9 \]

or

\[ Q = \frac{V_s\varepsilon^{2}\theta(\varepsilon)}{1 - \varepsilon} \quad 3.10 \]

Rearrangement of Eq.3.9 gives:

\[ r = \left( \frac{9Q\eta(1 - \varepsilon)}{2g(\rho_s - \rho_l)^2\varepsilon^{2}\theta(\varepsilon)} \right)^{1/2} \quad 3.11 \]

For spherical particles settling in the presence of an attached layer of immobile liquid

Steinour further modified this equation [9] to:

\[ Q = V_s \frac{(\varepsilon - W_1)^3\theta(\varepsilon)}{(1 - W_1)^2 - (1 - \varepsilon)} \quad 3.12 \]
Where, \( W_1 \) is the ratio of the volume of the immobile liquid to the total volume of solid (including the volume of the pores) plus immobile liquid as:

\[
W_1 = \frac{\alpha}{1+\alpha}
\]  \hspace{1cm} 3.13

Where, \((\alpha)\) is the quantity of liquid in millimeters per unit bulk volume of solid.

Steinour expressed this equation in another form:

\[
Q = V_s\varepsilon^2 10^{A(1-\varepsilon)}
\]  \hspace{1cm} 3.14

Where, \((A)\) is a characteristic constant. It can be calculated from plots of \(
\log \frac{Q}{\varepsilon^2}
\) against \((\varepsilon)\) for each experiment and fitted his experimental results with a constant calculated to be \(A=1.8\).

Comparison of the coefficients in Eq. 3.14 and Eq. 3.5 gives

\[
\left[ \frac{1-\varepsilon}{\varepsilon} \right] 10^{A(1-\varepsilon)} = \theta(\varepsilon)
\]  \hspace{1cm} 3.15

This can be rearranged to give:

\[
\frac{1-\varepsilon}{e^{B(\varepsilon)}} = 10^{A(1-\varepsilon)}
\]  \hspace{1cm} 3.16

which may be inserted into Eq.3.11 to give

\[
r = \left\{ \frac{9Q\eta 10^{A(1-\varepsilon)}}{2g(r_s-\eta_1)e^2} \right\}^{1/2}
\]  \hspace{1cm} 3.17

Taking the log of both sides and rearranging, Eq.3.14 gives the following:

\[
\log \frac{Q}{\varepsilon^2} = A\varepsilon + (\log V_s - A)
\]  \hspace{1cm} 3.18
In the equation of straight line, When \( \log (Q/\varepsilon^2) \) is plotted against \( \varepsilon \), the intercept of the equation is \( \log V_s - A \) and slope is \( A \). The particle size is calculated by extrapolating the relationship to unit porosity where \( Q = V_s \).

### 3.2.2 Richardson and Zaki’s equation:

Expressions derived in Richardson and Zaki’s \([10]\) equation, showed that \( n \) is proportional to \( \varepsilon_1 \). The value for \( [Q(1-\varepsilon)] \) is the maxima for the liquid volume fraction of a homogenous suspension. Where, \( Q \) is the rate of fall of supernatant interface and \( \varepsilon \) is the initial liquid volume fraction. The rate of settling is \( \varepsilon_1 \) which reaches the \( (V_s \exp^{-1}) \), in this case \( V_s \) is stokes limiting velocity for hindered settling after infinite dilution \( \varepsilon_1 \) approaches unity).

The empirical formula is as follows:

\[
Q = V_s \varepsilon^n
\]

If a graph is plotted between \([Q (1-\varepsilon)]\) and \( \varepsilon \), it will reach a maximum at \( \varepsilon_1 \) because the value of \( (1-\varepsilon) \) decreases with an increase in \( \varepsilon \) and which might eventually be zero.

The value for \([Q \ (1-\varepsilon)] \rho_s \) is the solid flux which is simply the mass transfer of solid per unit cross section per unit time. The maximum value for \([Q(1-\varepsilon)]\) is given by:

\[
\frac{d[Q(1-\varepsilon)]}{d\varepsilon} = 0
\]
Porosity at this point can be defined as \((\varepsilon_1)\) gives:

\[
V_s \varepsilon_1^n = V_s \varepsilon_1^n n\varepsilon_1^{-1}(1 - \varepsilon_1)
\]  \hspace{1cm} 3.21

It can be simplified as:

\[
\varepsilon_1 = \frac{n}{n+1}
\]  \hspace{1cm} 3.22

Therefore, \((n)\) in this case is a function of the porosity \((\varepsilon_1)\) where \([Q (1-\varepsilon)]\), and the maximum value for solid flux is attained for the system.

Richardson and Zaki’s equation can now be given as:

\[
Q = V_s \varepsilon_1^{\varepsilon_1/(1-\varepsilon_1)}
\]  \hspace{1cm} 3.23

While the log of the equation gives:

\[
\log Q = \log V_s + n\log \varepsilon
\]  \hspace{1cm} 3.24

The plot of \((\log Q)\) vs. \((\log \varepsilon)\) ideally should give a straight line.

This signifies, \((\varepsilon_1)\) is a crucial parameter in describing the sedimentation rate for suspensions. The magnitude of \(\varepsilon_1\) can be determined by the relationship between \((\varepsilon_1)\) and the chemical system parameters. Moreover, \((\varepsilon_1)\) is just as important as the initial suspension concentration for maximum solid flux.
The experimental relationship that $(Q/V_s)$ is proportional to $(\varepsilon)$ should be expected, which is even more important than the concentration dependence.

\[
\frac{(\text{liquid volume fraction})}{(\text{solid volume fraction})} \text{ which is } [\varepsilon_1(1-\varepsilon_1)]
\]

The solid volume fraction would appear in the numerator instead of the denominator of the power term, since the hindrance to settling was merely an effect of solid concentration, expressible as a multiple power law. There is an instant decrease in interface settling rate $(Q)$ with a decrease in initial porosity $(\varepsilon)$ according to equation 3.25, as $(\varepsilon_1)$ approaches its theoretical maximum value of infinity. Hindrance in settling occurs in systems with a high concentration of solids, which follows that the $(\varepsilon_1)$ is proportional to the hindered settling [11].

The range and intensity of forces acting within the system also affects hindrance. Davies et.al [12] stated that “hindrance would be expected to be at a maximum with charged particles of large surface areas per gram in polar solvents and at a minimum with uncharged solids of small specific surface in non-polar solvents”.

It could be suggested that hindrance occurs partly due to particle-liquid (including multi-centre particle-liquid-particle) interactions [13]. It applies to the concept related to the development of long range electrostatic interactions. However, this suggestion involves
the notion of particle-particle repulsions which acts only as one of the cause of hindrance, while the model also ascribes it to particle-liquid attractions. Electrostatic repulsions prevent particle-particle cohesion which leads to relatively slow settling. Particle-liquid attractions would lead to particle-liquid cohesion reducing the effective density of the solid. The charge density on the surface of the solid which is completely open to the liquid media is certainly another important factor in determining hindrance.

3.2.3 Dollimore-Mcbride’s equation:

The expression determines the settling parameters such as \((\varepsilon_1)\), \((n)\) and \((A)\). The following method calculates the weight to volume solids concentration for mass transfer for the maximum sedimentation. Dollimore and Mcbride [14] demonstrated that a suspension settling under hindered conditions provides valuable data about the particle size, packing factor and Sedimentation mechanism for both flocculated and non-flocculated systems. The equation proposed relates the rate of fall \((\text{cm sec}^{-1})\) of the interface between the slurry and supernatant to the concentration \((\text{g cm}^{-3})\) of particles in homogenously mixed suspension. A plot of \(\log Q\), where \(Q\) is designated as the rate of fall for hindered settling, against the initial concentration \((C)\) gave a straight line with “b” being the slope of the equation. The mean particle size for the suspension was derived
from the graph which was plotted; and provided the values for the mean particle radius in the slurry.

Log (Q) against Log (ε) plot discussed by Davies et al[14], where ε is stated as the initial liquid volume fraction of a homogenous suspension or it can also be called its initial porosity. The slope derived Davies shows the direct relation to the (ε) which corresponds to the maximum solid flux or the maximum mass transfer of the sedimentation volume.[15]

The linear equation for Dollimore and McBride can be written as:

$$\log Q = a - bC$$  \hspace{1cm} 3.25

At infinite dilution, then:

$$a = \log Q$$  \hspace{1cm} 3.26

Since,

$$Q = V_s$$  \hspace{1cm} 3.27

Therefore,

$$10^a = 10^{\log V_s} = V_s$$  \hspace{1cm} 3.28

And,

$$Q = V_s 10^{-bC}$$  \hspace{1cm} 3.29

The initial porosity (ε) can be expressed as:
\[ \varepsilon = \frac{V_{sn} - V_{sd}}{V_{sn}} \]  \hspace{1cm} (3.30)

where,

\[ V_{sn} = \text{volume of the suspension} \]

\[ V_{sd} \] is the volume of solid,

Since,

\[ V_{sd} = \frac{\text{mass of the solid}}{\text{density of solid}} = \frac{M_s}{\rho_s} \]  \hspace{1cm} (3.31)

Therefore,

\[ \varepsilon = \frac{V_{sn} - \frac{M_s}{\rho_s}}{V_{sn}} \]  \hspace{1cm} (3.32)

or it can be expressed as:

\[ \varepsilon = 1 - \frac{M_s}{\rho_s V_{sn}} \]  \hspace{1cm} (3.33)

Since, \[ \frac{M_s}{V_{sn}} = C \]

After substitution,

\[ \varepsilon = 1 - \frac{C}{\rho_s} \]  \hspace{1cm} (3.34)

Where, \( (\rho_s) \) = density of solids.

Substituting \( (C) \) by the initial porosity \( (\varepsilon) \),
\[ Q = V_s 10^{-b \rho_s (1 - \varepsilon)} \quad 3.35 \]

After taking the log on both sides of Equation 3.35,

\[ \log Q = \log V_s - b \rho_s (1 - \varepsilon) \quad 3.37 \]

Also,

\[ \log Q = \log V_s + 2 \log \varepsilon - A(1 - \varepsilon) \quad 3.38 \]

It can also be written as,

\[ b \rho_s (1 - \varepsilon) = A(1 - \varepsilon) - 2 \log \varepsilon \quad 3.39 \]

Therefore,

\[ A = b \rho_s + \frac{2 \log \varepsilon}{(1 - \varepsilon)} \quad 3.40 \]

Log \( \varepsilon \) becomes zero at infinite dilutions, therefore:

\[ A = b \rho_s \quad 3.41 \]

Results obtained using the Dollimore and Mcbride method fall in very close proximity of those derived from the Richardson and Zaki’s method. In a uniformly mixed suspension the Dollimore and McBride plot can calculate the weight to volume solids concentration.

Rearranging the equation

\[ \varepsilon = 1 - \frac{1}{2.303 \frac{b d}{d}} \quad 3.42 \]
When, \( C = C_{\varepsilon 1} \),

\[
2.303b\varepsilon_1 (1 - \varepsilon 1) = (1 - \varepsilon 1)
\]

3.43

\[
C_{\varepsilon 1} = \frac{1}{2.303b}
\]

3.44

Hence, a plot of \( \log(Q) \) against \( (C) \) (the solids concentration \( (C_{\varepsilon 1}) \) (g.cm\(^{-3}\)) for maximum solid flux) is obtained where \(-b\) is the slope using equation 3.44.

### 3.3 Packing Factor and Flow Units:

The solid particles undergoing settling are assumed to carry a certain amount of liquid down the laminar flow. It is supposed to be the important factor which determines the sedimentation behavior of the suspension. The increased sedimentation volume for the solids usually indicates the total amount of associated liquid, since the predicted value for solid volume from the actual solid weight and density differs markedly from the value obtained during the experiment.

McKay [4] asserted that the retention of liquid with the flocs or flow units is directly correlated with the surface morphology, packing of the solid into the flocs and distribution of the surface charge. The packing factor term was introduced by McKay[4] and considered not be associated with the flow units. The liquid is supposed to be the one which is present in the voids between the flow units.
Flow units were described by McKay as:

\[ p = \frac{(1-\epsilon')}{V} \]  

(\(\epsilon'\)) is the corrected volume of (\(\epsilon\)).

(p) is the packing factor.

(V) is the Final settled volume.

(1-\(\epsilon'\)) is the volume fraction of the flow unit.

By diluting the same master dispersion and preparing a series of dependent dispersions which differ only in the value of (c) by McKay’s equation, the packing factor (p) can be evaluated from (Q) and (v) data as follows:

\[ Q = \left(\frac{2g}{9\eta}\right) \left(\rho_s - \rho_l\right) \left(\frac{c}{pv}\right) (1 - \rho_{vs})^{2.7} (10^{-1.82pv}) \]  

Bhatty et al[3] and McKay [4] concluded that when P > 1, as the solid flux settles at the bottom as sediment the associated liquid is forced off. And in contrast, P < 1, there is a minor portion of associated liquid where there is close packing of incompressible solid spheres. This concludes that the larger amount of associated liquid corresponds to the larger p value and lower effective density of floc and greater hindrance.
3.4 Kozeny – Carman Permeability Approach:

Two sets of theories were proposed for the behavior of concentrated suspensions and the rate of fall. The First set of theories were essentially based on Stokes’ law while the second was for the suspension as a packed bed where the fluid flows through and is based on the concept of permeability.[16]

The equation of Kozeny – Carman[17] can be expressed as:

\[ \nu = \left[ \frac{\varepsilon^3}{K \eta^2 S^2} \right] \frac{\Delta P}{L} \]  

Where,

\( \nu \) = Apparent velocity of fluid through the total cross section of the container.

\( \varepsilon \) = volume of pore space per unit volume of bed (i.e., the porosity)

\( K \) = Kozeny constant, originally stated as 5.0

\( \eta \) = Fluid viscosity (gm.cm\(^{-1}\).s\(^{-1}\))

\( S \) = Particle surface area per unit bed volume (cm\(^{-1}\))

\( \Delta P \) = Pressure difference across the bed depth (gm.cm\(^{-1}\).s\(^2\))

\( L \) = bed’s depth

Under the influence of gravity, the particles in high concentration in a suspension tend to create some problems. Particles tend to move in a laminar flow and the Reynolds number
is assumed to be $\leq 0.2$. The relative velocity for that of solid flux is $(Q)$, which can be compared with the liquid at velocity $(v)$ through a motionless bed.

Happel[18] Proposed the following equation to overcome the problem in sedimentation:

$$Q = \left( \frac{1}{2K} \right) \left( \frac{\varepsilon^3}{1-\varepsilon} \right) V_s$$  \hspace{1cm} 3.48

It can also be expressed as:

$$Q(1 - \varepsilon) = \left( \frac{1}{2K} \right) V_s \varepsilon^3$$  \hspace{1cm} 3.49

In the case of a settling bed, the particles can’t adjust themselves in the fluid flow but rather the particles tend to sediment mass. The particles participating in the hindered settling, which are flowing in the laminar flow is comparable to fluidized bed. Since, the particles of different size are undergoing hindered settling, they also settle with same velocity. Bhatty et al [5] demonstrated that, porosity is dependent on $(Q)$, and when $(\varepsilon_1)$, changes from exponential to a sigmoid curve. With a decrease in Porosity above $(\varepsilon_1)$ the maximum rate of mass transfer occurs until the settling plug is formed where there is a decrease in porosity below $(\varepsilon_1)$. 
At some value \((\varepsilon_K)\) which is less than \((\varepsilon_1)\), Dollimore and Mcbride have shown that \((K)\) reaches its minimum value \((K_{\text{min}})\). The relationship between \((\varepsilon_K)\) to \((\varepsilon_1)\) is as follows:

\[
\varepsilon_K = \frac{4\varepsilon_1 - 3}{3\varepsilon_1 - 2}
\]

It follows that the values for \((\varepsilon_K)\) and \((\varepsilon_1)\) converge as \((\varepsilon_1)\) increases and attain virtual identity when \((\varepsilon_1)\) is equal to unity (i.e., in highly hindered systems).

For such suspensions, \((K)\) varies inversely with \((\varepsilon)\) virtually all the way up to \((\varepsilon_1)\).

Figure 3-2 Kozeny-Carman parameter \(k\) dependence on Porosity for various parameters, A, n=4; B, n=7; C, n=10.

Davies and Dollimore [19] concluded that, the mass of particles undergoing hindered settling is equivalent to fluidization, which is proportional to the laminar flow of the
fluid. The Kozeny Carman equation’s variable (k) is not inversely related to the liquid volume fraction of the suspension. A solid volume fraction of 25% and more would not give the maximum rate, given the relation between the Kozeny Carman and Richardson’s and Zaki equation.

3.5 Determination of Particle size:

The particle can essentially be derived from the rate of settling. The sedimentation phenomenon is carefully studied physical properties of the system such as viscosity, shape and density can help deriving the particle size of the settling particles in a uniformly mixed suspension. Modification of Stokes’ principle helps determining the average particle size.

3.5.1 Steinour’s method:

Considering Q (average setting rate) as the most important parameter for calculating particle size, Steinour stated:

\[ Q = V_s \epsilon^2 10^{-A(1-\epsilon)} \]  \hspace{1cm} 3.51

Taking log,

\[ \log \frac{Q}{\epsilon^2} = A(\epsilon) + (\log V_s - A) \]  \hspace{1cm} 3.52
A plot constructed between \( \log (Q/\varepsilon^2) \) and \( \varepsilon \), as indicated in figure 3.3, should be linear. Slope and intercept could be derived which gives the exact values for the \( (A) \) and \( (V_s) \)

\[ \text{Figure 3-3: Plot of } \log [(Q/\varepsilon^2)] \text{ against } (\varepsilon)[3] \]

### 3.5.2 Limiting Stokes Velocity:

Stenour derived the relation between \( (V_s) \) and \( (Q) \) :

\[ Q = V_s \cdot \varepsilon^2 \varphi(\varepsilon) \quad 3.53 \]
Particle diameter is related to the function “$\phi \varepsilon$”, which depends on the relative size and shape of the flow space. After infinite dilution the function $\phi \varepsilon$ becomes unity.

\[ V_s = \frac{2g}{3\eta} \cdot (\rho_s - \rho_l) \cdot r^2 \quad 3.54 \]

$\rho_s$ and $\rho_l$ = Densities of solids and liquid respectively.

$\eta$ = Viscosity of the liquid

g = Acceleration due to gravity

$r$ = Particle radius

The above equation does not solve for the uniform particle size of the suspension, but also solves for non-uniform particle sizes. In such cases it gives an average particle size.

The only modification could be done is replacing the “r” with hydraulic radius \[20\], which can also be defined as the flow volume wetted surface. It can be expressed as:

\[ h_r = \frac{r(\varepsilon)}{\frac{\varepsilon}{1-\varepsilon}} \quad 3.55 \]

The expression changes by the introduction of the equation 3.55:

\[ Q = V_s \left[ \frac{\varepsilon^3}{(1-\varepsilon)} \right] \cdot \varepsilon \theta \quad 3.56 \]

Where, $\theta(\varepsilon)$, $\varepsilon/(1-\varepsilon) = \phi(\varepsilon)$.

\[ Q = \frac{0.123 V_s}{(1-w_1)^2} \cdot \frac{(\varepsilon-w_1)}{(1-\varepsilon)} \quad 3.57 \]

Where, $w_1$ = ratio of volume of the liquid to the total volume of the solids.
3.5.3 Richardson and Zaki Method:

The plot of log (Q) against log (ε) is used to calculate the (Vs) and (r). the slope obtained is (n) and the intercept is Vs.

\[ \log Q = \log V_s + n \log \epsilon \]  

3.5.4 Dollimore and Mcbride’s Method:

The plot of (log Q) against concentration (C) for the total solid flux is obtained linear. The extrapolation of the data to zero concentration and Q (terminal velocity) were equated to (Vs) in order to obtain the particle size.

\[ \log Q = \log V_s + n \log(C) \]  

Hindered settling proves to be the best possible method to perform particle size analysis studies. Physical and chemical changes in the precipitation may cause some interference in particle size determination. Dollimore and McBride [19] have demonstrated that nucleation is controlled by the degree of supersaturation which consequently derives the particle size. Rate of addition of reagents is important in controlling particle size, which controls the precipitation.
3.6 Final Settled Volume:

The final settled volume consists of the total solids and volume of the voids present in between the particles. Bulk density varies throughout the height of the settled bed, it is not uniform. The number of pores per unit volume is much higher in the upper zone as compared to the lower zone, where density is higher as compared to the upper zone. The upper zone has more liquid trapped in the pores; this liquid tends to move from the settled bed during the compressive phase of sedimentation.

The total volume of the solid, volume of space between particles and pore volume makes up the total bulk volume. Moreover, the surrounding matrix also adds up to the bulk volume.

The shape of the particle affects the final settled volume. In the three dimensional packing of solids in a matrix, the packing spheres arrange primitive cubic, extended hexagonal and body centered. All particle packing were differentiated and explained according to their coordination numbers. The cubic packing or hexagonal packing creates coordinates of six, which makes the system regular. Coordinates less than six have more void spaces, due to which instability increases. In the case of very fine particle system’s settled volume, the coordination number is from four to six. The coordination number moves further down as the particles become even finer.
The presence of electrostatic interaction between particles may decrease the coordination number. According to Steinour, for higher concentrations, the particle porosities vary from 0.26 to 0.95 only if the shape factor (A) is known. It was also concluded that the particle size could also be determined by having knowledge of the sedimentation volume.

Robinson and Ward and Kammermeyer [21] suggested that the sedimentation volumes were recorded as the ratio of the final height (Hf) of the settled bed, to the initial height (Ho).

\[
\text{Sedimentation Volume} = \frac{H_f}{H_o}
\]  

Dintenfass (1959)[22] derived a n equation where he utilized the ratio of the final settled volume to the original volume.

\[
F = \frac{V_u}{V_o}
\]  

The surfaces of two adjacent particles and the cohesive force between them determine the surface energy. Surface energy is directly proportional to the adhesive force between the particle surfaces. The force of adhesion decreases as the particle size increase. Similarly, smaller particles exhibit a higher degree of adhesion compared to the weight of the individual particles causing adhesion. Therefore, fine particles do not break into fragments or dust as compared to larger and coarse particles. A system of large voidage is present between the small particle’s points of contact. [23] In order to sustain stability, the particles must have a finer geometry and high voidage. In other words, the systems
with finer particles produce large sedimentation volume compared to larger ones. It was finally concluded by Dollimore and McBride [19], “sedimentation volume is a function of porosity and also depends on the voidage”. Associated liquid along with the settling particle plays a vital role in sedimentation volume. Liquid attached to the particle forms a floc of greater diameter. Density of this aggregate is the mean weight of its liquid and solid content.

The density ($\rho_c$) of the particles, surrounded by liquid can be expressed as:

$$\rho_c = \frac{\rho_s + \rho_l \partial}{1 + \partial}$$  \hspace{1cm} (3.61)

Where, ($\partial$) is the quantity of bound liquid per centimeter cubed of solid. The value of ($\partial$) is calculated by monitoring the final settled volume and computing the quantity of solid surface bound liquid and free liquid contained in the flocs.

The nominal porosity ($\varepsilon$) is changed to a value ($\varepsilon_m$), since as ($\partial$) increased for small values of ($\varepsilon$), ($\varepsilon_m$) was apparently negative (for a value equal to 1, the calculated values for ($\varepsilon_m$) corresponding to an ($\varepsilon$) below 0.5 which are negative). The quantity of bound liquid fell into the two extremes for the total settled volume. The upper limit will be represented by the final settled volume and it will be increasingly high depending upon the larger voids between the particles and the settled associated liquids. Therefore, the
mean spherical radii are equal to the mean equivalent particle or floc together with its bound liquid along with the solids.
Chapter 4

Flocculation and Particle Interactions

4.1 Overview

The suspension formulation should be homogenous after shaking the container in order to dispense the optimum amount of dosage. However, the particles dispersed in the system will begin settling as soon as the agitation stops and gravity becomes the absolute force. The rate of settling can be decreased by introducing several excipients into the formulation such as viscosity enhancers. The ideal stable suspension formulation must be uniformly distributed in the dispersion media and, if the settling occurs, it should not form aggregates and should be easily redistributed after a gentle shaking or agitation with no signs of caking.

4.2 Wetting of the Suspension

The addition of any favorable excipients causes flocculation or deflocculation of the suspension. The magnitude of the force of attraction and repulsion decides whether the suspension will or will not flocculate. Compared to the flocculated system, deflocculated systems have a slow sedimentation rate and are considered to be a more homogenous dosage form. However, there is a disadvantage for aggregated settled bed formations,
which is difficult to re-disperse. On the other hand, flocculated system is easy to redisperse, but there is a higher chance for dosage errors.

The requirement of using an appropriate wetting agent is necessary for obtaining the desired suspension formulation. During and after the solid particle’s contact with liquid, the surface energy decreases. [24] Depending on the hydrophobicity of the particles, wetting agents may be used. HLB (Hydrophilic-Lipophilic balance) is the factor to be taken into consideration. The HLB range of value from 7 – 9 selected surfactants will decrease the interfacial tension between the solid and the liquid to the greater extent and considered to be optimum. Colloids which are hydrophilic in nature also act as protective colloids by layering the solid particle from the surface. Some examples are acacia, bentonite, tragacanth, and other cellulose derivatives. Some other wetting agents which are frequently used include alcohols, glycols (PEG) etc.

4.3 Flocculation of Suspension and Double layer

Particle size is the major factor governing the rate of fall.[25] According to Stokes’ principle, settling rate decreases with an increase in Particle flocculation or an increase in particle size. Surface energy is higher with the smaller particles and therefore the small particles form flocs (aggregates) to decrease the surface area and thus reduce the surface free energy. These flocules stay together with the help of weak forces of Van der Waal.[26] The force of attraction which holds the aggregates is so weak that it can be broken and particles would be easily dispersible. In contrast higher forces of attraction resulting in the formation of aggregates and redispersibility is difficult. The phenomenon which is responsible for the free movement of the particles across the dispersion is known as Brownian motion. Due to the larger particle size in deflocculated suspensions, the
gravitational force nullifies the Brownian movement and thus sedimentation occurs. Particles have a tendency to flocculate to become thermodynamically stable.

Repulsive forces are produced due to the electrical double layer surrounding the particles. The double layer demonstrates how the electrical repulsive forces occur in the vicinity of a charged colloid. The model is visualized as ionic environment where neutralizing ions of negative colloids suddenly get detached. At the surface of the colloid, negatively charged particles create and attract positively charged particle to form a counter-ion layer known as the stern layer. The positive layer on the surface of the colloids repels further approaching positively charged ions and creates a condition of dynamic equilibrium. On the other hand negatively charged ions, around the surface are repelled by negative ions present on the surface. The negative ions are also called co-ions since the colloid is also negatively charged.

The difference in the concentration of positive and negative ions at any point is equal to the charge density at that point which diminishes as the distance from the colloids increased and concentration of positive and negative ions merge together. A double layer is nothing more than positive ions attached to the surface of colloids and ions present in the diffused layer.

4.4 Zeta Potential and the DLVO Theory:

An electrokinetic potential is developed between any point surrounding the colloid and the surface of the colloid, which neutralizes the charge on the colloid, this phenomenon is known as the formation of the double layer. The potential developed is referred to as surface potential with millivolts as its units. The Surface charge and the thickness of the double layer are the critical factors which govern the magnitude of the potential on the
As shown in Fig 4.2, the magnitude of the surface potential decreases almost linearly in the stern layer followed by an exponential drop in the diffuse layer which finally reaches the value of zero at an imaginary boundary of the double layer. The mobility of the particles is related to the dielectric constants, electric potential between the liquid and solid particles and viscosity of the suspending liquid. The electric potential between the junction where the Stern layer and diffuse layer meet is called the “Zeta potential” and the zone is called the Slip plane.[28]
Fig 4-2 Variation of ion density in the diffuse layer, (Upper) The variation in positive and negative ion concentration with distance from a negative colloid; (Lower) Net effect of charge density.
The DLVO theory was named after Derjaguin, Landau, Verwey and Overbeek. This theory explains the stability of colloids in suspensions. The relation between the particle agglomeration with forces such as electrostatic repulsion and Van der Walls attraction is revealed in this theory. In a homogenous suspension when two colloids come close together, their double layers begin to interface, Electrostatic repulsion becomes significant.[29] The amount of energy required to separate two colloids can be derived from the electrostatic repulsion curve. Van der Waals attraction occurs due to attraction
between the colloids and molecules present in them. Van der Waals forces are additive in nature and the value is the total amount of force applied by individual molecules.[30] The curve seen in Figure 4.4, provides an insight into the variation in forces with respect to distance between the particles. Particle agglomeration is an event when particles on either side must carry sufficient kinetic energy with the mass to cross the barrier and collide. Depending upon the type of study and research goals, changes can be applied which include altering the ionic strength, pH or the addition of any surfactant to directly affect the charge of the colloid. [31]

Fig. 4–4 The net interaction curve (Attraction curve – Repulsion curve)

4.5 Surface Active Agents:

Surface active agents are also called surfactants. These are the excipients added in low concentration which act as modes for changing the surface tension and the surface free energy. They tend to adsorb on the surface of the particles suspended and reduce the
interfacial energy which is required to form the interface between two phases during hindered settling.

### 4.5.1 Properties and Behavior of Surfactants

The molecules which are present in the interior of the suspension system require higher amounts of work to move to the surface. Thus, the potential energy of the molecules on the surface is higher than the molecules present in the interior. The reason is that the molecules on the surface have a higher degree of interaction with molecules in the interior as compared to the interaction with the free air outside the system. The structure of surfactants is such that they have both a lyophilic group and a lyophobic group. Thus, they are also referred to as being amphiphatic in nature.

Hydrophobic groups which are also called lyophobic when dissolved in a solvent increase the free energy by creating a distortion of the solvent. This means that a lesser amount of work is required to bring the surfactant molecule to the surface due to an increase in free energy. Due to the amphipathic structure of the surfactant, its concentration rises to the surface and also reduces the surface tension of water. For different conditions such as temperature or electrolyte a change in the surfactant is necessary to maintain the optimum surface activity.

### 4.5.2 Types of Surfactants and Flocculation Properties

The hydrophobic group present in the surfactant is a hydrocarbon chain residue or an oxygenated hydrocarbon or siloxane chain. The hydrophilic group is the factor which differentiates several surface active agents. They may be classified as:
1. Anionic surfactants:

2. Cationic surfactants

3. Zwitterionic surfactants

4. Nonionic Surfactants

Properties of polymers such as functional group attached, molecular weight, ionic strength of the particle and the solvent system are the major factors governing adsorption of the polymer on the particles and efficiency of flocculation. Cationic polymers are responsible for increasing flocculation in china clay suspensions. On the other hand negatively charged anionic surfactants get repelled by the china clay.[32] Non ionic suspension can also flocculate the suspension. The adsorption will be stronger, if the electrostatic charge on the particle and polymer are opposite with higher magnitude. The polymeric chains of the surfactants are responsible for keeping the particles separated to avoid heavy agglomerate formation. The polymers intend to form a protective layer around the particle which is called the steric protection. They also minimize the probability of particle link formation by reducing the uncoated areas.

4.5.3 Electrolytes

Electrolytes are responsible for bringing the particles together to form floccules. The charge on the particles creates repulsive forces which keeps the suspension stable. The aggregation of particles occurs with multi-valent ions attaching on to the surface. In such cases, electrolytes act as a deflocculating agent by inducing a negative charge. In the cases of a highly charged species trivalent or higher electrolytes can be utilized. Although, trivalent electrolytes are most efficient, trivalent electrolytes are not commonly
used because of their toxic nature. The concentration of electrolyte to be used depends upon the desired degree of flocculation.

4.5.4 Adsorption of strongly charged particles

The ion–exchange mechanism led adsorption of surface active counterions doesn’t change the electrostatic potential of the adsorbent.[33] But the potential at the stern layer may decrease if the adsorption through ion-pair mechanism continues and eventually becomes neutralized. When the charge neutralizes, the particles with a similar charge stop repelling each other. Therefore, the particles suspended earlier due to similar charge tend to flocculate together as the charge neutralizes. The orientation of the hydrophobic end of the surfactant adsorb on the aqueous region to make the surface highly hydrophobic. The contact angle at the solid-water-air interface increases to the extent where zeta potential reaches zero.[33]

4.5.5 Adsorption of Polar group

Adsorption of surfactants at any concentration on a substrate with a polar group on the surface occurs where the hydrophilic group of the surfactant attaches to the aqueous phase. Hydrophilicity increases with this adsorption. For ionic surfactants, there is an increase in its surface charge density, making it more wettable by the polar phase. “In case of polyoxyethylenated nonionics, adsorption may produce a steric barrier to the close approach of another similarly covered particle since such approach would result in the restriction of the movement of the randomly coiled polyoxyethylene chains with consequent decrease in entropy”.[2]
Chapter 5

Instrumentation

5.1 Laser Diffraction Analysis

Laser diffraction is both a highly recommended and most popular technique for particle size analysis. It is capable of analyzing broad size range in a variety of dispersion media citing this primary reason.[34] User convenience and ease of standard operating procedure are its other advantages. It shows agreement with the sieving method and has high efficiency with fine particles.[35]

5.1.1 Principle of Laser Diffraction

Laser diffraction based particle size analysis relies on the fact that particles passing through a laser beam will scatter light at an angle that is directly related to their size. In simple words, analysis is based on light and particle interaction. The light incident on the particle gets scattered at a given angle. With a decrease in particle size, the angle of scattering increases logarithmically. [36] Large particles therefore scatter light at narrow angles with high intensity whereas small particles scatter at wider angles but with low intensity. This behavior is exploited in the determination of particle size by laser diffraction. [37, 38] The diffracted light is focused by two Fourier lenses which position the beam angle toward the same detector. Therefore, the position of the particle in the
sample cell does not influence the measurement. A stream of particles can pass through to produce a series of diffraction patterns.[35]

Lorentz-Mie theory [39] and Fraunhofer diffraction theory [40, 41] have been used to solve for the particle size determination with respect to the diffracting wavelength pattern. Although, Fraunhofer diffraction theory has a limitation in that it proves inappropriate for the particle size closer to the wavelength of light. In this technique, the particle size distribution is calculated by comparing a sample’s scattering pattern with an appropriate optical model. This theory works for the primary scattering occurring from surface of the particle, and allows for calculating the difference between the refractive indices of the particle and the dispersion medium. The errors occurring due to scattering of light wavelength in the particle itself due to its morphology, can also be calculated.

Figure 5-1: Schematic representation of the Laser diffraction particle sizing analysis.[42]
The Fraunhofer approximation theory assumes that the particles being measured are opaque and scatter light at narrow angles, hence it is mostly applicable for the particle size distribution of larger particles [43].

5.1.2 Instrumentation

The Malvern Mastersizer 2000 Laser Diffraction Grain Size Analyzer has a fully optimized optical design which allows particles in the size range 0.02 - 2000 micron to be characterized effectively. The instrument is composed of two components, the main body and two dispersion units. In most cases, the small dispersion unit (the Hydro SM manual small volume sample dispersion unit, sets the pump/stir speed at 3000 rpm on the stand-alone tacho control unit) is recommended for small samples. If you have a large amount of sediment, the large dispersion unit (the Hydro MU large volume manual sample dispersion unit using standard laboratory beakers as the sample container, pump/stir speed at 3000 rpm) can be used.

The Helium neon laser as a laser source which emits coherent wavelengths which hits the particle stream moving inside the chamber after being homogenized by homogenizer attached. During the travel of each particle, they are exposed to certain wavelength of laser beam which after scattering from the surface detected by beam detector and the scattering signals are further calculated by the computer for the mean particle size. [44, 45].

5.1.3 Sample Preparation

The sample is dispersed in any media can be used and there is no requirement for a special sample procedure. Care must be taken with respect to the addition of sample in
the homogenizer. For uniform particle distribution an appropriate dispersion medium is necessary.[45] Dilution of sample is required to get correct results and minimize the scattering through haze produced by viscous dispersions. The usual concentration of solids dispersed in a liquid is between 0.001 to 1% (w/v).

5.1.4 Applications

The major application of this instrument is the determination of particle size of any type of particle whether dry or wet in nature. [46]. Determination of mean particle size and analysis of particle size distributions of pharmaceutical formulations like solids, sprays, dry powders, suspensions and emulsions can be efficiently done. The data obtained is usually a volume based particle size distribution which is equivalent to a weight distribution [38].

5.2 Nicomp ZLS 380:

The device responsible for the quantitative measurement of charge and electrical mobility of a particle suspended in the dispersion medium is called Electrophoretic light scattering.[47]. The potential difference between the surface of the tight diffusion layer and the stern layer region is calculated as the zeta potential by Electrophoretic mobility. The Dynamic light scattering is the instrument which follows the same principle for electrophoretic light scattering and technically well suited.

5.2.1 Principle of Electrophoretic Light Scattering [48, 49]

The particles suspended in the liquid media carry a charge on their surface [31] This is measured under the effect of an electrical field generated in the cell of the DLS chamber.
A laser light on the right shaft is irradiated in order to scatter the light from the particle surface and subsequently the particle velocity vector is detected. The frequency of the scattered light is shifted from the incident light in proportion to the speed of the particle’s movement. The electrophoretic mobility of the particles can be measured from the frequency shift.

According to the Helmholtz-Smoluchowski equation [50] zeta potential can be calculated by:

\[ \zeta = \frac{\eta \mu}{\varepsilon} \]

Where:

- \( \zeta \) is the zeta potential
- \( \eta \) is the viscosity of the solvent
- \( \mu \) is the electrophoretic mobility of the particle
- \( \varepsilon \) is the dielectric constant of the solvent.

### 5.2.2 Instrumentation

A laser, delivering optics, electrophoretic cell, collecting optics and a photomultiplier tube are the key components of the instrument. Via an electrophoresis cell, a laser beam irradiates the particles dispersed in it and consequently the particles exhibiting random Brownian motion[16] start colliding and scattering back the signals. The scattered light is detected by the photo multiplier tube. There is always room for Doppler shift which depends on the stability of the suspension. The fluctuations might affect the results in the end due to a Doppler shift.
5.2.3 Sample Preparation

No special sample preparation techniques are necessary. The sample should be dilute enough to prevent particle-particle interaction. Dry samples should be suspended in a liquid before measurement.

5.2.4 Applications

Zeta potential can be utilized in estimating their stability against subsequent aggregation [16]. Multi angle particle size analysis is possible along with low angle zeta potential
analysis. Zeta potential serves as an important parameter in characterizing the electrostatic interaction between particles in dispersed systems as well as the properties of the dispersion which are affected by this electrical phenomenon [50]. Zeta potential is mainly used in the formulation of particulate dispersions.

5.3 X-Ray Diffraction

5.3.1 Theory

X-rays are a form of electromagnetic spectrum that have their wavelength range from 0.01- 1 nm. Diffraction is a phenomenon that occurs when light is scattered by a crystal, in which atoms are arranged in periodic arrays, producing constructive interference between two waves, at specific angles [51]. In X-ray diffraction, X-rays are diffracted by the electron cloud of atoms. Incident X-rays interact with a crystalline material to produce constructive interference when conditions satisfy Bragg’s law [52] as mentioned in Figure 5-3.

Figure 5-3: Diffraction of X-rays by a crystal surface

![Diffraction Diagram](image-url)
According to Bragg’s law [52],

\[ n\lambda = 2dsin\theta \]  \hspace{1cm} 5.2

Where, \((\lambda)\) is the wavelength of X-rays; \((\theta)\) is the diffraction angle; \((d)\) is the lattice spacing or distance between the parallel planes of atoms in a crystal; and \((n)\) is an integer.

### 5.3.2 Powder X-ray Diffraction

Powder X-ray diffraction or PXRD is an analytical technique that is used to identify phases present in the sample and provide information about its crystal structure. The scattering of X-rays from atoms produce a diffraction pattern which contains useful information about the atomic arrangement within the crystalline material. An amorphous material will not produce a diffraction pattern and the data will appear as a flat line.

### 5.3.3 Instrumentation

An X-ray diffractometer consists of three basic parts: an X-ray tube, a sample stage and a detector. A cathode ray tube is used as an X-ray source which generates X-rays when the filament, usually composed of tungsten is heated, due to which high energy electrons are produced. These are further accelerated towards the target material by applying voltage and hence, electrons collide with the target material. [53] The inner shell electrons from the target material are removed when the electrons with sufficient energy collide and characteristic X-ray spectra are produced. The wavelength of X-rays produced depends upon the target material. The most common target material used is the copper with CuK\(_\alpha\) radiation of 1.5418 Å.

Powder diffractometers typically use Bragg- Brentano geometry. The geometry is such that the sample rotates in the path of collimated X-ray beam at an angle \(\theta\), while X-ray
detector rotates at an angle $2\theta$ to collect the diffracted X-rays. The measuring device used to rotate the sample and maintain the angle is referred to as goniometer. [51]

PXRD data was collected using Panalytical’s X’pert Pro X-ray diffractometer which has Bragg- Brentano geometry typically $\theta:2\theta$ geometry, in which the sample stage is fixed and the tube and detector rotate at the rate of $-\theta^\circ$/min and $\theta^\circ$/min, respectively.

5.3.4 Sample Preparation

A sample for PXRD should have a flat smooth surface and be homogeneous. The crystallites should be ground to a fine powder and randomly oriented. Rough surface and non-random orientations lead to peak intensity variations. The powder with a crystallite size $< 10 \, \mu m$ is preferred in order to obtain an optimum powder diffraction pattern [51]. Around 100 mg of sample is packed on an aluminium sample holder which contains a shallow well. Sample is pressed down the well using a glass slide to create a smooth flat surface to achieve randomly oriented crystallites [54].
5.3.5 Applications

PXRD is a widely used analytical technique for phase identification of crystalline materials [55]. It is extensively used to characterize the composition of different pharmaceuticals. PXRD is used extensively in the design and development of drug delivery systems [56]. It is an important technique for solid-state drug analysis, benefiting all stages of drug development, testing and production. Both quantitative and qualitative analysis of pharmaceuticals can be carried out using PXRD.

Figure 5-4: Panalytical X’pert Pro X-ray Diffractometer
Figure 5-5: Schematic representation of a Bragg-Brentano X-ray diffractometer.

5.4 Scanning Electron Microscopy (SEM)

SEM is a significant analytical technique used to study the morphology of samples and determine their particle shapes and sizes. Particles with size ranges from micrometers (μm) to nanometers (nm) can be characterized using SEM. It is based upon the interaction of electrons with the surface of the solid samples. Images with a resolution of few nanometers are obtained to characterize the samples using SEM.

5.4.1 Instrumentation:

A scanning electron microscope consists of a column that has a tungsten filament cathode used to generate electrons. High voltage is applied between the cathode and anode
through the column in order to accelerate these electrons on the surface of the sample. Condenser lenses are used to focus the electron beam and convert it into a narrower beam. The sample is mounted on the anode, and a set of scanning coils allows scanning a rectangular portion on the surface of the sample. [57] The instrument needs to be under high vacuum to avoid the loss of electrons and to reduce background noise. The electrons interact with the sample surface and the depth of the electrons reaching the sample depends upon the accelerated voltage and on sample’s composition and density. A three dimensional image depends upon the detection of secondary electrons which are emitted by the sample when the incoming beam has sufficient energy to dislodge the electrons. [58]

Secondary electrons are basically low energy electrons. They contribute to the image by originating no lower than a few nm below the surface. Image quality strongly depends upon the accelerating voltage, condenser lens (probe current) and objective lens aperture size. High resolution is usually obtained using high accelerating voltage. If the sample is not conductive in nature, then high accelerating voltage may result in a charging effect and burn the sample. A soft tone image is obtained at low accelerating voltage. The electron beam size is smaller with lower probe current. Signal to noise ratio is better at higher probe current. SEM data was collected on a JEOL 7500F field emission scanning electron microscope during this research.
5.4.2 Sample Preparation

Conductive samples do not require special sample preparation for SEM. Usually high purity aluminum pin stubs are used for the sample preparation [59]. Carbon tape is applied on the aluminum pin stub and then the sample is sprinkled onto the carbon tape for scanning. Electronic insulators tend to accumulate surface charges and require coating with a conductive layer, such as gold or carbon, to produce a clear image in the secondary electron mode.
5.4.3 Applications

SEM is one of the most extensively used techniques in the field of pharmaceutics. Morphological investigations including size, shape, texture and composition for pharmaceuticals can be explored using SEM [60]. Scanning for inorganic as well as organic specimens can be explored. Structural images of a specimen in the micrometer and nanometer size range can be obtained using SEM.

5.5 Thermogravimetric Analysis (TGA)

5.5.1 Principle of Thermogravimetric Analysis:

Thermogravimetric analysis (TGA) is one of the most widely used thermal-analytical techniques. The principle of TGA is to measure the change in mass of a substance as a function of temperature, when a substance is continuously heated at a uniform rate.

Thermogravimetric curve (TG curve) as seen in Figure 5-6, is a graph or plot of mass change versus temperature. This plot aids determining the thermal stability of an analytical sample and provides information about the extent of transformation (decomposition, melting, volatility etc.) in a sample [61]. In a TG curve with a single stage decomposition, the variation in the mass \( m \) of the sample with the temperature \( T \) or time \( t \) is represented. Normally, a mass loss is plotted downward on the y-axis and mass gain upwards along x-axis. In Figure 5-6, the region A represents a plateau of constant weight, region B is the mass loss portion and region C is again a constant weight portion. This figure also includes a derivative thermogravimetric curve (DTG) shown by the dotted line. DTG curve represents the rate of mass change \( (dm/dt) \) as a function of temperature, when the sample is heated at constant rate. [4]
5.5.2 Instrumentation

The instrument used to carry out thermogravimetric analysis is called a thermobalance. Basic components of a thermobalance include a balance for measuring weight, a furnace for heating, a programmer for temperature measurement and control and a recorder to record the mass and temperature changes. The whole of the balance system is present in a glass to protect it from dust and provide an inert atmosphere. There is a control mechanism to regulate the flow of inert gas to the sample atmosphere and water to cool the furnace. The temperature sensor of the furnace is linked to the program to control the heating rates, etc. The balance output and thermocouple signal may be fed to a recorder to record the TG Curve. Thermogravimetric and differential thermal analysis experiments were carried out on a SDT 2960 DTA-TGA from TA Instruments.

![Thermogravimetric curve](image)

Figure 5-7: A typical thermogravimetric curve (TG curve).
5.5.3 Sample Preparation

The sample is usually packed into a deep crucible or pan which can accommodate 8 to 10 mg of the solid sample. The pans are made of different metals including aluminium, platinum etc. The sample should be spread out on the bottom of the pan in a uniform
manner such that the weight loss resolution and temperature reproducibility is easily obtained [62].

5.5.4 Applications

TGA is extensively studied to understand the chemistry of decomposition of a various pharmaceutical drugs, excipients and other adjuants [63]. TGA also provides information about the temperature range over which a particular sample appears to be stable or unstable. TG curves can be very useful in predicting the relative quantities of components in a mixture. TGA is also used to elucidate the kinetics of decomposition for a sample reaction [61].

5.6 Differential Scanning Calorimetry (DSC)

5.6.1 Principle of DSC:

Differential scanning calorimetry (DSC) is a thermal method that is used to study various thermal transitions including solid-solid and solid-liquid phase transitions. DSC measures the temperature and heat flow associated with the transitions in materials as a function of time and temperature in a controlled atmosphere. Quantitative as well as qualitative analysis of physical and chemical changes involving endothermic (when heat flows out of the sample) or exothermic (when heat flows into the sample) processes in heat capacity can be carried out using DSC. In other words, DSC measures the heat absorbed or released by a material as a function of temperature or time (isothermally). Important thermal characteristics such as transition temperatures, for example, melting and boiling points as well as other transition temperatures such as glass transition temperature (TG), and crystallization temperature (Tc) can be determined using DSC [64].
5.6.2 Instrumentation

A DSC instrument includes both a sample chamber and a reference chamber. The reference chamber consists of a solvent and the sample chamber consists of the solid sample along with equal amount of solvent, whose change in enthalpy ($\Delta H$) is recorded. The $\Delta H$ for solvent is constant in both chambers, so any difference between the two can be attributed to the presence of the substance of interest [65]. Each chamber should be of
equal temperatures due to the heat obtained from separate sources. The temperature of each chamber is controlled by using thermocouple sensor. The heating rate used to maintain equivalent temperatures is logged as a function with respect to the temperature [65].

5.6.3 Sample Preparation

Both liquid and solid samples are analyzed using DSC. About 1 to 10 mg of sample is added to the pan and lid is used to cover the pan. The pans usually made of aluminium, if the temperature is not to exceed 550 °C. After weighing the sample in a pan with lid, both pan and lid are crimped together. Empty pan and lid are crimped together and used as the reference pan.

5.6.4 Applications

In the pharmaceutical industry, DSC is used to study ‘aging’ and shelf life of pharmaceuticals, as well as other basic research and development [64]. It is also used in the development of dosage forms to determine the choice of the salt form, phase diagrams, drug substance and excipient interactions, physical changes on processing or during storage and even in the analysis of the dosage form [66]. DSC can also be used to study many different fields including biopolymer energetics where it is used to find the enthalpy of the protein denaturation process. DSC is also used in conjunction with differential thermal analysis. Through the combination of these two techniques, thermal behavior of inorganic compounds can be studied while the melting, boiling and decomposition points of organic compounds and polymers are found [65].
Chapter 6

Material and Methods

6.1 Chemical Constituents:

The following are the ingredients used to prepare the “Never Dried” Calcium Carbonate suspensions:

6.1.1 Sodium Bicarbonate

Sodium bicarbonate is a white fine powder and is crystalline in nature. It exhibits salty to alkaline taste, similar to that of sodium carbonate. It is widely present in mineral springs, as a constituent of Natron. Its natural mineral form is also known as nahcolite.

6.1.1.1 Physical properties

Source: Fischer Scientific BP328-500,

pH: 8.3 (0.1M solution)

CAS-No: 144-55-8

Lot No: E63164

Chemical name: Sodium Hydrogen Carbonate

Chemical formula: NaHCO3

Melting point: 270°C / 518°F
Boiling point: 851°C

Molecular weight: 84.01 gm/mole

Specific gravity: 2.20 g cm$^{-3}$

![Figure 6-1:Structure of Sodium bicarbonate](image)

### 6.1.1.2 Chemical properties:

Sodium bicarbonate decomposes in humid conditions and remains stable under dry conditions. It is moderately water soluble. Decomposition in water is accelerated by agitation. Exothermic reactions of Sodium bicarbonate occur with acids and results in the formation of carbon dioxide gas. It is incompatible with acids, acidic salts (dopamine hydrochloride, pentazocine lactate, and many alkaloidal salts) aspirin and bismuth salicylate.

### 6.1.1.3 Uses

Sodium bicarbonate is highly used in the field of chemistry, pharmacy as well as in the household. There are various medical uses for sodium bicarbonate such as in the treatment of indigestion, acidosis, urinary alkalinization, Hyperkalemia, etc. In general for household usage it is called baking powder has been used for baking purposes. It is a very potent cleaning agent because of its anti fungal activity.
6.1.2 Calcium Chloride dihydrate.

Calcium chloride is used mainly as a source of calcium ion in chemical reactions. It has few characteristics of ionic halides. It appears as a white powder. It readily absorbs water from the air. Calcium chloride dihydrate occur in nature in mineral form as Sinjarite. It is highly soluble in water. It is also soluble in ethanol and methanol. Stability is maintained when stored in sealed and closed containers.

6.1.2.1 Physical properties

Source: LETCO Medical, LOT No. 11070634

CAS No. 10035-04-8               Vapor density: >1
Chemical name: Calcium Chloride dihydrate               Chemical formula: CaCl$_2$.2H$_2$O
Molecular weight: 147.01g/mole               Density: 0.83 g/ml
Boiling point: 174°C               Melting point: 176°C

6.1.2.2 Chemical properties

Calcium chloride dihydrate is extremely hygroscopic in nature. Calcium chloride dihydrate after reacting produces heat energy i.e. undergoes exothermic reaction. When calcium chloride is reacted with water it produces chlorine gas and calcium hydroxide with the libration of heat energy. Calcium chloride dihydrate is non-flammable in most cases, but in the presence or reacting with metal ions such as zinc or sodium, it produces flammable hydrogen. It is soluble in both organic and inorganic solvents.
6.1.2.3 Uses

Calcium chloride dihydrate is used in the Pharmaceutical and chemical industries for manufacturing several salts, where it acts as a source of calcium ion. It is also used as water desiccant. When it is added in a solution, it removes bound and unbound water. Due to its hygroscopic nature, it is used to keep the dew on roads’ surface by keeping the dust down. It is also used to increase the water hardness. It is helpful in lowering the freezing point of liquids due to its exothermic reactivity.

6.1.3 Poloxamer 407

Poloxamer 407 is a hydrophilic non ionic surfactant. It is a white, coarse powder with a specific odor. It is readily soluble in water but requires agitation and shaking when added in large quantities. It is insoluble in ether, paraffin and fatty oils. It is a synthetic triblock copolymer. Due to its inverse thermo sensitivity, it dissolves at low temperature. However it forms gel at high temperatures. [67]

6.1.3.1 Physical properties

Source: BASF, LOT No. WPAF580B

Specific gravity: 1.05

CAS No. 9003-11-6

Viscosity: 3100cps

Chemical name: Triblock copolymer of polypropylene glycol and polyethylene glycol

Melting point: 56°C

pH: 6-9 (50gms/L of solution)

Chemical formula: \((C_3H_6O.C_2H_4O)_x\)
Surface tension: 41 dynes/cm (of a 0.1% solution at 25°C)

Molecular weight: 12,600 Daltons

Bulk density: 500 kg/m³

HLB value: 18-23

Soluble in cold water (>175gms/L)

\[
\text{CH}_3 \\
\text{HO} \{\text{CH}_2 - \text{CH}_2 \cdot \text{O}\}_a \{\text{CH}_2 - \text{CH} - \text{O}\}_b \{\text{CH}_2 - \text{CH}_2 - \text{O}\}_a \cdot \text{H}
\]

Figure 6-2: Structure of Lutrol F127 (Poloxamer 407) where a=101 and b=56

6.1.3.2 Chemical properties

Poloxamer 407 is both non-ionic and non toxic in nature. Apart from surfactant activity, poloxamer helps in increasing the permeability of the anti-cancer nanoparticles. It decreases the enzymatic degradation of the drug (SLN based Nanoparticles). [68] Poloxamer is available in different grades, according to the molecular weight. [69] The third digit in the molecular name when multiplied by 10 gives the percentage by weight of the polyoxypropylene portion.

6.1.3.3 Uses

Poloxamer 407 has tendency to increase the adhesive properties of hydro gels prepared with it. Poloxamer 407 is a thermosensitive so it is used accordingly at a variety of temperatures. It decreases the surface tension of substances to be emulsified and helps other excipients and substances to become dissolved in solutions which they are normally are immiscible or poorly soluble. It is also used as a flocculating agent in pharmaceutical suspensions and several cosmetic preparations. It is mainly used as a viscosity enhancers
and co-emulsifier in creams and liquid emulsions. When used to prepare nanoparticles and microemulsions, it helps in increasing drug permeability and efficacy.

**6.1.4 De-Ionized water (DI) water**

DI water is used to prevent the impurities or ions having an effect on the system being studied. It was obtained from the University of Toledo, DI water system.

**6.2 Equipments used**

Graduate cylinders were used to study the rate of fall of the interface. A 250 mL measuring cylinder made of pyrex glass manufactured by Fisher Scientific, Fairlawn, NJ were used.

A 100 mL volumetric flask was used to make the 1% polymer solution.

An electronic balance, ER 120A, made by American Scientific Products was used for all weighing.

An Ostwald-Viscometer, E.H. Sergent & Co. No. S-83305, Chicago, IL was used for the viscosity measurements.

A pycnometer, 25ml, Kimble brand, Item No. 15123-ST, USA was used for density and specific gravity measurements.

A stop watch, Fisher Scientific, Fairlawn, NJ was used to time the experiments

Parafilm, American National Can Co. Chicago, IL was used to prevent liquid loss through evaporation and environmental contamination.

A long glass stirring rod, pyrex was used and manufactured by the UT glass blower Sputter Coater –Denton vacuum, Desk II and JSM 5200 Scanning Electron Microscope, The University of Toledo.
Laser diffraction instrument, Malvern Metasizer 2000®, The University of Toledo

Zeta potential measurement, Nicomp 380 ZLS, Particle Sizing Systems, CA, University of Toledo

Differential Scanning Calorimeter, DSC 822® Mettler Toledo, University of Toledo

X-ray powder diffractometer, PANalytical X’Pert Pro MPD, University Of Toledo

6.3 Methods

6.3.1 Preparation of polymer solutions

A stock solution of 2% Poloxamer 407 was prepared in 1000 mL of distilled water.

Various concentrations of Poloxamer 407 were prepared such as 0.1%, 0.5%, 1% and 2% were prepared by adding 10 mL, 50mL, 100mL and 200 mL respectively, to the 200mL volumetric flask. The solution of Poloxamer 407 was sonicated to eliminate the froth produced. The bubbles may interfere with the hindered settling studies and other analytical studies.

6.3.2 Determination of density

The density of the poloxamer solution was determined using a 25 mL pycnometer. The empty bottle was weighed and filled with the solution to the brim and stopper was inserted; and weighed again. The measurement was done in triplicate. The difference in the weights was calculated and the density determined using the formula:

\[
\text{Density (gm/ml)} = \frac{\text{difference in weights}}{\text{volume (25 ml)}}
\]
6.3.3 Determination of viscosity

The viscosity of the solutions was measured using an Ostwald’s viscometer. The principle underlying this method is to measuring the time of fall of the liquid from one mark at the top to other mark at the bottom of the bulb. This is usually compared with the time it takes for water to fall between these same markings. The same procedure was repeated for all solutions of known density. The viscosity of the solutions was calculated using the formula:

\[
\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}
\]

Where,

- \(\eta_1\) is the viscosity of water
- \(\rho_1\) is the density of water
- \(\eta_2\) is the viscosity of the solution
- \(\rho_2\) is the density of the solution

6.3.4 Hindered settling experiments

Calcium Carbonate was prepared stoichiometrically, using 1M Calcium chloride dihydrate and 1M Sodium Bicarbonate as given in the equation. The titration was carried out in 200 mL graduated measuring cylinders. Various weights were prepared for the hindered settling study, such as 2g, 4g, 6g, and 10g but hindered settling was observed at 16g CaCO\(_3\). A stock solution of calcium chloride dihydrate was prepared. A 500 g weight of Calcium Chloride dihydrate was dissolved in 500 mL water (given that the solubility of CaCl\(_2\). 2H\(_2\)O = 1000 g/1000 mL). Due to the rise in volume after the addition of 500 mL water in 500 g of CaCl\(_2\).2H\(_2\)O, 1 mL portion of stock solution was equivalent to 0.7526 g CaCl\(_2\).2H\(_2\)O.
The Titration was carried out and the “never dried” suspension was prepared using water as a vehicle. The suspension was shaken well and left overnight for complete settling. Decantation of the supernatant was done repeatedly for three - four times until the suspension is free from NaCl. The presence of NaCl can be determined with the aid of silver nitrate, which combines with the chloride ions to form a cloudy precipitate. The volume was made up to 200 mL with water and the suspension was shaken for 30-40 times and placed upright on flat surface for hindered settling measurements. The rate of fall was monitored every 30 seconds and the readings noted. The experiment of monitoring the rate of hindered settling was repeated thrice. The rate of fall of the interface is plotted as height of interface (mm) vs. Time (min) curve and the straight line from the curve is extrapolated for further calculations which included Particle size determination.

### 6.3.5 Flocculation of suspensions

Poloxamer 407 was dissolved in the required quantity of water to prepare the stock solution. The appropriate amount was removed from the stock solution and diluted with water to obtain the desired poloxamer concentration and was then added to the final suspension solution. Before adding the poloxamer solution to the suspension, the suspension was decanted at least four times to make the suspension sodium chloride free. Flocculation occurred due to the addition of poloxamer to the suspension. Poloxamer increases the attraction between the calcium carbonate particles and tends to produce flocules.
6.3.6 Determination of percentage yield

A known volume of calcium carbonate suspension was filtered and transferred to a glass plate. It was dried in an oven overnight at 30°C. Next day the dried powder was weighed and the percentage yield was calculated using the formula:

\[
\text{Percentage yield} = \frac{\text{Actual weight}}{\text{Theoretical weight}} \times 100
\]

6.3.7 Scanning electron microscopy (SEM)

Morphologic studies were performed using a JSM – 5200 SEM. Calcium Carbonate suspension prepared in water and various poloxamer concentrations were exclusively dried and transferred to a metal sample holder. The samples were obtained with taking special care so as to avoid any cross contamination, since the sample holder was carrying different samples at once. The sample was made conductive by coating it with gold using a vacuum sputter coater.

6.3.8 Laser Diffraction (LD)

A Malvern Metasizer 2000\textsuperscript{c} was used for the determination of particle size. The respective samples were homogenized using vortex mixer. The water was filled 2/3 of the capacity of the homogenizer connected to the analyser and small quantity of the suspension was added. It should be noted that the particles must be in the designated range and should not exceed the normal particle size range. The particle size analysis was done in triplicate for 20 g CaCO\textsubscript{3} suspension prepared in water as well as in, 0.1%
poloxamer, 0.5% poloxamer, 1% poloxamer and 2% poloxamer. Comparative results were reported and the graph was plotted.

6.3.9 Zeta potential measurement

A Nicomp 380 ZLS, particle sizing system was used to measure the zeta potential of the suspensions. Suspension from each dispersion concentration was taken and further diluted to obtain an accurate zeta potential measurement. Durex borosilicate glass culture tube was used to perform the experiment. The zeta potential was determined by placing the sample in the path of a Helium Neon laser of wavelength 658 nm at a scattering angle of 90° and at a temperature of 23°C.

6.3.10 Differential Scanning Calorimetry (DSC)

Suspension samples prepared in their respective reference dispersion media were analyzed. Samples were carefully weighed in pre-weighed 100 µL aluminum crucibles. The weight of the reference aluminum pan was 75.407 mg. The sample pan weight was noted and the lid was pierced for the gas to escape during high temperature treatment. A DSC 822° Mettler Toledo was used to perform the studies equipped with TS0800GCI gas flow system attached to a Nitrogen gas cylinder. Nitrogen gas was used as the Purge gas. The method was divided into three dynamic temperature segments. First segment was from 25°C to -20°C at 1°C/min. The second segment was from -20°C to 50°C at 1°C/min and third segment was from 50°C to 200°C at 5°C/min. The method was kept constant for all the samples. The flow of Purge gas, Nitrogen, was kept at rate of 20ml/min. After the completion of the experiment, the curves were saved and further evaluated using
STAR software. The rationale behind the study was to analyze the amount of bound and unbound water which might be found in the suspensions.

6.3.11 X-ray Powder Diffraction (PXRD)

Calcium carbonate suspended in various poloxamer media and water was dried for comparative study using PANalytical X'Pert Pro MPD. X-ray spectra were recorded using a Cu X-ray source, a voltage of 45 kV, a current of 40 mA, with 0.04 rad Soller slits, 1/4° divergence slit, 10 mm mask, 1/2° anti scattered slit, Nickel filter and X'Celerator detector over a 2Θ range of 10° to 70° with a continuous speed of 4°/min. The powder was trituated to obtain a uniform particle size and was placed on an aluminum sample holder. The Peak pattern for each sample was evaluated using the X'Pert Data High Score Plus software.

6.3.12 Thermogravimetry (TG)

The 20 g Calcium carbonate dispersed in various media was analyzed using a SDT 2960 DTA-TGA from TA Instruments. Approximately 8 to 10 mg of the sample was weighed and placed into a 100 µL platinum pan. The lid was pierced for the evolution of water vapor. The sample was heated from 22°C to 1000°C at 10°C/min. Air was used as the gas at a flow rate of 100 mL/min. The results were evaluated using Microsoft excel.
Chapter 7

Results and Discussion

7.1 Rate of Hindered Settling

7.1.1 Physical Property calculation:

The density and viscosity of the suspending media was calculated based on the method as described in Chapter 6 Sections 6.3.2 and 6.3.3. The results are given in Table 7.1. The value for the density of Calcium Carbonate used in this study is 2.72 gm/cm$^3$ and was obtained from the literature. After suspending the calcium carbonate in the dispersion media such as water and concentrated poloxamer, the clear interface was observed. However, lower concentrations other than 0.1% were unable to produce a clear interface.

Table 7.1: Densities and Viscosities for various dispersion media

<table>
<thead>
<tr>
<th>Suspending media</th>
<th>Density (gm/cm$^3$)</th>
<th>Viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified water</td>
<td>0.9857</td>
<td>0.00091</td>
</tr>
<tr>
<td>0.1% w/v Poloxamer</td>
<td>1.0282</td>
<td>0.0328</td>
</tr>
<tr>
<td>0.5% w/v Poloxamer</td>
<td>1.0299</td>
<td>0.3483</td>
</tr>
<tr>
<td>1% w/v Poloxamer</td>
<td>1.0323</td>
<td>0.0361</td>
</tr>
<tr>
<td>2% w/v Poloxamer</td>
<td>1.0354</td>
<td>0.0416</td>
</tr>
</tbody>
</table>
7.1.2 Hindered Settling:

The Experiments were performed by strictly following the procedures explained in chapter 6. The sodium chloride ions were washed out carefully and this was verified by performing a limit test with silver nitrate which reacts with the chloride ions to cause a cloudy precipitate. The poloxamer concentrated solutions were prepared and added in the suspension media; Foam observed while and after the graduated cylinder with the suspension was shaken. The rate of sedimentation was observed as the clear interface was observed.

The poloxamer concentrated solutions were prepared namely 0.1%, 0.5%, 1% and 2%. The plot of hindered settling could be divided into three phases as described in Chapter 3. These included the Initial zone, linear zone and compressive zone among which the linear part is considered in the calculation of rate of fall (Q). The plot established between the heights of the interface (mm) against time (min.). The concentration range which showed the hindered settling was 16gm - 20gm of calcium carbonate. The plots are illustrated in Figures 7.1 to 7.5 for the hindered settling experiments conducted for each concentration of calcium carbonate. The terminal velocity (Q) and average rate were calculated from the slope of the linear zone. Tables 7.2 to 7.6 give the values calculated for (Q) and (ε).

The initial porosity (ε) can be expressed as:

\[ \varepsilon = 1 - \frac{C}{\rho_s} \] 7-1

Where, C = The concentration of Suspension (gm/mL);

\[ \rho_s = \text{Density of the solid suspended (gm/cm}^3\)]
Figure 7-1: A plot of height of the interface (mm) against time (min) for Never-dried Calcium Carbonate suspensions in purified water. Where,

- 16 gm
- 17 gm
- 18 gm
- 19
- 20 gm
Figure 7-2: A plot of height of the interface (mm) against time (min) for Never dried Calcium Carbonate suspensions in 0.1% Poloxamer solution. Where,
Figure 7-3: A plot of height of the interface (mm) against time (min) for Never-dried Calcium Carbonate suspensions in 0.5% Poloxamer solution. Where,

20 g  19 g  18 g  17 g  16 g
Figure 7-4: A plot of height of the interface (mm) against time (min) for Never-dried Calcium Carbonate suspensions in 1% Poloxamer solution. Where,
Figure 7-5: A plot of height of the interface (mm) against time (min) for Never-dried Calcium Carbonate suspensions in 2% Poloxamer solution. Where,

- 20 g
- 19 g
- 18 g
- 17 g
- 16 g
Table 7.2: Hindered settling values for concentration, $Q_1$, $Q_2$, $Q_3$, $Q_{\text{avg}}$. Standard deviation and porosity derived from different weights of Never-dried Calcium Carbonate suspended in water.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>C (g/mL)</th>
<th>$Q_1$ (mm/min)</th>
<th>$Q_2$ (mm/min)</th>
<th>$Q_3$ (mm/min)</th>
<th>$Q_{\text{avg}}$ (mm/min)</th>
<th>SD</th>
<th>$\varepsilon = 1 - C/\rho_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.08</td>
<td>3.109</td>
<td>3.0727</td>
<td>3.0613</td>
<td>3.0810</td>
<td>0.0203</td>
<td>0.9705</td>
</tr>
<tr>
<td>17</td>
<td>0.085</td>
<td>2.6181</td>
<td>2.6545</td>
<td>2.6243</td>
<td>2.6323</td>
<td>0.0159</td>
<td>0.9686</td>
</tr>
<tr>
<td>18</td>
<td>0.09</td>
<td>2.5636</td>
<td>2.5818</td>
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<td>2.5551</td>
<td>0.0260</td>
<td>0.9668</td>
</tr>
<tr>
<td>19</td>
<td>0.095</td>
<td>2.4727</td>
<td>2.5818</td>
<td>2.4652</td>
<td>2.5066</td>
<td>0.0533</td>
<td>0.9649</td>
</tr>
<tr>
<td>20</td>
<td>0.1</td>
<td>2.3818</td>
<td>2.5818</td>
<td>2.3791</td>
<td>2.4476</td>
<td>0.0949</td>
<td>0.9631</td>
</tr>
</tbody>
</table>

Table 7.3: Hindered settling values for concentration, $Q_1$, $Q_2$, $Q_3$, $Q_{\text{avg}}$. Standard deviation and porosity derived from different weights of Never-dried Calcium Carbonate suspended in 0.1% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>C (g/mL)</th>
<th>$Q_1$ (mm/min)</th>
<th>$Q_2$ (mm/min)</th>
<th>$Q_3$ (mm/min)</th>
<th>$Q_{\text{avg}}$ (mm/min)</th>
<th>SD</th>
<th>$\varepsilon = 1 - C/\rho_S$</th>
</tr>
</thead>
<tbody>
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<td>16</td>
<td>0.08</td>
<td>2.3243</td>
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</tr>
<tr>
<td>17</td>
<td>0.085</td>
<td>2.1081</td>
<td>2.1145</td>
<td>2.1663</td>
<td>2.1296</td>
<td>0.0261</td>
<td>0.9686</td>
</tr>
<tr>
<td>18</td>
<td>0.09</td>
<td>2.0405</td>
<td>2.0810</td>
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<td>2.0604</td>
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</tr>
<tr>
<td>19</td>
<td>0.095</td>
<td>1.9865</td>
<td>1.9913</td>
<td>1.9659</td>
<td>1.9812</td>
<td>0.0110</td>
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</tr>
<tr>
<td>20</td>
<td>0.1</td>
<td>1.9324</td>
<td>1.9577</td>
<td>1.9211</td>
<td>1.9371</td>
<td>0.0153</td>
<td>0.9631</td>
</tr>
</tbody>
</table>
Table 7.4: Hindered settling values for concentration, $Q_1$, $Q_2$, $Q_3$, $Q_{\text{avg}}$, Standard deviation and porosity derived from different weights of Never-dried Calcium Carbonate suspended in 0.5% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>C  (g/mL)</th>
<th>$Q_1$ (mm/min)</th>
<th>$Q_2$ (mm/min)</th>
<th>$Q_3$ (mm/min)</th>
<th>$Q_{\text{avg}}$ (mm/min)</th>
<th>SD</th>
<th>$\varepsilon = 1 - C/\rho_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.08</td>
<td>3.0909</td>
<td>3.1130</td>
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<tr>
<td>17</td>
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<td>2.7818</td>
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<td>2.7002</td>
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<tr>
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<td>2.1240</td>
<td>2.3088</td>
<td>0.1333</td>
<td>0.9631</td>
</tr>
</tbody>
</table>

Table 7.5: Hindered settling values for concentration, $Q_1$, $Q_2$, $Q_3$, $Q_{\text{avg}}$, Standard deviation and porosity derived from different weights of Never-dried Calcium Carbonate suspended in 1% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>C  (g/mL)</th>
<th>$Q_1$ (mm/min)</th>
<th>$Q_2$ (mm/min)</th>
<th>$Q_3$ (mm/min)</th>
<th>$Q_{\text{avg}}$ (mm/min)</th>
<th>SD</th>
<th>$\varepsilon = 1 - C/\rho_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
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<td>3.1147</td>
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<tr>
<td>17</td>
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<td>2.818</td>
<td>2.7630</td>
<td>2.8310</td>
<td>2.8040</td>
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<td>0.9686</td>
</tr>
<tr>
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<tr>
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<td>2.667</td>
<td>2.5410</td>
<td>2.6011</td>
<td>2.6030</td>
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<tr>
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<td>0.1</td>
<td>2.536</td>
<td>2.4260</td>
<td>2.3460</td>
<td>2.4360</td>
<td>0.0779</td>
<td>0.9631</td>
</tr>
</tbody>
</table>
Table 7.6: Hindered settling values for concentration, $Q_1$, $Q_2$, $Q_3$, $Q_{avg}$, Standard deviation and porosity derived from different weights of Never-dried Calcium Carbonate suspended in 2% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>C (g/mL)</th>
<th>$Q_1$ (mm/min)</th>
<th>$Q_2$ (mm/min)</th>
<th>$Q_3$ (mm/min)</th>
<th>$Q_{avg}$ (mm/min)</th>
<th>SD</th>
<th>$\varepsilon = 1 - C/\rho_S$</th>
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</thead>
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<td>10.34</td>
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<td>10.7300</td>
<td>10.5367</td>
<td>0.1592</td>
<td>0.9686</td>
</tr>
<tr>
<td>18</td>
<td>0.09</td>
<td>7.45</td>
<td>7.8320</td>
<td>6.0217</td>
<td>7.1012</td>
<td>0.7791</td>
<td>0.9668</td>
</tr>
<tr>
<td>19</td>
<td>0.095</td>
<td>5.5</td>
<td>5.8400</td>
<td>5.4200</td>
<td>5.5867</td>
<td>0.1821</td>
<td>0.9649</td>
</tr>
<tr>
<td>20</td>
<td>0.1</td>
<td>3.8056</td>
<td>3.9960</td>
<td>3.4520</td>
<td>3.7512</td>
<td>0.2254</td>
<td>0.9631</td>
</tr>
</tbody>
</table>

The results indicate that the rate of settling marginally decreased as the concentration of the suspension increased. The particles in higher concentration tend to hinder the following particles and thus decrease the rate of settling. [1]

Stokes’ law is used to calculate particle size using hindered settling data. The Parameters required for the calculation of particle size were derived from the data in Tables 7.2 to 7.6.

**7.1.3 Particle size determination**

**7.1.3.1 Steinour’s equation:** The equation is given as:

$$\log \frac{Q}{\varepsilon^2} = A(\varepsilon) + \log V_s - A \quad 7.2$$

Log ($Q/\varepsilon^2$) against $\varepsilon$ when plotted, gives a straight line with a slope equal to $(A)$ and an intercept of $(\log V_s - A)$. The linear plots for this equation using four different media are
given in Figures 7.6 to 7.10 and the parameters obtained from the plot are given in Tables 7.7 to 7.11.

**7.1.3.2 Richardson & Zaki equation:** The equation is given by:

\[ \log Q = \log V_s + n \log \epsilon \]  

7.3

A graph of \([\log Q]\) against \([\log \epsilon]\) when plotted, gives a straight line with a slope of \((n)\) and an intercept of \([\log V_s]\). The linear plots for this equation using four different media are given in Figures 7.11 to 7.15 and the parameters obtained from the plot are given in Table 7.12.

**7.1.3.3 Dollimore & McBride equation:**

The equation is given by

\[ \log Q = \log V_s - b\rho_s (1-\epsilon) \]  

7.4

A plot of \([\log Q]\) against \([1-\epsilon]\) gives a linear curve with a slope of \((-b\rho_s)\) and an intercept of \([\log V_s]\). The linear plots for this equation using four different media are given in Figures 7.16 to 7.20 and the parameters obtained from the plot are given in Table 7.13.

Following the concepts discussed in Chapter 3, particle size was then calculated using Stokes’ Law as follows

\[ r = \sqrt{\frac{9\eta V_s}{2g(\rho_s-\rho_l)}} \]  

7.5

The particle radius found for the various poloxamer concentrations can be calculated by substituting the values for settling velocity determined by the various equations with the density and viscosity.

The values obtained are given in the Tables 7.14 to 7.17
Table 7.7: The values for $Q_{\text{avg}}$, $\log Q$, $\varepsilon$, $\log(Q/\varepsilon^2)$, $\log \varepsilon$ and $1-\varepsilon$ derived from different weights of Never-dried for the hindered settling of different concentrations of Never-dried Calcium Carbonate suspended in water.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>$Q_{\text{avg}}$ (mm/min)</th>
<th>$\varepsilon$</th>
<th>$\log(Q/\varepsilon^2)$</th>
<th>$\log \varepsilon$</th>
<th>$\log Q$</th>
<th>$1-\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>3.0810</td>
<td>0.97048</td>
<td>0.51472</td>
<td>-0.013</td>
<td>0.48869</td>
<td>0.02952</td>
</tr>
<tr>
<td>17</td>
<td>2.6323</td>
<td>0.96863</td>
<td>0.44802</td>
<td>-0.0138</td>
<td>0.42034</td>
<td>0.03137</td>
</tr>
<tr>
<td>18</td>
<td>2.5551</td>
<td>0.96679</td>
<td>0.43674</td>
<td>-0.0147</td>
<td>0.4074</td>
<td>0.03321</td>
</tr>
<tr>
<td>19</td>
<td>2.5066</td>
<td>0.96494</td>
<td>0.43007</td>
<td>-0.0155</td>
<td>0.39908</td>
<td>0.03506</td>
</tr>
<tr>
<td>20</td>
<td>2.4476</td>
<td>0.96310</td>
<td>0.42139</td>
<td>-0.0163</td>
<td>0.38873</td>
<td>0.0369</td>
</tr>
</tbody>
</table>

Table 7.8: The values for $Q_{\text{avg}}$, $\log Q$, $\varepsilon$, $\log(Q/\varepsilon^2)$, $\log \varepsilon$ and $1-\varepsilon$ derived from different weights of Never-dried for the hindered settling of different concentrations of Never-dried calcium carbonate suspended in 0.1% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>$Q_{\text{ave}}$ (mm/min)</th>
<th>$\varepsilon$</th>
<th>$\log(Q/\varepsilon^2)$</th>
<th>$\log \varepsilon$</th>
<th>$\log Q$</th>
<th>$1-\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2.3506</td>
<td>0.9704797</td>
<td>0.39721</td>
<td>-0.013</td>
<td>0.37118</td>
<td>0.02952</td>
</tr>
<tr>
<td>17</td>
<td>2.1296</td>
<td>0.96863469</td>
<td>0.35598</td>
<td>-0.0138</td>
<td>0.3283</td>
<td>0.03137</td>
</tr>
<tr>
<td>18</td>
<td>2.0604</td>
<td>0.96678967</td>
<td>0.34329</td>
<td>-0.0147</td>
<td>0.31396</td>
<td>0.03321</td>
</tr>
<tr>
<td>19</td>
<td>1.9812</td>
<td>0.96494465</td>
<td>0.32793</td>
<td>-0.0155</td>
<td>0.29693</td>
<td>0.03506</td>
</tr>
<tr>
<td>20</td>
<td>1.9371</td>
<td>0.96309963</td>
<td>0.3198</td>
<td>-0.0163</td>
<td>0.28715</td>
<td>0.0369</td>
</tr>
</tbody>
</table>

Table 7.9: The values for $Q_{\text{avg}}$, $\log Q$, $\varepsilon$, $\log(Q/\varepsilon^2)$, $\log \varepsilon$ and $1-\varepsilon$ derived from different weights of Never-dried for the hindered settling of different concentrations of Never-dried Calcium Carbonate suspended in 0.5% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>$Q_{\text{ave}}$ (mm/min)</th>
<th>$\varepsilon$</th>
<th>$\log(Q/\varepsilon^2)$</th>
<th>$\log \varepsilon$</th>
<th>$\log Q$</th>
<th>$1-\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>3.1720</td>
<td>0.9704797</td>
<td>0.52736</td>
<td>-0.013</td>
<td>0.50133</td>
<td>0.02952</td>
</tr>
<tr>
<td>17</td>
<td>2.7002</td>
<td>0.96863469</td>
<td>0.45908</td>
<td>-0.0138</td>
<td>0.4314</td>
<td>0.03137</td>
</tr>
<tr>
<td>18</td>
<td>2.5027</td>
<td>0.96678967</td>
<td>0.42774</td>
<td>-0.0147</td>
<td>0.3984</td>
<td>0.03321</td>
</tr>
<tr>
<td>19</td>
<td>2.4077</td>
<td>0.96494465</td>
<td>0.4126</td>
<td>-0.0155</td>
<td>0.38161</td>
<td>0.03506</td>
</tr>
<tr>
<td>20</td>
<td>2.3088</td>
<td>0.96309963</td>
<td>0.39604</td>
<td>-0.0163</td>
<td>0.36338</td>
<td>0.0369</td>
</tr>
</tbody>
</table>
Table 7.10: The values for $Q_{\text{avg}}$, log Q, $\varepsilon$, log $(Q/\varepsilon^2)$, log $\varepsilon$ and 1-$\varepsilon$ derived from different weights of Never-dried for the hindered settling of different concentrations of Never-dried Calcium Carbonate suspended in 1% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>$V_{\text{final,ave}}$ (mm)</th>
<th>$Q_{\text{ave}}$ (mm/min)</th>
<th>$\varepsilon$</th>
<th>log$(Q/\varepsilon^2)$</th>
<th>log$\varepsilon$</th>
<th>logQ</th>
<th>1-$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>33.0</td>
<td>3.1147</td>
<td>0.97048</td>
<td>0.51944</td>
<td>-0.013</td>
<td>0.49341</td>
<td>0.02952</td>
</tr>
<tr>
<td>17</td>
<td>50.0</td>
<td>2.8040</td>
<td>0.96863</td>
<td>0.47546</td>
<td>-0.0138</td>
<td>0.44778</td>
<td>0.03137</td>
</tr>
<tr>
<td>18</td>
<td>54.0</td>
<td>2.6412</td>
<td>0.96679</td>
<td>0.45114</td>
<td>-0.0147</td>
<td>0.4218</td>
<td>0.03321</td>
</tr>
<tr>
<td>19</td>
<td>58.1</td>
<td>2.6030</td>
<td>0.96494</td>
<td>0.44647</td>
<td>-0.0155</td>
<td>0.41548</td>
<td>0.03506</td>
</tr>
<tr>
<td>20</td>
<td>62.0</td>
<td>2.4360</td>
<td>0.96310</td>
<td>0.41933</td>
<td>-0.0163</td>
<td>0.38668</td>
<td>0.03690</td>
</tr>
</tbody>
</table>

Table 7.11: The values for $Q_{\text{avg}}$, log Q, $\varepsilon$, log $(Q/\varepsilon^2)$, log $\varepsilon$ and 1-$\varepsilon$ derived from different weights of Never-dried for the hindered settling of different concentrations of Never-dried Calcium Carbonate suspended in 2% Poloxamer.

<table>
<thead>
<tr>
<th>W (g)</th>
<th>$V_{\text{final,ave}}$ (mm)</th>
<th>$Q_{\text{ave}}$ (mm/min)</th>
<th>$\varepsilon$</th>
<th>log$(Q/\varepsilon^2)$</th>
<th>log$\varepsilon$</th>
<th>logQ</th>
<th>1-$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>33.0</td>
<td>18.3463</td>
<td>0.97048</td>
<td>1.28958</td>
<td>-0.013</td>
<td>1.26355</td>
<td>0.02952</td>
</tr>
<tr>
<td>17</td>
<td>50.0</td>
<td>10.5367</td>
<td>0.96863</td>
<td>1.05038</td>
<td>-0.0138</td>
<td>1.0227</td>
<td>0.03137</td>
</tr>
<tr>
<td>18</td>
<td>54.0</td>
<td>7.1012</td>
<td>0.96679</td>
<td>0.88067</td>
<td>-0.0147</td>
<td>0.85133</td>
<td>0.03321</td>
</tr>
<tr>
<td>19</td>
<td>58.1</td>
<td>5.5867</td>
<td>0.96494</td>
<td>0.77815</td>
<td>-0.0155</td>
<td>0.74715</td>
<td>0.03506</td>
</tr>
<tr>
<td>20</td>
<td>62.0</td>
<td>3.7512</td>
<td>0.96310</td>
<td>0.60683</td>
<td>-0.0163</td>
<td>0.57417</td>
<td>0.0369</td>
</tr>
</tbody>
</table>
Figure 7-6: The linear plot of the Steinour equation for different weights of Never-dried Calcium Carbonate in water. Where, slope = 11.089, intercept = 10.271 and $R^2 = 0.7497$

Figure 7-7: The linear plot of the Steinour’s equation for different weights of Never – dried Calcium Carbonate in 0.1% Poloxamer. Where, slope = 9.9115, intercept = 9.2335 and $R^2 = 0.9033$
Figure 7-8: The linear plot of the Steinour’s equation for different weights of Never-dried calcium carbonate suspended in 0.5% Poloxamer. Where, slope = 16.754, intercept = 15.753 and $R^2 = 0.891$

Figure 7-9: The linear plot of the Steinour’s equation for different weights of calcium carbonate suspended in 1% Poloxamer. Where, slope =12.422, intercept = 11.547 and $R^2 = 0.9282$
Figure 7-10: The linear plot of the Steinour’s equation for different weights of calcium carbonate suspended in 2% Poloxamer. Where, slope = 88.765, intercept = 84.896 and $R^2 = 0.981$

Table 7-12 The values for the hindered settling parameters (A), (log $V_s$) and ($V_s$) obtained using Steinour's Equation for Never-dried Calcium Carbonate suspended in various media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>A</th>
<th>log $V_s$</th>
<th>$V_s$ (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>12.702</td>
<td>0.869</td>
<td>7.396</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>16.754</td>
<td>0.678</td>
<td>10.023</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>12.422</td>
<td>1.001</td>
<td>7.499</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>9.912</td>
<td>0.875</td>
<td>4.952</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>8.928</td>
<td>0.695</td>
<td>4.764</td>
</tr>
</tbody>
</table>
Fig. 7-11 The linear plot for the Richardson & Zaki equation for different weights of Never-dried calcium carbonate in water. Where, slope is 26.672, intercept is 0.8121 and $R^2$ is 0.777.

Figure 7-12: The linear plot for the Richardson & Zaki equation for different weights of never dried Calcium Carbonate in 0.1% Poloxamer. Where, slope is 24.057, intercept is 0.8121 and $R^2 = 0.917$
Figure 7-13: The linear plot for the Richardson & Zaki equation for different weights of Never-dried Calcium Carbonate in 0.5% Poloxamer. Where, slope is 39.282, intercept is 0.9915 and $R^2 = 0.9001$.

Figure 7-14: The linear plot of the Richardson & Zaki equation for different weights of Never-dried Calcium Carbonate in 1% Poloxamer. Where, slope is 29.647, intercept is 0.8679 and $R^2 = 0.9366$. 
Figure 7-15: The linear plot of the Richardson & Zaki equation for different weights of Never-dried Calcium Carbonate in 2% Poloxamer. Where, slope is 199.58, intercept is 3.8195 and $R^2 = 0.9814$.

Table 7.13: The values for the hindered settling parameters (n), $(\log V_s)$ ($V_s$) obtained by Richardson & Zaki equation for Calcium Carbonate suspended in different media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>n</th>
<th>$\log V_s$</th>
<th>$V_s$ (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>30.263</td>
<td>0.869</td>
<td>7.396</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>39.282</td>
<td>0.672</td>
<td>9.806</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>29.647</td>
<td>0.992</td>
<td>7.885</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>24.057</td>
<td>0.897</td>
<td>4.875</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>21.761</td>
<td>0.688</td>
<td>4.073</td>
</tr>
</tbody>
</table>
Figure 7-16: The linear plot for the Dollimore & McBride equation for different weights of Never-dried Calcium Carbonate in water. Where, slope is -11.988, intercept is 0.819 and $R^2 = 0.7778$.

Figure 7-17: The linear plot of the Dollimore & McBride equation for different weights of Calcium Carbonate in Poloxamer 0.1% solution. Where, slope is -10.81, intercept is 0.6785 and $R^2 = 0.9175$
Figure 7-18: The linear plot of the Dollimore & McBride equation for different weights of Calcium Carbonate in Poloxamer 0.5% solution. Where, slope is 17.652, intercept is 1.001 and $R^2 = 0.9007$.

Figure 7-19: The linear plot of the Dollimore & McBride equation for different weights of Calcium Carbonate in Poloxamer 1% solution. Where, slope is 13.321, intercept is 0.8754 and $R^2 = 0.934$
Figure 7-20: The linear plot of the Dollimore & McBride equation for different weights of Calcium Carbonate in Poloxamer 2% solution. Where, slope is 89.664, intercept is 3.8695 and $R^2 = 0.9817$

Table 7.14: The values for the hindered settling parameters ($n$, $\log V_s$) and $(V_s)$ obtained for the Dollimore & McBride equation for Never-dried Calcium carbonate suspended in different media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>b</th>
<th>$\log V_s$</th>
<th>$V_s$ (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4.423</td>
<td>0.8689</td>
<td>7.394</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>6.513</td>
<td>0.6785</td>
<td>10.034</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>4.915</td>
<td>1.0015</td>
<td>7.505</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>3.988</td>
<td>0.8754</td>
<td>4.959</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>3.079</td>
<td>0.6954</td>
<td>4.769</td>
</tr>
</tbody>
</table>

Table 7.15: Particle size calculated using the three different equations for Never dried Calcium Carbonate suspended in water
<table>
<thead>
<tr>
<th>Equation</th>
<th>$V_s$ (cm/s)</th>
<th>$r$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;Z</td>
<td>0.01211</td>
<td>6.422</td>
</tr>
<tr>
<td>S</td>
<td>0.01233</td>
<td>6.480</td>
</tr>
<tr>
<td>D&amp;M</td>
<td>0.01232</td>
<td>6.479</td>
</tr>
<tr>
<td>Average</td>
<td>0.01225</td>
<td>6.460</td>
</tr>
</tbody>
</table>

Table 7.16: Particle size calculated using the three different equations for Never dried Calcium Carbonate suspended in 0.1% Poloxamer.

<table>
<thead>
<tr>
<th>Equation</th>
<th>$V_s$ (cm/s)</th>
<th>$r$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;Z</td>
<td>0.00784</td>
<td>5.167</td>
</tr>
<tr>
<td>S</td>
<td>0.00794</td>
<td>5.201</td>
</tr>
<tr>
<td>D&amp;M</td>
<td>0.00795</td>
<td>5.204</td>
</tr>
<tr>
<td>Average</td>
<td>0.00791</td>
<td>5.191</td>
</tr>
</tbody>
</table>

Table 7.17: Particle size calculated using the three different equations for Never Dried Calcium Carbonate suspended in 0.5% Poloxamer.

<table>
<thead>
<tr>
<th>Equation</th>
<th>$V_s$ (cm/s)</th>
<th>$r$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;Z</td>
<td>0.00813</td>
<td>5.261</td>
</tr>
<tr>
<td>S</td>
<td>0.00825</td>
<td>5.302</td>
</tr>
<tr>
<td>D&amp;M</td>
<td>0.00827</td>
<td>5.306</td>
</tr>
<tr>
<td>Average</td>
<td>0.00821</td>
<td>5.290</td>
</tr>
</tbody>
</table>

Table 7.18: Particle size calculated using the three different equations for Never dried Calcium Carbonate suspended in 1% Poloxamer.
Table 7.19: Particle size calculated using the three different equations for Never dried Calcium Carbonate suspended in 2% Poloxamer.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Vs (cm/s)</th>
<th>r (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;Z</td>
<td>0.01634</td>
<td>7.462</td>
</tr>
<tr>
<td>S</td>
<td>0.01671</td>
<td>7.544</td>
</tr>
<tr>
<td>D&amp;M</td>
<td>0.01672</td>
<td>7.548</td>
</tr>
<tr>
<td>Average</td>
<td>0.01659</td>
<td>7.518</td>
</tr>
</tbody>
</table>

The observation was made that, as the poloxamer concentration increased, the average particle size of the never dried calcium carbonate also increased. The poloxamer or any surfactant has the property to decrease the surface energy and make the particles flocculate.[70] The polymer tends to make polymer bridges which initiate the flocculation. The plot constructed for all the equations were linear and there is substantial similarities in the data collected from the various equations.

**7.1.4 Determination of Permeability:**

The hindered settling plug can be considered to be stationary with the fluid moving upwards through the pores in the bed of granular solids. This phenomenon is called permeability (K). The value of (K) can be calculated by using the rate of fall (Q) and settling velocity (Vs) or by using (n) obtained from the Richardson Zaki method as shown in the equations below.

Where:

$$ K = \left( \frac{1}{2Q} \right) \left( \frac{\varepsilon}{1-\varepsilon} \right) V_s $$  \hspace{1cm} (7.6)
Equation 7.6 was used to calculate the values for the Kozeny Carman constant ($K$). These ($K$-values) for each suspension are plotted against $\varepsilon$ as seen in the Figure 7.22. At a value of $\varepsilon = \varepsilon_K$ the ($K$-values) pass through a minimum ($K_{min}$). ($\varepsilon_K$) and ($K_{min}$) are calculated from Equations 7.8 and 7.9, respectively. The ($K$-value) is inversely proportional at values of $\varepsilon$ above $\varepsilon_K$ and it is directly proportional to $\varepsilon$ when $\varepsilon$ is below $\varepsilon_K$.

The value $\varepsilon_1$ is the initial volume fraction of the suspension at which hindered settling commences. Therefore $\varepsilon_1$ is calculated using the equation

$$\varepsilon = \frac{n}{n+1} \quad 7.10$$

The higher the value of $\varepsilon_1$, the more the system tends to be hindered. $\varepsilon_K$ is always less than $\varepsilon_1$ and a plot of $\varepsilon_K$ and $\varepsilon_1$ gives a straight line as seen in Figure 7.23.

From Figure 7.20, it can be seen that the Kozeny Carman constant for permeability ($K$) increases when ($\varepsilon$) is greater than ($\varepsilon_K$) and ($K$) increases when ($\varepsilon$) is less than ($\varepsilon_K$). This pattern is observed for all the suspensions.
From Table 7.20, it was observed that permeability decreased when the Poloxamer was added to the suspension. This could be due to the flocculation of suspensions resulting in fewer pores through which the fluid could move. The (K value) for water is the highest when compared to the other poloxamer media.
Table 7.20: The values for permeability parameters \((K)\), \((\varepsilon_K)\) and \((K_{\text{min}})\) for various weights of never-dried calcium carbonate suspended in various media

### Case I

<table>
<thead>
<tr>
<th>Medium</th>
<th>Weight (g)</th>
<th>K</th>
<th>(\varepsilon_K)</th>
<th>K_{\text{min}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>16</td>
<td>37.16418</td>
<td>0.964618</td>
<td>0.51834</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>40.70021</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>39.38152</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>37.8074</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>36.57801</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Case II

<table>
<thead>
<tr>
<th>Medium</th>
<th>Weight (g)</th>
<th>K</th>
<th>(\varepsilon_K)</th>
<th>K_{\text{min}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poloxamer 0.1%</td>
<td>16</td>
<td>30.97589</td>
<td>0.954663</td>
<td>0.523745</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>31.99599</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>31.05519</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>30.42203</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>29.39043</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium</td>
<td>Weight (g)</td>
<td>K</td>
<td>$\varepsilon_K$</td>
<td>Kmin</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>---------</td>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>Poloxamer 0.5%</td>
<td>16</td>
<td>47.86089</td>
<td>0.973177</td>
<td>0.513781</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>52.61382</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>53.30777</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>52.19336</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>51.41308</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Medium</th>
<th>Weight (g)</th>
<th>K</th>
<th>$\varepsilon_K$</th>
<th>Kmin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poloxamer 1%</td>
<td>16</td>
<td>39.19107</td>
<td>0.96383</td>
<td>0.518764</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>40.73919</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>40.61454</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>38.818</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>39.18011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Case V

<table>
<thead>
<tr>
<th>Medium</th>
<th>Weight (g)</th>
<th>K</th>
<th>$\varepsilon_K$</th>
<th>Kmin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poloxamer 2%</td>
<td>16</td>
<td>4.113966</td>
<td>1.119325</td>
<td>0.446698</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>6.703452</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>9.34029</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>11.18334</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15.732</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.21: The values for initial ($\varepsilon_1$) porosity and minimum porosity ($\varepsilon_k$) for Never-dried Calcium Carbonate suspended in various media

<table>
<thead>
<tr>
<th>Medium</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.9705</td>
<td>0.96461</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>0.9686</td>
<td>0.993</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>0.9668</td>
<td>0.97318</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>0.9649</td>
<td>0.96383</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>0.9631</td>
<td>0.95466</td>
</tr>
</tbody>
</table>
Figure 7-22: A plot of initial porosity and minimum porosity for Never dried Calcium Carbonate suspended in different media. Where, slope = 6.7517, intercept = 5.55 and $R^2 = 0.9564$

### 7.2 Percentage Yield Calculation:

The calculation for the percentage yield of Never-dried calcium carbonate was calculated by using the method explained in Chapter-6. The theoretical weight along with the actual weight obtained after the Calcium Carbonate and percentage yield calculated is given in Table 7.22. For convenience theoretical weights have been used in all the calculations for the hindered settling experiments.

Table 7.22: Percentage yield calculated from actual weight and theoretical weight

<table>
<thead>
<tr>
<th>Theoretical weight (gms)</th>
<th>Actual weight (gms)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>14.741±2.84</td>
<td>92.1</td>
</tr>
<tr>
<td>17</td>
<td>16.853±0.27</td>
<td>99.13</td>
</tr>
<tr>
<td>18</td>
<td>17.546±0.112</td>
<td>97.3</td>
</tr>
<tr>
<td>19</td>
<td>18.881±0.262</td>
<td>99.3</td>
</tr>
<tr>
<td>20</td>
<td>19.721±0.054</td>
<td>98.6</td>
</tr>
</tbody>
</table>
7.3 Scanning Electron Microscopy:

The method was followed as provided in Chapter 6. The respective results for the never dried Calcium Carbonate prepared in various media with unique concentrations are given in the figure 7.24 – 7.29.

Figure 7-23: SEM image of dried Calcium Carbonate dispersed in water.
Figure 7-24 SEM image of dried Calcium carbonate dispersed in 2% Poloxamer.
Figure 7-25 SEM image of dried Calcium carbonate dispersed in 2% Poloxamer
Figure 7-26: SEM image of dried Calcium carbonate dispersed in 1% Poloxamer
Figure 7-27: SEM image of dried Calcium carbonate dispersed in 0.5% Poloxamer
Figure 7-28: SEM image of dried Calcium carbonate dispersed in 0.1% Poloxamer.

The SEM study was carried out to analyze the effect of polymer on particle size. As the particle size affects the flocculation and thus alternatively leads to hindered settling, the requisites for the sample preparation does not help determine it. The sample preparation requires a dried product which was obtained from the suspensions dried overnight in an Oven at 30 -40 °C. The drying of the liquid suspension might have broken the large flocs and we can’t state the effect of higher concentrations for the poloxamer on the flocculation. Although the particle cluster did not break completely and the difference in particle cluster can be seen as the poloxamer concentration increased.[32] The aggregate
size at 10000x magnification was estimated to 1µm. Further studies such as laser
diffraction were performed to compare the data for accurate results.

7.4 Laser Diffraction (LD) Results:

Laser diffraction was performed on 20 gm never dried Calcium Carbonate suspensions in
various media as described in Chapter 6. The numbers are assigned according to the
presence of Poloxamer in the medium as 0% (Water), 1%, 0.5%, and 0.1% poloxamer
concentration respectively. The mean particle size for each suspension is given in Table 7.21.

Table 7.23: Mean particle size from never dried Calcium Carbonate suspended in various
poloxamer media.

<table>
<thead>
<tr>
<th>Poloxamer Concentration (%)</th>
<th>Particle radius in µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.255</td>
</tr>
<tr>
<td>1</td>
<td>22.999</td>
</tr>
<tr>
<td>1</td>
<td>23.381</td>
</tr>
<tr>
<td>1</td>
<td>23.212</td>
</tr>
<tr>
<td>0.5</td>
<td>22.179</td>
</tr>
<tr>
<td>0.5</td>
<td>22.115</td>
</tr>
<tr>
<td>0.5</td>
<td>23.45</td>
</tr>
<tr>
<td>0.5</td>
<td>22.57</td>
</tr>
<tr>
<td>0.1</td>
<td>19.395</td>
</tr>
<tr>
<td>0.1</td>
<td>20.017</td>
</tr>
<tr>
<td>0.1</td>
<td>20.849</td>
</tr>
<tr>
<td>0.1</td>
<td>20.07</td>
</tr>
<tr>
<td>0</td>
<td>16.50</td>
</tr>
<tr>
<td>0</td>
<td>16.932</td>
</tr>
<tr>
<td>0</td>
<td>17.521</td>
</tr>
<tr>
<td>0</td>
<td>16.976</td>
</tr>
</tbody>
</table>
Table: 7.24 Mean Particle size parameters with upper and lower limits for plotting the Particle radii (µm) against the Concentration of Poloxamer curve for never dried Calcium carbonate suspension.

<table>
<thead>
<tr>
<th>Concentration of Poloxamer (%)</th>
<th>1</th>
<th>0.5</th>
<th>0.1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Particle Size</td>
<td>23.212</td>
<td>22.57</td>
<td>20.07</td>
<td>16.976</td>
</tr>
<tr>
<td>Maximum Particle Size</td>
<td>23.381</td>
<td>23.45</td>
<td>20.849</td>
<td>17.521</td>
</tr>
<tr>
<td>Minimum Particle Size</td>
<td>22.999</td>
<td>22.115</td>
<td>19.397</td>
<td>16.5</td>
</tr>
<tr>
<td>+ error</td>
<td>0.169</td>
<td>0.88</td>
<td>0.779</td>
<td>0.545</td>
</tr>
<tr>
<td>- error</td>
<td>0.213</td>
<td>0.455</td>
<td>0.673</td>
<td>0.476</td>
</tr>
</tbody>
</table>

Figure 7-29: Plot of particle radii (µm) against the Concentration of Poloxamer for the never dried Calcium carbonate suspensions.
The Laser diffraction results indicate that, with an increase in the concentration of the poloxamer the particle size increases. Similarly the surface weighted mean also increases. The never dried Calcium carbonate in water when passed through the homogenizer of the instrument resulted in a consistent particle size when compared to the hindered settling experiment data. However, the results for the never dried calcium carbonate dispersed in the flocculating agent did not give results comparable to the hindered settling experiment. The reason could be the breaking of the flocs when the appropriate amount of suspension added in the homogenizer of the instrument.

7.5 Thermal Analysis:

7.5.1 Differential Scanning Calorimetry (DSC) Results:

The Method stated in Chapter 7 was used to perform the studies. Both methods of sample preparation namely, extraction from the final settled volume and filtered precipitate gave promising results. The exothermic peaks observed in the respective plots obtained indicates the crystallization of water, eventually followed by endothermic peak at ~4°C representing the melting of the ice crystal formed at a lower temperature; Another endothermic peak for the vaporization of water was reported at ~110°C. Table 7.25 shows all the results for the heat of crystallization ($\Delta H_c$), fusion ($\Delta H_m$), vaporization ($\Delta H_v$) and degradation ($\Delta H_d$).
Table 7.25: Thermogram data namely heat of crystallization ($\Delta H_c$), fusion ($\Delta H_m$), vaporization ($\Delta H_v$) and degradation ($\Delta H_d$), and temperatures at $T_c$, $T_m$ and $T_v$ for never dried Calcium Carbonate Suspension in water and different concentrations of poloxamer.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_v$ (J/g)</th>
<th>$T_v$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>257.61</td>
<td>-7.69</td>
<td>264.88</td>
<td>2.87</td>
<td>1644.70</td>
<td>100.85</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>236.75</td>
<td>-4.69</td>
<td>249.78</td>
<td>3.30</td>
<td>1304.47</td>
<td>98.78</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>258.81</td>
<td>-10.85</td>
<td>255.47</td>
<td>4.51</td>
<td>1363.60</td>
<td>104.54</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>159.15</td>
<td>-9.94</td>
<td>173.38</td>
<td>5.82</td>
<td>1319.79</td>
<td>110.4</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>235.23</td>
<td>-6.17</td>
<td>247.48</td>
<td>2.71</td>
<td>1554.99</td>
<td>102.22</td>
</tr>
</tbody>
</table>
Figure 7.30: DSC thermogram for 20 g of Never Dried Calcium Carbonate suspended in Water.
Figure 7-31: DSC thermogram of 20 g for Never Dried Calcium Carbonate suspended in 0.1% Poloxamer.
Figure 7.32: DSC thermogram of 20 g for Never Dried Calcium Carbonate suspended in 0.5% Poloxamer.
Figure 7.33: DSC thermogram of 20 g for Never Dried Calcium Carbonate suspended in 1% Poloxamer.
Figure 7-35: DSC thermogram of 20 g for Never Dried Calcium Carbonate suspended in 2% Poloxamer.
Figure 7-35: DSC thermogram comparison of triplicate run for unbound water analysis in 20 g for Never Dried Calcium Carbonate suspended in 1% Poloxamer.
Differential Scanning Calorimetry was performed to analyze the unbound and bound water present in the never dried calcium carbonate suspension with various media. The heat of crystallization and fusion observed in figures 7.31 to 7.36 were carefully analyzed and it was found that with the increase in concentration of the Poloxamer in the suspension dispersion, the water bound on the surface of the particle decreased. This can be seen through the decrease in peak intensity as the concentration of poloxamer decreases in the suspension media.

In Figure 7.36, the consistency in the results for the substantial decrease in the bound water peak at the heat of crystallization are compared, which gives evidence of poloxamer’s affinity toward particles as compared to water and how they compete for the site of adsorption.

7.5.2 Thermogravimetry (TG) Results:

A TG curve acts to characterize the purity of the compound being analyzed. The mass lost due to thermal degradation can be related to the stoichiometry involved when the quantitative composition of a compound is known. [61] The chemistry involved in the thermal decomposition of calcium carbonate:

\[ \text{CaCO}_3 \rightarrow \text{CaO (s)} + \text{CO}_2 (g) \]  

Calcium carbonate roughly decomposes between 800°C to 950°C and forms CaO and CO\(_2\) as indicated in the equation above. Stoichiometrically, 1 mole of CaCO\(_3\) gives 1 mole of CO\(_2\) and which is can be expressed as:

\[ 1 \text{ mole CO}_2 = \frac{(m_1-m_2)}{d} \times M_r \text{CaO} \]
Where, $M_r$(CaO) is relative molar mass of CaO.

$$m_3 = \left(\frac{m_1-m_2}{44}\right) \times 56 \quad 7.13$$

Here $m_3$ is mass of CaO formed.

$$m_3 = 1.27(m_1 - m_2) \quad 7.14$$

The amount of calcium in calcium carbonate and calcium oxide can be calculated by:

$$= 1.27(m_1 - m_2) \times \frac{A_r(Ca)}{M_r(CaO)} \quad 7.15$$

$$= 1.27(m_1 - m_2) \times 40/56 \quad 7.16$$

$$= 0.19(m_1 - m_2) \quad 7.17$$

Calcium carbonate, after calcinations, forms calcium oxide, which is used extensively in high temperature applications. TGA was performed on 20 g for Never-dried calcium carbonate suspended in water, 1% and 2% Poloxamer as described in Chapter-6.

Thermograms for all three suspensions are given in Figures 7.37 to 7.39. The first derivative of the thermogram was obtained to determine the water loss. Three different temperatures where water loss is observed for each of the suspensions is given in Table 7.26.
Figure 7-36: TG thermogram for dried form of Never-dried Calcium carbonate suspension dispersed in water.
Figure 7-37: TG thermogram for dried form of Never-dried Calcium carbonate suspension dispersed in 1% Poloxamer.
Figure 7-38: TG thermogram for dried form never dried Calcium carbonate suspension dispersed in 2% Poloxamer.
Figure 7-39: The TGA plot of Weight (mg) Vs Temperature (°C) for CaCO3 in water; the points highlighted indicate the specific events during the thermal decomposition.
Table 7.26: Weight loss for Never dried calcium carbonate suspension in water due to Thermal decomposition during the TGA cycle.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.11</td>
<td>8.60</td>
</tr>
<tr>
<td>22.17</td>
<td>8.60</td>
</tr>
<tr>
<td>188.58</td>
<td>8.57</td>
</tr>
<tr>
<td>293.65</td>
<td>8.55</td>
</tr>
<tr>
<td>454.08</td>
<td>8.51</td>
</tr>
<tr>
<td>622.48</td>
<td>8.20</td>
</tr>
<tr>
<td>649.29</td>
<td>7.85</td>
</tr>
<tr>
<td>683.52</td>
<td>6.92</td>
</tr>
<tr>
<td>708.43</td>
<td>5.71</td>
</tr>
<tr>
<td>716.02</td>
<td>5.25</td>
</tr>
<tr>
<td>722.40</td>
<td>4.88</td>
</tr>
<tr>
<td>741.66</td>
<td>4.63</td>
</tr>
<tr>
<td>790.92</td>
<td>4.62</td>
</tr>
<tr>
<td>867.67</td>
<td>4.61</td>
</tr>
<tr>
<td>955.52</td>
<td>4.61</td>
</tr>
<tr>
<td>991.67</td>
<td>4.61</td>
</tr>
</tbody>
</table>
Figure 7-40: The TGA plot of Weight (mg) Vs Temperature (°C) for Never dried CaCO3 in 1% poloxamer; the black points indicate the specific events during the thermal decomposition.

Table 7.27: Weight loss for Never dried calcium carbonate suspension in 1% poloxamer due to Thermal decomposition during the TGA cycle.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318.672</td>
<td>9.679</td>
</tr>
<tr>
<td>390.504</td>
<td>9.295</td>
</tr>
<tr>
<td>584.519</td>
<td>9.172</td>
</tr>
<tr>
<td>641.247</td>
<td>8.752</td>
</tr>
<tr>
<td>731.826</td>
<td>5.189</td>
</tr>
<tr>
<td>911.11</td>
<td>5.155</td>
</tr>
</tbody>
</table>
Figure 7-41: The TGA plot of Weight (mg) Vs Temperature (°C) for Never- dried CaCO3 in 2% Poloxamer; the highlighted points indicate the specific events during the thermal decomposition.

Table 7.28: Weight loss for calcium carbonate suspension in 2% poloxamer due to Thermal decomposition during TGA cycle.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>335.305</td>
<td>7.395</td>
</tr>
<tr>
<td>391.409</td>
<td>7.138</td>
</tr>
<tr>
<td>617.68</td>
<td>6.923</td>
</tr>
<tr>
<td>722.303</td>
<td>3.949</td>
</tr>
</tbody>
</table>
The weight loss for calcium carbonate dispersed in water substantially started at ~622°C and it kept increasing until 722.40 °C after which it became almost constant. In the case of the calcium carbonate sample which was prepared and dispersed in 1% poloxamer before drying, gives two peaks at different intervals. It was found to be the decomposition peak at ~318.672 till 390.504 is of Poloxamer followed by the peak of calcium carbonate decomposition at 614.247 °C.

Similarly, 2% poloxamer containing dried calcium carbonate sample’s thermogram revealed a peak onset at 335.305 °C till 391.409; this peak is also considered to be produced by 2% poloxamer. The peak onset at 617.68 till 722.303 was produced by Calcium carbonate thermally decomposed products such as CaO and carbon dioxide.

7.5 Average Zeta Potential Results:

Zeta potential measurements were performed on 20 g of Never-dried calcium carbonate suspended in water and various concentrations of Poloxamer solution. The method described in Chapter 6 was used. The zeta potential values for Never-dried calcium carbonate dispersed in various media is given in the Table 7.26.

Table 7.29: Zeta potential values for 20 g Never-dried calcium carbonate suspended in various media.

<table>
<thead>
<tr>
<th>Dispersion Media</th>
<th>Average zeta potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-24.383</td>
</tr>
<tr>
<td>0.1% Poloxamer</td>
<td>-4.29</td>
</tr>
<tr>
<td>0.5% Poloxamer</td>
<td>-4.91</td>
</tr>
<tr>
<td>1% Poloxamer</td>
<td>-7.77</td>
</tr>
<tr>
<td>2% Poloxamer</td>
<td>-11.69</td>
</tr>
</tbody>
</table>
Figure 7-42: Average Zeta potential analysis of 20g of Never dried Calcium Carbonate suspended in water.
Figure 7-43: Average Zeta potential analysis of 20 g of Never-dried Calcium Carbonate suspended in 0.1% Poloxamer.
Figure 7-44: Average Zeta potential analysis of 20 g of Never-dried Calcium Carbonate suspended in 0.5% Poloxamer.
Figure 7-45: Average Zeta potential analysis of 20 g of Never-dried Calcium Carbonate suspended in 1% Poloxamer.
Figure 7-46: Average Zeta potential analysis of 20 g of Never-dried Calcium Carbonate suspended in 2% Poloxamer.

The Average zeta potential results were extremely necessary for this research. Poloxamer is a non-ionic surfactant which doesn’t alter the electrical charge of the dispersion media at low concentrations up to 0.05%. It was determined that Never-dried calcium carbonate, being a heavy molecule requires a higher poloxamer concentration of 0.1 % and higher to achieve flocculation. Poloxamer as discussed in Chapter 4 works by creating bridges between molecules to cause flocculation. The results found in this research suggest that, at higher concentrations of 0.1 to 2% poloxamer there is marked change in the average zeta potential. As the poloxamer concentration increases the flocculation magnitude
increases and due to higher bridging, higher positive ions become attracted toward the negative core and hence average zeta potential decreases.

With water as a dispersion media the never-dried calcium carbonate suspension shows the average zeta potential within the stable suspension range. A rise in the poloxamer concentration in the dispersion media pushes the value for the average zeta potential near to the value of zero; this implies that there is more force of attraction between particles and consequently a higher rate of flocculation. This pattern continues until 0.5% poloxamer, increases further at 1% poloxamer concentration and beyond. The average zeta potential value again starts moving towards higher negative values which implies more negative charge sites on the particles. This retrieval of average zeta potential toward the -7.11 to -11.81 indicates the higher viscosity gradient which decreases the rate of settling although the flocculation is still occurring. There is another theory which suggests, as the core of the particle is negative and the positive ions from other particles are attracted toward them, which leads to flocculation. With higher concentrations of poloxamer, the surface of the particle becomes occupied with the poloxamer and positive ions are unable to pair up. This increases the surface tension and yet facilitates the flocculation without changing the potential toward the positive side.

7.7 X-ray Powder Diffraction (PXRD) Results:

PXRD was performed as described in Chapter 6. PXRD was performed on oven dried form of Never-dried Calcium carbonate suspended in water and calcium carbonate suspended in various Poloxamer concentrates. The diffractograms observed implies change in morphology of the calcium carbonate powder for different dispersion mediums. The results can be seen below in figure 7.47.
Figure 7-47: Diffractogram for calcium carbonate powder dispersed in Water and different poloxamer concentration. Where, (A) = Diffractogram for Calcium carbonate + 2% Poloxamer; (B) Diffractogram for Calcium carbonate + 1% Poloxamer; (C) Diffractogram for Calcium carbonate + 0.5% Poloxamer; (D) Diffractogram for Calcium carbonate + 0.1% Poloxamer; and (E) Diffractogram for Calcium carbonate + water.
Figure 7-48: Diffractogram of Calcium carbonate powder dispersed in Water and different poloxamer concentration. (4X Zoomed). Where, (A) = Diffractogram for Calcium carbonate + 2% Poloxamer; (B) Diffractogram for Calcium carbonate + 1% Poloxamer; (C) Diffractogram for Calcium carbonate + 0.1% Poloxamer; (D) Diffractogram for Calcium carbonate + 0.5% Poloxamer; and (E) Diffractogram for Calcium carbonate + water.

In the beginning, the diffractograms seems to be overlapping for all the different samples. But then gave distinct patterns when magnified and watched closely. The results revealed that with an increase in poloxamer concentration the peak shifts forward. The reason could be due to polymer coating on the particles and thus an increase in concentration of the poloxamer the peaks come distinct from each other. Although this could not be possible due to flocculation since the powder was triturated with pastel mortar and the particles in absence of moisture are unable to flocculate. This theory proved that the
crystal structure does not affect this peak shift when the only change made to the suspension sample was the poloxamer concentration.

Figure 7-49: Peak prototype comparison between of the sample and reference.
Figure 7-50: Peak prototype comparison of the sample with reference.
Chapter 8

Conclusions and Future Work

8.1 Conclusions

Calcium carbonate suspensions prepared in the “never dried” state exhibit hindered settling at 16g/200ml concentration (w/v). The suspension after sedimentation was easily redispersible and there were no signs of caking. Stokes’ parameters helped explaining and evaluate the particle size of the particles which were calculated by hindered settling. Steinour, Richardson & Zaki and Dollimore & McBride equation results were consistent with the various concentration samples with strong correlation between the respective laws.

Poloxamer 407 used as a surfactant was very effective in flocculating the suspension. The concentration range optimum for the comparative study of flocculation was found to be 0.1%, 0.5%, 1% and 2%. The flocculation of the suspended particles was found to be a function of the concentration of the surfactant. Deflocculation took place in an excess of poloxamer concentration resulting in a slower rate of sedimentation. Non-ionic surfactants tend to create cross polymer bridging which was responsible for the flocculation and subsequent increase in particle size. Zeta potential measurements
showed that with an increase in concentration of poloxamer, the average zeta potential changed from that obtained with water as the dispersion medium.

The theory suggested that the nonionic surfactant does not make any zeta potential changes at smaller concentration of 0.05% since the flocculation is the result of polymer bridging with the calcium carbonate particles without influencing the electrical double layer. However, with the extensive increase in the concentration of poloxamer in the range of 0.1% to 2%, there was a substantial deviation in the average zeta potential. This suggests that the steric stability and electrical double layer has been affected due to the significantly higher concentration of the poloxamer above the 0.05%. The permeability of the suspension decreased substantiality with an increase in the flocculation of the suspension. The theory suggests that an increase in particle size and porosity decreases the permeability.

SEM images provided the information necessary to discern surface morphology which clearly indicates the flocculation; however, the real flocculation found in the liquid dispersion could not be replicated since the sample prepared was dried in an oven and pretreated for SEM compatibility. Laser Diffraction results were found to be in agreement with the hindered settling results and SEM images, since there were some morphological changes or change in lattice structure which imparted an increase in particle size analysis. The sample while being processed by the laser diffraction instrument, passed through a homogenizer which was capable of breaking the flocules; however some of floccles and particles managed to keep their integrity which was reflected in the results.
DSC studies documented the hypothesis that suggested that there was a decrease in the unbound water with an increase in the poloxamer concentration. The results indicated that the exothermic peak was markedly of lower magnitude in the case of the suspension formulated in the poloxamer than that the ones formulated with water. The assertion could be possibly made that the poloxamer particles compete with the water molecules to cover the surface of the calcium carbonate particles. Calcium carbonate degraded into its thermal by products, CaO and carbon dioxide which were visible at ~740°C to 810°C.

8.2 Future studies:

More techniques must be applied for formulation preparation and evaluation. In addition to the non-ionic surfactants, viscosity enhancers can also be employed to better understand polymer affinity towards the particles. Moreover, cationic and anionic surfactant can be used as suggested by literature. Cationic surface active agents have greater affinity and higher stability with the basic suspensions. Similarly, pH modification and its influence can be monitored to determine its effect on flocculation and settling behavior. Cationic and anionic surfactants could cause higher floccule formation because of ion pair interactions and if not used in appropriate quantities, it would not form stable a suspension.

The polymer with chromophore group could be employed for flocculation. The suspension thus formulated can be centrifuged and the supernatant could be extracted to study the concentration of unbound surfactant. This will show the affinity of a polymer toward the calcium carbonate particle and might reveal other veiled aspects of this research.
References

Chapter 3


References

Chapter 4


References

Chapter 5


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Chapter 6


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Chapter 7


