

**CHAPTER THREE:  
RESULTS AND DISCUSSION**

### 3.1 STABILITY OF TiO<sub>2</sub> NANOPARTICLE SUSPENSION IN DISPERSING AGENTS

Protection of skin against UV-radiation has developed from protection against skin burning to include UV protection. A combination of organic filter and/or physical filters (nanoparticles of TiO<sub>2</sub>) has been the main actives. To make a product with acceptable texture and storage stability it is important to use dispersing agent. Importance of dispersing agent is to disperse the powder of TiO<sub>2</sub>, minimising aggregation and maximizing the surface area of the powder. While cream texture and its flow properties are paramount in giving marketable products, their storage stability and biocompatibility are equally important.

Most dispersed systems show low stability, even if the degree of their dispersion is high. Solid particles in a suspension show a tendency to aggregate and then sediment. Stability of aqueous dispersions depends upon the balance of interactions between the particles of the dispersed phase, which are of attractive London dispersion forces and repulsive electrostatic interactions between the electrical double layers at the solid/solution interface, as well as the interactions caused by the presence of the adsorbed layers (steric stabilization) and hydration forces.

Stability of such systems can be modified by changing the electrostatic interactions and the structure of adsorbed layers. To obtain stable suspensions of titanium dioxide, ionic and nonionic surfactants are added. (Megoro, 1988) Obviously, the stability of TiO<sub>2</sub> dispersions depends also on various parameters, i.e., the density and size of the particles, particle size distribution, type of electrolyte and ionic strength.

The aim of this work was to compare the effect of anionic ( $\lambda$ -Carrageenan, dodecyl- $\beta$ -D-maltoside – DDM, sodium dodecyl sulfate – SDS) and nonionic (PEG

10,000 and Brij 35P) and glycolipids on the stability of titanium dioxide suspensions on the different concentration and chain length.

### 3.1.1 Settled volume

As far as surfactant type is concerned five surfactants were tested. The molecular architecture of three (3) surfactants suggests that they contain same number of carbon atoms in their hydrophobic tail, but differ in their head group polarities which are DDM, SDS and Brij 35P. It means that these surfactants possess same degree of affinity for oil phase, whilst differ in their affinity to aqueous phase. The result is that they differ in their HLB values, thereby stabilizing oil droplets in water at varying degree. The less polar the surfactant, the less water soluble it is, thereby showing greater interfacial activities. Whereas for PEG 10,000 and  $\lambda$ -Carrageenan irrespectively because they contain different number of carbon and head group polarity as well.

It is widely known that the important surface tensions are for characteristics of the surfactant and functionality itself and that have correlation with settled volume phenomenon by increasing surfactant concentration of dispersing agents it actually decreased the surface tensions, and each surface tension curve had a breaking point, which was taken as the critical micelles concentration. As can be seen in **Figure 3.1**, Brij 35P stabilized titanium oxide was found to be less stable compared to SDS stabilized titanium oxide. As evident from this figure, Brij 35P stabilized titanium oxide showed lower stability compared to SDS (**Figure 3.2**) to stabilized titanium oxide.

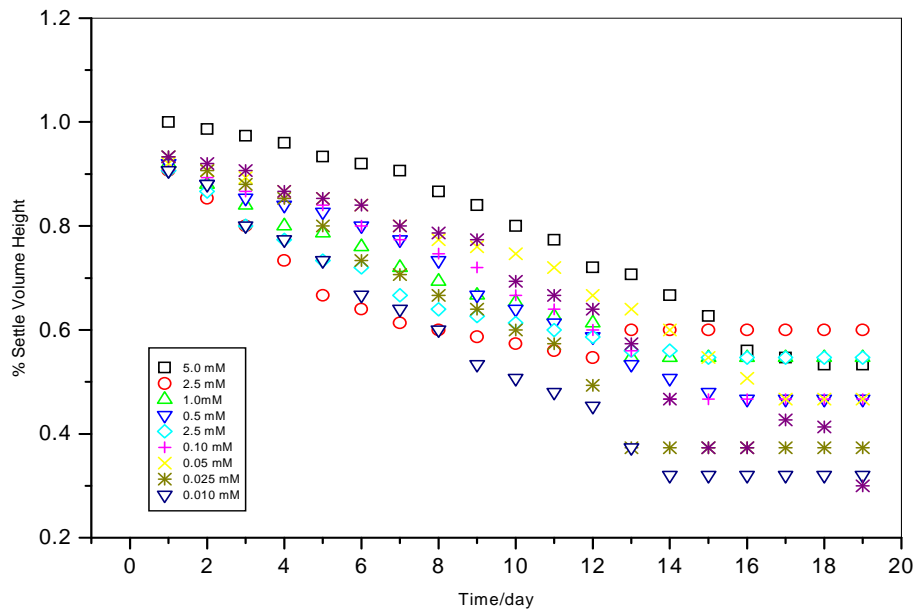
This probably happened because of SDS is higher polarity due to the hydrophilic (electrostatic repulsions from  $\text{SO}_4^{-2}$ ) of head group, the monomer molecules of this ionic surfactant tend to formed micelles at higher concentration. Typically the micelles have a closely spherical shape in a rather wide concentration range above the CMC state.

Single alkyl chain of SDS is possible to pack the molecule in micelles with rather distinct separation between the hydrophobic parts and the aqueous medium (Thomas, 1992). The area occupied per polar group in a spherical micelle is rather large so there is inevitable rather extensive hydrocarbon-water contact at the surface.

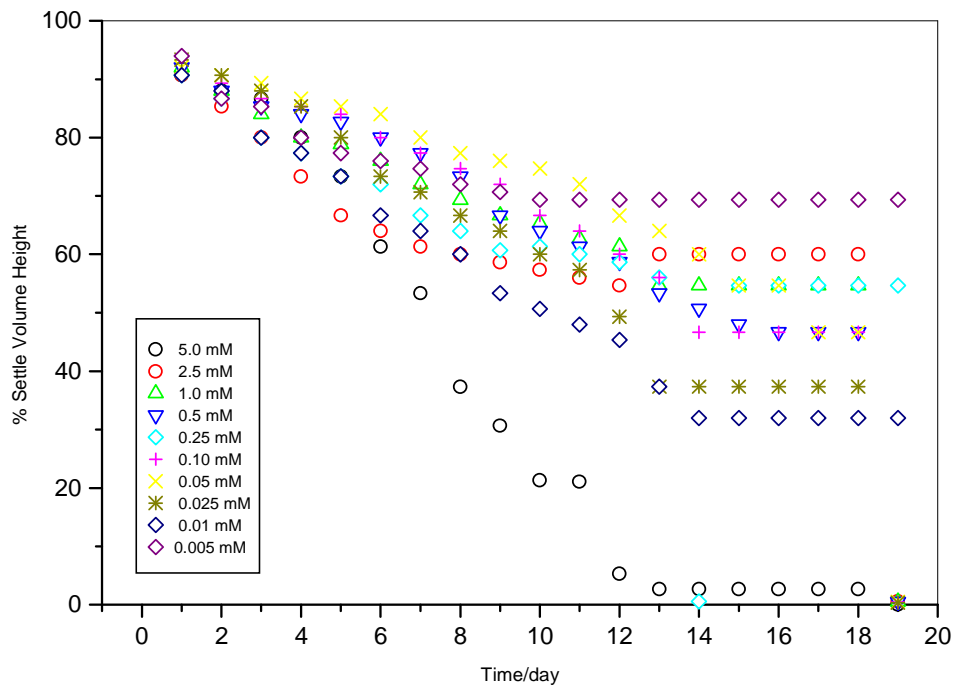
Meanwhile, Brij 35P is sugar-based nonionic surfactant which is slightly dependent on the anomeric configuration of glycosidic linkage. Hereby, is highly affected by the chain length of the hydrophobic tail of the surfactant and even has the same number of carbon with SDS but this surfactant is less polar and it clearly is not affected by head group. Much like Brij 35P and SDS stabilized titania suspensions, the PEG 10,000 stabilized TiO<sub>2</sub> showed a time independent stability past 15 days (**Figure 3.3**), as well as showing higher stability with the increase in its concentration. It could be due to the fact that polymeric ethylene oxide adsorbed more efficiently onto titanium oxide particle surface. Furthermore, the settled volume of the given stability of titania decreased with the increase in chain length of the hydrophobic tail. This can be accounted for the fact that with the increase in chain length aqueous phase, solubility of the surfactant decreases. It is the part of the electrostatic repulsions effect from polarity is absent and cooperatively in association is much greater as manifested inter alia in the much lower CMC (Lindman, 1984).

However, the threshold time-independent stability shifted to longest time with the increase in surfactant concentration DDM (**Figure 3.4**) and  $\lambda$ -Carrageenan (**Figure 3.5**). This difference also could be related with appears in the feasibility of closer packing of the head groups of  $\lambda$ -Carrageenan as is required in the transformation from monomer molecule into micelles (micellar growth). In these micellar growth, the water molecule are very mobile when bound to the micelles molecule, they rotate almost isotropically at a rate which is two or three times faster than in pure water and exchange

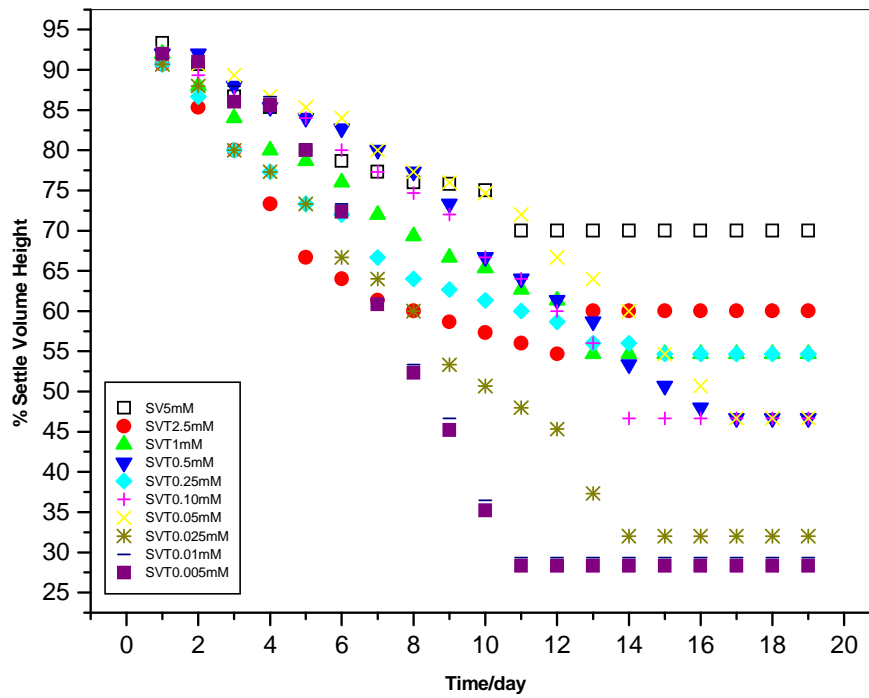
rapidly with the intermicellar solution (life time of water in the micelles of order of  $10^{-8}$  second) (Lindman, 1984; Couper, 198). These properties enhance the tendency of the stability of the suspension which is increased with surfactant concentration. It also could be probably due to the existence of anionic sulfate groups of  $\lambda$ -Carrageenan can interact strongly with oppositely charged cationic by ionic interaction (Aguzzi et al., 2002; Bonferoni et al., 2004)



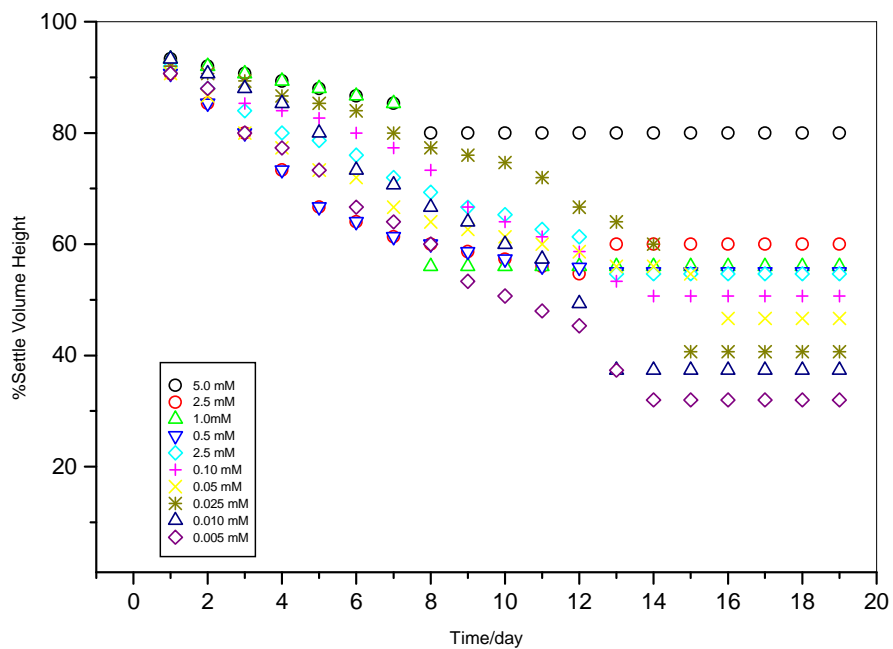
**Figure 3.1:** Settled volume-time profiles of Brij 35P stabilized titanium oxide colloidal systems as a function of Brij 35P



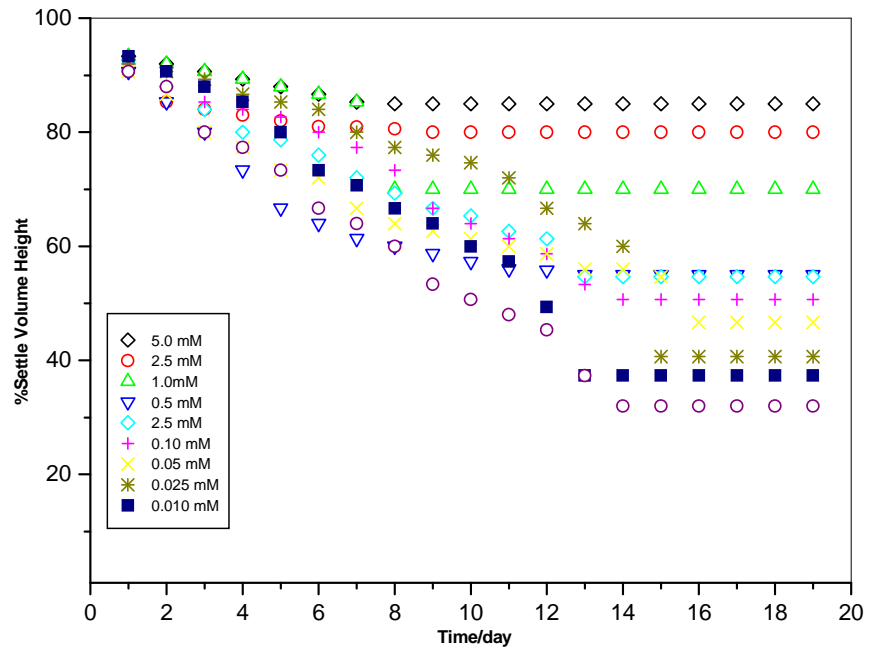
**Figure 3.2:** Settled volume-time profiles of SDS stabilized titanium oxide colloidal systems as a function of SDS



**Figure 3.3:** Settled volume-time profiles of PEG 10,000 stabilized titanium oxide colloidal systems as a function of PEG 10,000

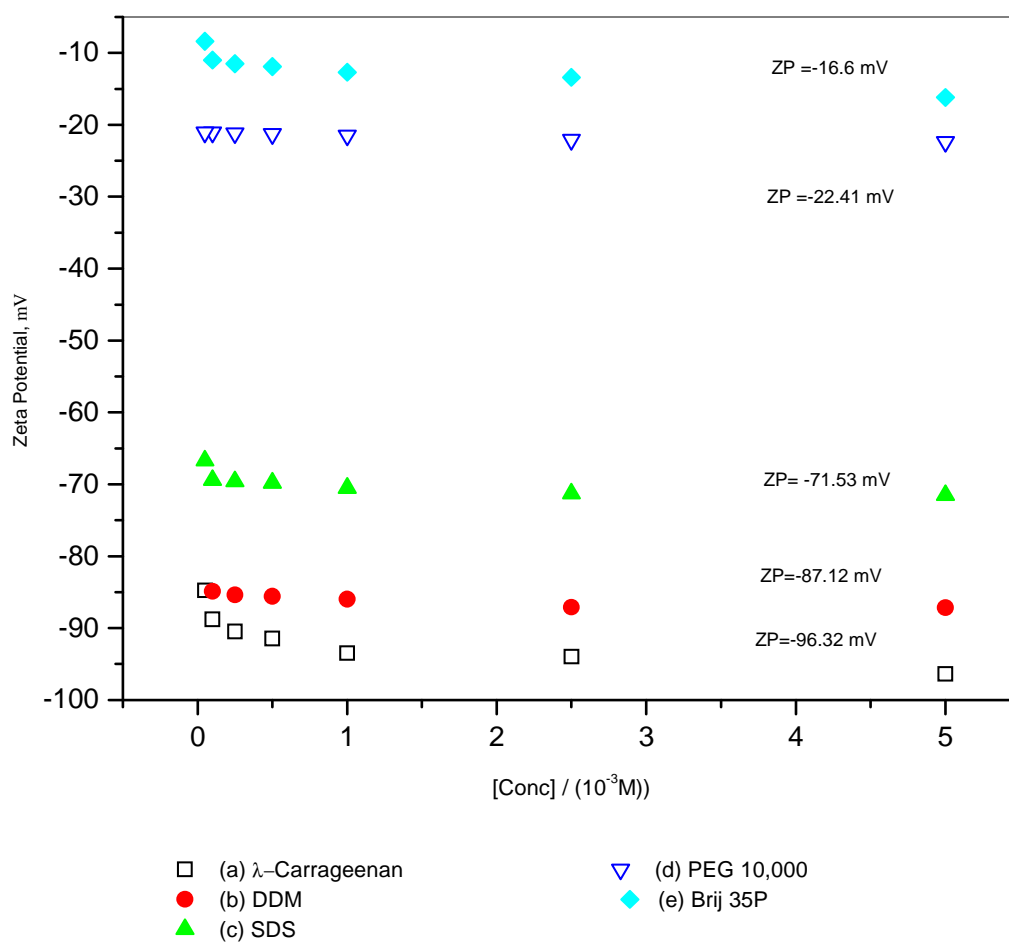


**Figure 3.4:** Settled volume-time profiles of DDM stabilized titanium oxide colloidal systems as a function of DDM concentration



**Figure 3.5:** Settled volume-time profiles of  $\lambda$ -Carrageenan stabilized titanium oxide colloidal systems as a function of  $\lambda$ -Carrageenan concentration.





**Figure 3.6:** Zeta potential profiles of different dispersing agents stabilized titanium oxide colloidal systems at 25°C.

### 3.1.2 Zeta potential

Advantages of zeta potential are that its value can be related to the stability of colloidal dispersions. The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles of dispersing agents in a dispersion. For molecules and particles that are smaller, a high zeta potential will confer stability, i.e. the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with higher negativity of zeta potential are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate (Delgado et al., 2005).

As can be seen from the **Figure 3.6**,  $\lambda$ -Carrageenan shows higher zeta potential than other dispersing agents respectively. The results of these zeta potential values has been compared to the literature and portrayed in **Table 3.1** and **Table 3.2**. This clearly indicates that  $\lambda$ -Carrageenan, DDM and PEG 10,000 show excellent stability because the zeta potential values are more than 60mV and whereas this is so for SDS and Brij 35P.

Analyzing the zeta potential changes, it can be seen that values of TiO<sub>2</sub> suspension and at the same concentration of dispersing agents. These phenomena strictly have correlation between salt contents, dynamic interfacial tension, HLB and head-tail surfactant itself. As can be seen, stronger effect is observed in the presence of  $\lambda$ -Carrageenan, where the shift towards higher negative values of the zeta potential already appears in **Figure 3.6**, and its behavior is in good agreement with that reported previously for concentration higher than  $5.0 \times 10^{-3}$  M.

Dispersing agents	Zeta Potential (mV)
$\lambda$ -Carrageenan	-96.32
DDM	-87.12
PEG 10,000	-71.53
SDS	-22.41
Brij 35P	-16.6

**Table 3.1:** Values of zeta potential for dispersing agents stabilized titanium oxide colloidal systems at 25°C.

Zeta Potential (mV)	Stability behavior of the colloid
from 0 to $\pm 5$	Rapid coagulation or flocculation
from $\pm 10$ to $\pm 30$	Incipient instability
from $\pm 30$ to $\pm 40$	Moderate stability
from $\pm 40$ to $\pm 60$	Good stability
more than $\pm 61$	Excellent stability

**Table 3.2:** Literature data of zeta potential values referring for stability behavior of the colloid

When more  $\lambda$ -Carrageenan is added, the nanoparticles become negative, well known is higher polarity from electrostatic repulsion from  $\text{OSO}_3^-$  of  $\lambda$ -Carrageenan, the monomer molecules of this ionic surfactant particles in dispersion tend to repel one another and therefore do not agglomerate (Teleki et al., 2007). In addition, in chemical reaction, sulphate group was reacted with water to produce sulfuric acid as a salt content, herewith it make more acidic solution and shows higher zeta potential. It also contain polysaccharide that has ability to performed better emulsifying properties due to the reduced of surface energy to form a thin layer between the aqueous and oil surface compared to DDM (disaccharide) and others dispersing agents respectively.

On the other hand for DDM is an anionic glycolipid which is less polar head and show a slightly greater degree of surface and interfacial tension reduction and increase proportionally with the flow rate (misni et al., 2005). These enhancements of interfacial tension were due to lessen time of surfactants at high flow rate region to interpenetrating (absorption) aqueous-oil interfacial (Garrett et al., 1972). Since the hydrophobic tail of DDM, SDS and Brij 35P surfactants is same it is evident that head group polarity (*HLB* value) is differ, it means based on this *HLB* surfactants possess same degree of affinity for oil phase, whilst differ in their affinity to aqueous phase. The result is that they differ in their *HLB* values, thereby stabilizing oil droplets in water at varying degree., and therewith in adsorption kinetics and rate of diffusion from the bulk solution to the liquid-liquid interface and as a general rule, surfactants with good oil solubility produce water-in-oil (w/o) emulsions while more water soluble surfactants produce oil-in-water (o/w) emulsions. Interestingly of this *HLB* values because is a good indicator of behavior of surfactants in water.

The fact that SDS is more polar DDM and Brij 35P, it is evident that performance at oil-in-water (o/w) interface is poor. The less polar the surfactant, the

least water soluble it is, thereby showing greater interfacial activities. Nevertheless, SDS when reacted with water produced a sodium salt which is an alkaline solution and spontaneously hydroxyl ions are released in the SDS adsorption process. (Chen, 1999). It seems that electrostatic repulsions still play an essential role for system stability. The data supported ligand exchange as a possible mechanism for SDS adsorption (Chibowski et al., 2007)..

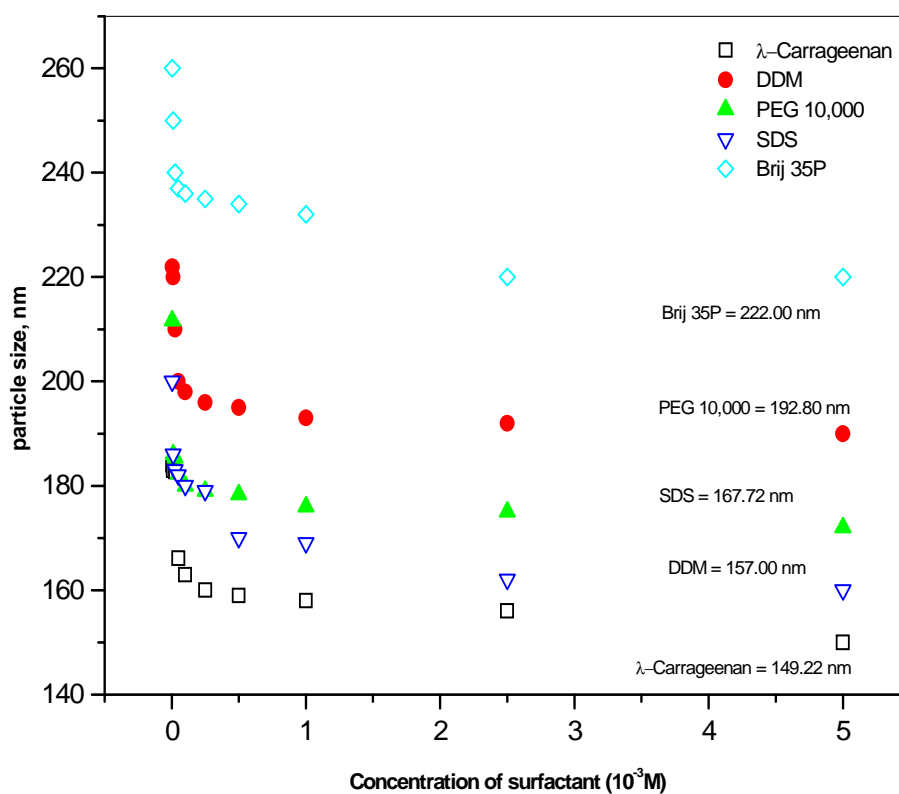
Meanwhile, PEG 10,000 and Brij 35P- are nonionic surfactants which are that no reaction with water to contribute charges unless form water (OH<sup>-</sup>) itself to give negative zeta potential values. The differences just the hydrocarbon tail and this hydrocarbon group is the hydrophobic part while they have the same chain of ethylene oxide groups which is the hydrophilic part of these surfactants and its obviously also play an essential role to zeta potential values because have an active free radical between oxygen atoms. This ethylene oxide chain is controlled by the relative amounts of reactants used and determines how hydrophilic the surfactant is and from this figure it clearly shown PEG 10,000 is higher stability than Brij 35P. This also probably happen due to the mechanical bridging by Brij 35P polymers is higher than PEG 10,000 and it can be an effective flocculating technique and large enough to adsorb to the surface of titana particles at the same time, binding them together in spite of the electrostatic forces that would normally make them repel each other

However, the changes in the mean size distribution as shown in **Figure 3.7**, caused by these dispersing agents are not easy to interpret in relation to the zeta potential changes. Despite the electrostatic repulsion, hydrophobic (dispersion) n-alkane chain-chain interactions have also to be considered, as well as steric stabilization. Obviously the zeta potential increases with higher concentration of dispersing agents. In practice, particles suspended in a liquid are never stationary. The particles are constantly moving due to Brownian motion. Brownian motion is the movement of particles due to the

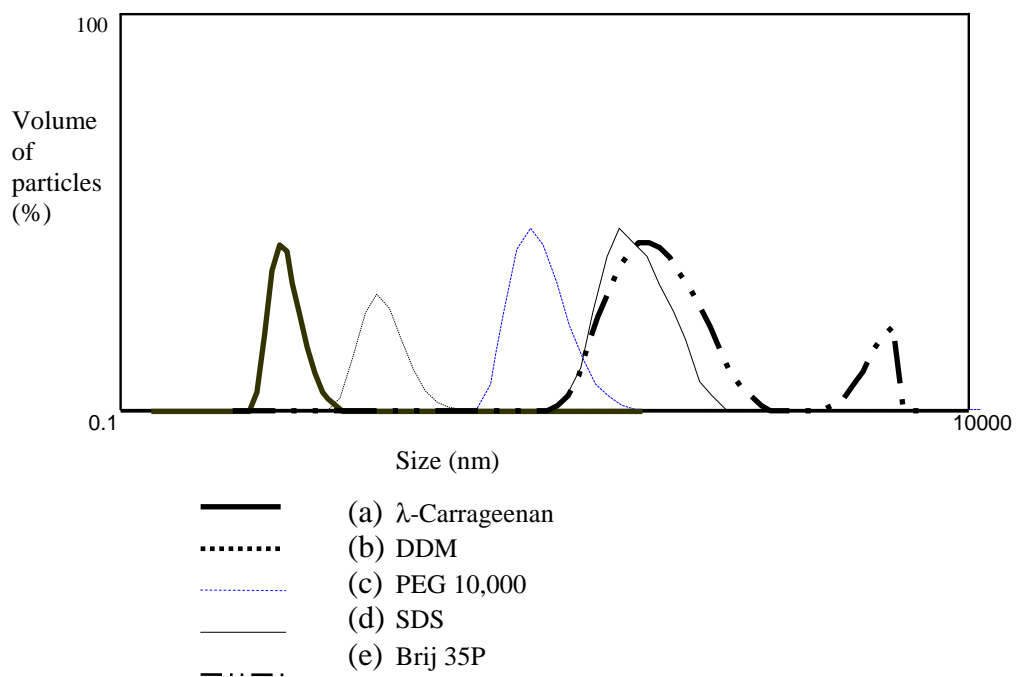
random collision with the molecules of the liquid that surrounds the particle. An important feature of Brownian motion for DLS is that small particles move quickly and large particles move more slowly. The relationship between the size of a particle and its speed due to Brownian motion is defined in the Stokes-Einstein equation. (Bohren et al., 1983)

By considering **Figure 3.8**, the degree of similarity between two signals over a period of time (correlation function) is shown for large and small particles. As can be seen, the rate of decay for the correlation function is related to particle size as the rate of decay is much faster for small particles than it is for large. If large particles are being measured, then, as they are moving slowly, the intensity of the speckle pattern will also fluctuate slowly as can be seen for Brij 35P and PEG 10,000 due to the evolution of a slow mode of long relaxation time and bimodal distribution.

What is interesting here is that, the appearance of a slow mode for PEG 10,000 and Brij 35P at 5.0 mM though small in amplitude, is an indication of uniaxial growth of the particle thereby approaching the semi-dilute regime. (Gunjan, 2006). The shift of the correlation function to larger times with different dispersing agents is an indication of the growth of the particles aggregation. Previous report, they have a lower percentage of settled volume due to particles with bigger size were not stabilized efficiently as opposed to particles of smaller size. And similarly if small particles are being measured then, as they are moving quickly, the intensity of the speckle pattern will also fluctuate quickly as can be seen for  $\lambda$ -Carrageenan, DDM and SDS. At  $\lambda$ -Carrageenan concentration the cumulants method gives a reasonably good fit to the data and a unimodal distribution of the relaxation times was observed.



**Figure 3.7:** Mean size profiles versus different concentration of dispersing agents stabilized  $TiO_2$  colloidal systems.



**Figure 3.8:** Volume of particles profiles versus different concentration of dispersing agents stabilized  $\text{TiO}_2$  colloidal systems.



### 3.2 RHEOLOGICAL PROPERTIES OF GLYCOLIPID BASED CREAMS FOR PHARMACEUTICAL AND COSMETIC APPLICATIONS

Sugar-based surfactants are gaining interest owing to their excellent surface-active property, non-toxic and biodegradable in nature (Misni, 2002) derived from renewable resources (Baker et al., 2000) and show good surface activity (Giffin, 1949). Another important advantage of sugar based emulsifiers is that they are much less sensitive to temperature variation than other nonionic emulsifiers (Stunbenrauch et al., 1996). These sugar-based surfactants are also soluble in both polar and non-polar solvents (Barnes, 2000). Due to these properties, sugar-based surfactants find increasing attention from cosmetic and pharmaceutical industries.

Considering their potential application this work explores the emulsifying behaviors of  $\lambda$ -Carrageenan, Dodecyl- $\beta$ -D-Maltoside (DDM), polyethylene glycol 10,000 (PEG 10,000), Sodium Dodecyl Sulphate (SDS) and polyethylene glycol dodecyl ether (usually referred to as Brij 35P) with the addition of UV- protect and moisturizing active ingredient that stabilized oil in water (o/w) emulsion using rheological properties.

There are two rheological properties of particular importance to emulsion that are their gel and flow properties. Their flow profiles are often intermediate between solid-like and liquid-like prototype fluids. A liquid-like behavior in a steady shear flow is characterized by the absence of shear thinning property at low shear rate domain. In this case the shear viscosity ( $\eta$ ) is independent of shear rate ( $\dot{\gamma}$ ). This means that the stress increases linearly with  $\dot{\gamma}$ .

On the other hand, while solid-like complex fluid is identified by  $\dot{\gamma}$  independent  $\sigma$  responses, thermodynamically stable emulsions in steady shear regime show non-Newtonian shear thinning behavior, where the shear viscosity ( $\eta$ ) in  $\eta(\dot{\gamma})$  profiles decays exponentially as a function of shear rate ( $\dot{\gamma}$ ) as  $\eta \propto \dot{\gamma}^{-n}$ , where the Power law index ( $n$ ) is used for the estimation of the degree of shear thinning (Larson, 1999). The lower the value of  $n$  the higher the degree of shear thinning and vice versa, whereas the higher the degree of shear thinning the better stabilized are the emulsions.

Materials showing shear thinning property always show resistance to flow. Flow can only be induced to these materials with the application of a certain minimum external stress ( $\sigma$ ) referred to as yield stress ( $\sigma_y$ ). The higher the  $\sigma_y$  the better stabilized are the emulsions, and the better they are structured materially (Barry, 1974).

On the other hand, in an oscillatory shear regime, where the dynamic moduli are plotted against oscillatory frequency ( $\omega$ ), the domination of loss modulus ( $G''$ ) response over storage modulus ( $G'$ ) response at a high  $\omega$  domain indicates greater degree of emulsion stability with longer storage life, whereas domination of  $G'$  response over  $G''$  response ( $G' > G''$ ) at a low frequency domains indicates that emulsion are easily spread when applied to human skin (Blazer et al., 1995).

In addition, in a prototype Maxwell model representation of  $\omega$  dependence of dynamic moduli, a liquid-like emulsion is characterized by  $G'$  response which is much lower than the  $G''$  response, and that it scales with  $\omega$  as  $G' \propto \omega^2$ , while the  $G''$  is a linear function of  $\omega$ , as  $G'' \propto \omega$ . Frequency dependence of dynamic moduli usually obeys these laws at low frequency domain and the  $\omega$  domain associated with it is called the terminal region (Bower et al., 1999). On the other hand, solid-like emulsion is

characterized by  $G'$  response, which is much higher than  $G''$  response,  $G' \gg G''$ , and that  $G'$  is nearly independent of  $\omega$ .

Similarly, emulsion showing semi-circled shaped Cole-Cole plot in combination with small phase angle ( $\delta$ ) over a wide range of  $\omega$  indicates that the samples under investigation are viscoelastic in nature. The consequence is that their flow behavior can be characterized by Maxwell model type fluid flow behavior (Barnes, 1994). The  $\delta$  which is the ratio of loss and storage modulus  $\tan^{-1} \left[ \frac{G''}{G'} \right]$  ranges from  $0^\circ$  for ideal elastic solid to  $90^\circ$  for ideal viscous liquid over a wide range of  $\omega$ . Higher value of  $\delta$  indicates that the emulsions are more liquid-like in nature, whereas lower values of  $\delta$  indicates that emulsions are more solid-like in nature.

This work also reports structure and viscoelastic property of dispersing agents stabilized o/w emulsions, whose dispersed phase contains molecular aggregates of surfactant in addition to emulsified droplets in it.

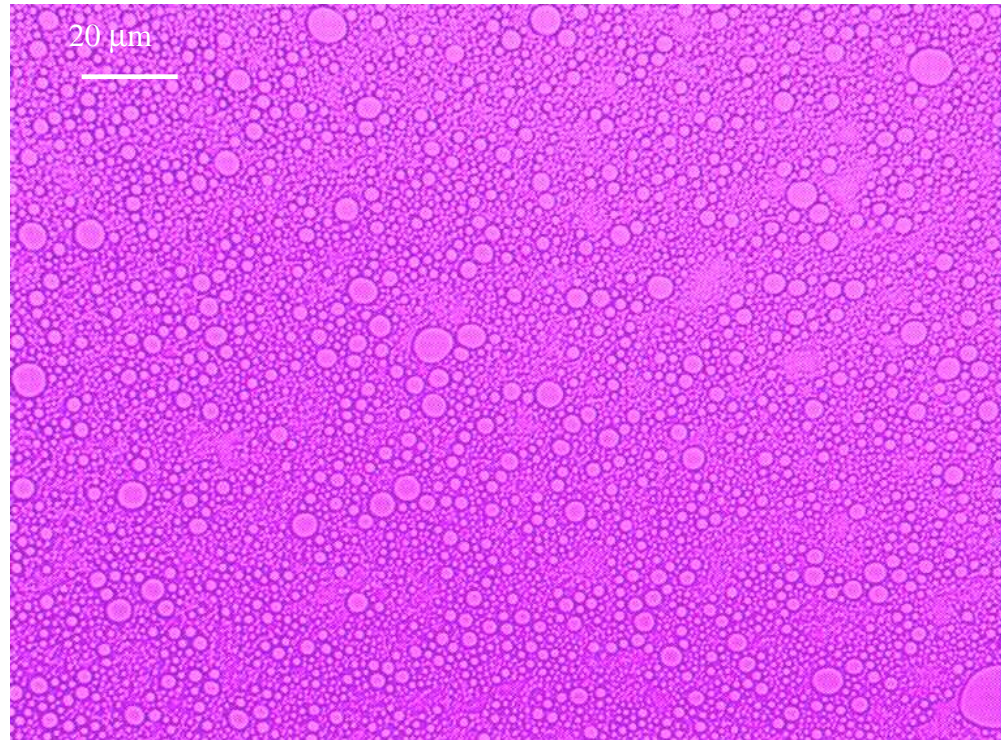
### 3.2.1 Morphological Studies

The rheological properties of emulsion used in pharmaceutical and cosmetics industries can be directly related to emulsion stability and product quality. The emulsion stability and product quality largely depend on the property of dispersed phase, namely droplet sizes. Phase separation frequently occurs from inter-droplet interaction, due to coalescence, deformation and followed by rupture of droplets (Isrealachvili, 1976). These may happen any time from the emulsion formulation to storage. Microscopy helps us to observe and evaluate emulsion structure.



**Figure 3.9:** Light micrograph image of  $\lambda$ -Carrageenan based cream at 25°C



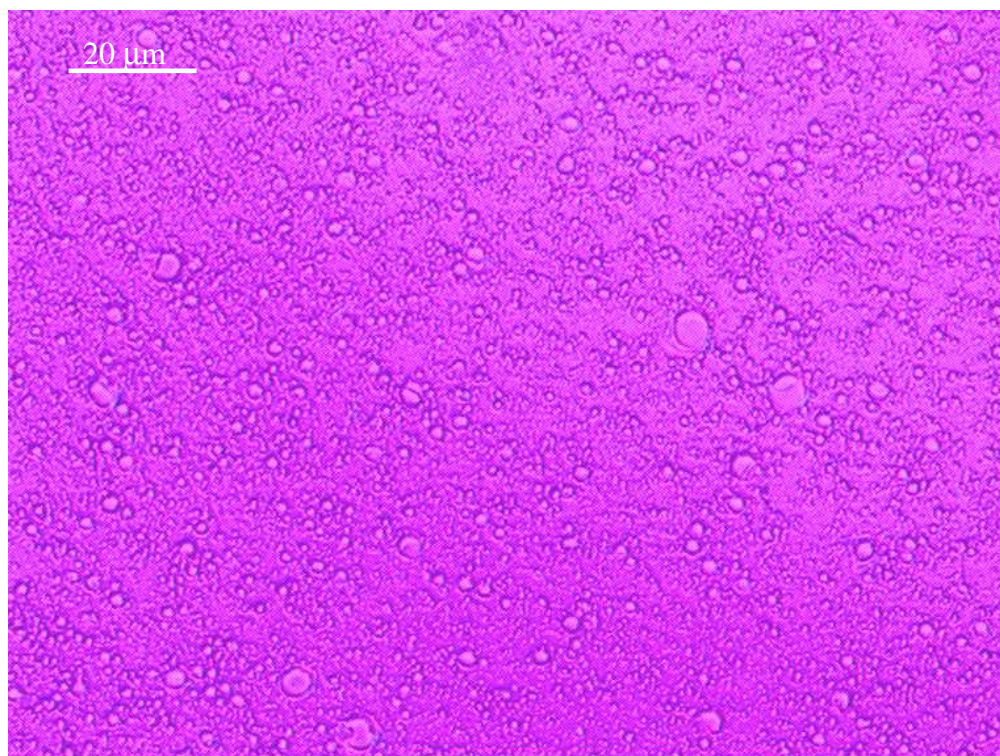


**Figure 3.10:** Light micrograph image of DDM based cream at 25°C.



**Figure 3.11:** Light micrograph image of SDS based cream at 25°C.





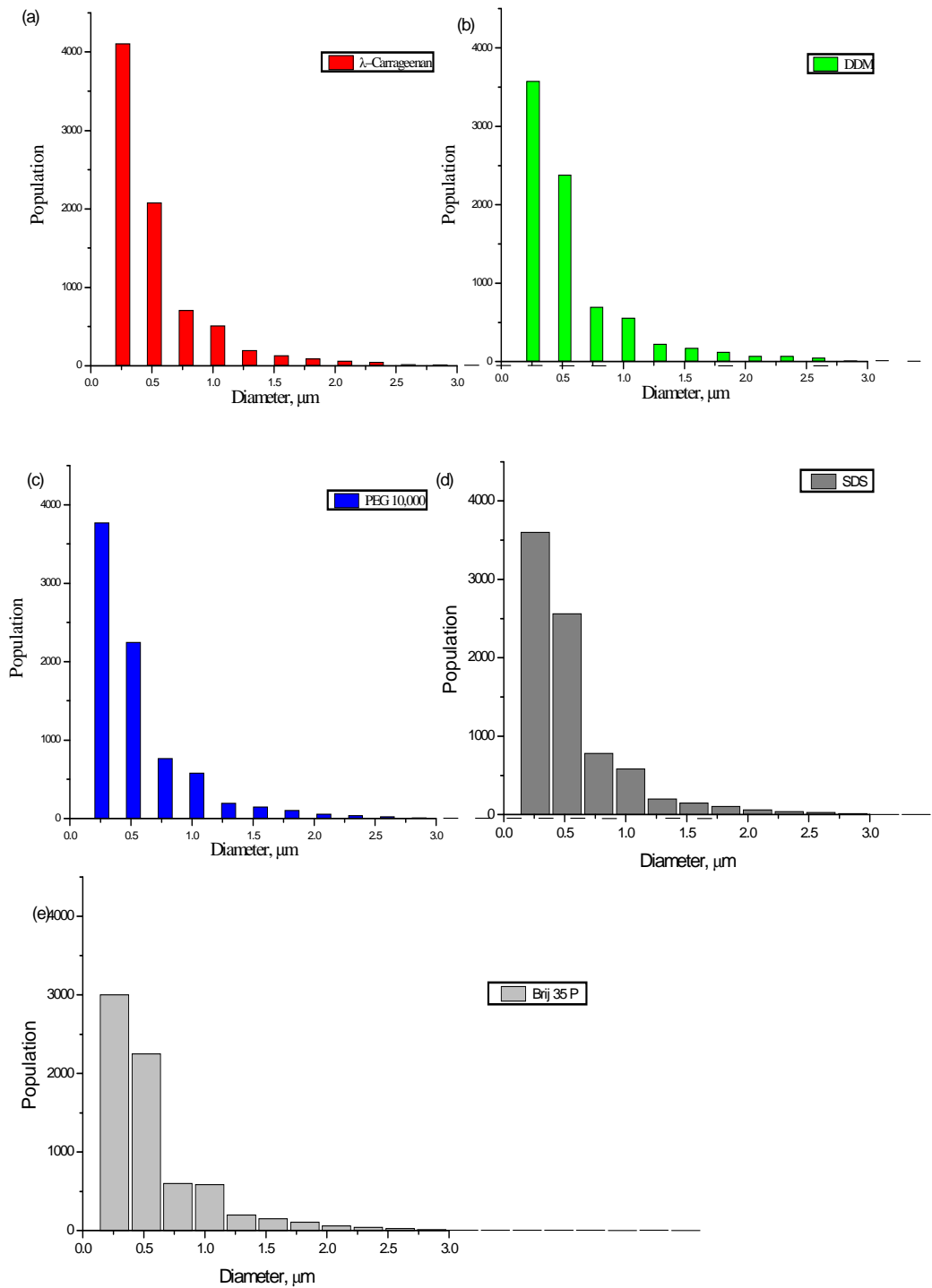
**Figure 3.12:** Light micrograph image of PEG 10,000 based cream at 25°C.



**Figure 3.13:** Light micrograph image of Brij 35P based cream at 25°C.

**Figure 3.9-3.13** showed typical micrograms of  $\lambda$ -Carrageenan, DDM, PEG 10,000, SDS and Brij 35P stabilized emulsions. These micrograph images were scanned after one-day preparation of the emulsion and stored at 45.0 °C in an oven. These microscopic images suggest that emulsified droplets were poly-dispersed. The emulsion droplets are relatively small with mean sizes for  $\lambda$ -Carrageenan, DDM, PEG 10,000, SDS and Brij 35P emulsion droplets as 0.60  $\mu\text{m}$ , 0.67  $\mu\text{m}$ , 0.70  $\mu\text{m}$ , 0.80  $\mu\text{m}$  and 0.97  $\mu\text{m}$  respectively. Creams with smaller droplets, behaved more viscoelastic than creams with larger droplets. Viscoelasticity increased with decrease in droplets sizes.

It is known that the dispersed phase of surfactant stabilized emulsion plays a vital role in both the emulsion stability and its rheological properties. In particular, density of dispersed phase and its droplet sizes plays an important role in emulsion stability. As evident from **Figure 3.8** and **Figure 3.14**, droplet sizes highly depended on surfactant concentration respectively with or without o/w emulsion. It means that surfactant itself clearly plays an essential part that influences each property even with or without o/w emulsion. These typical micrograms suggested that the emulsions prepared in the presence of higher surfactant concentration were better stabilized as the smaller droplets tend to be more rigid with better rheology properties as evident from both the rheology and microscopy results.

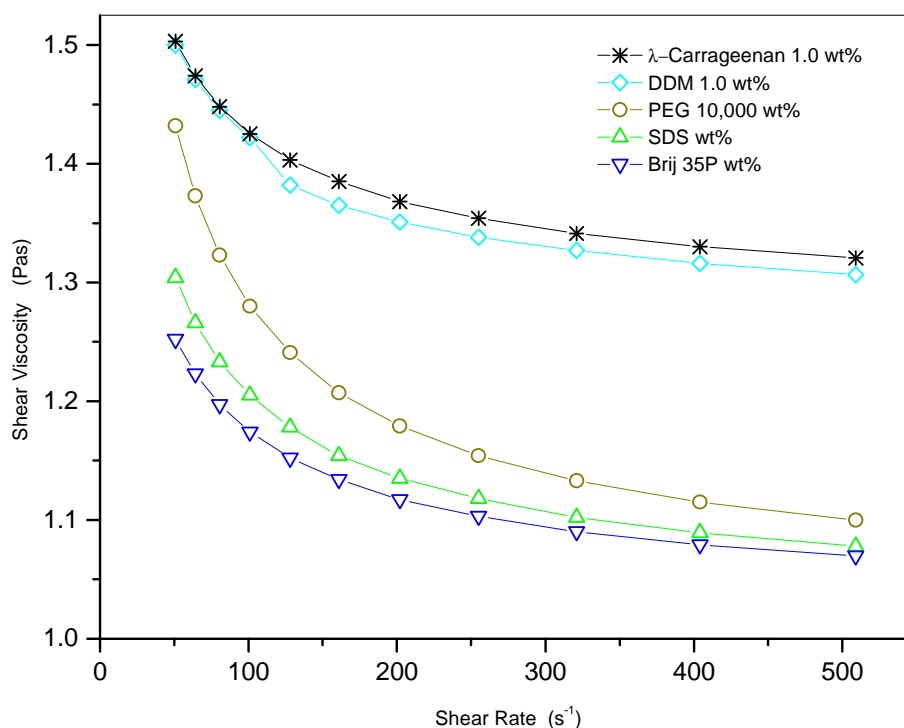


**Figure 3.14:** Droplets size distribution of different surfactant to formulate based creams. (Total 8000 droplets).(a)  $\lambda$ -Carrageenan, (b) DDM, (c) PEG 10,000, (d) SDS and (e) Brij 35P



### 3.2.2 Steady Shear Sweep Rheometry

**Figure 3.15** showed  $\eta(\dot{\gamma})$ -  $\dot{\gamma}$  profiles of different types of 1.0 wt% surfactant stabilized creams and titania concentration as a function of shear rate. . As depicted in this figure, depending upon the rate of decay of the shear viscosity, these flow profiles can be divided into two regions. Low shear rate region and high shear rate region. In the low shear rate region, all samples examined here showed a steep decay in the shear-viscosity as a function of shear rate (with a steep slope of line), suggesting a shear thinning behavior. It means that the viscosity in low shear rate region is shear rate dependent, and can be characterized as non Newtonian flow behavior. As depicted the viscosity decay follow a typical power law dependency on shear rates with an exponent. In contrast, at high shear rates, the viscosity is only slightly dependent on shear rates, suggesting a close to the Newtonian flow behavior. This is turn suggested that the creams under investigation undergo structural changes with applied shear or deformation.



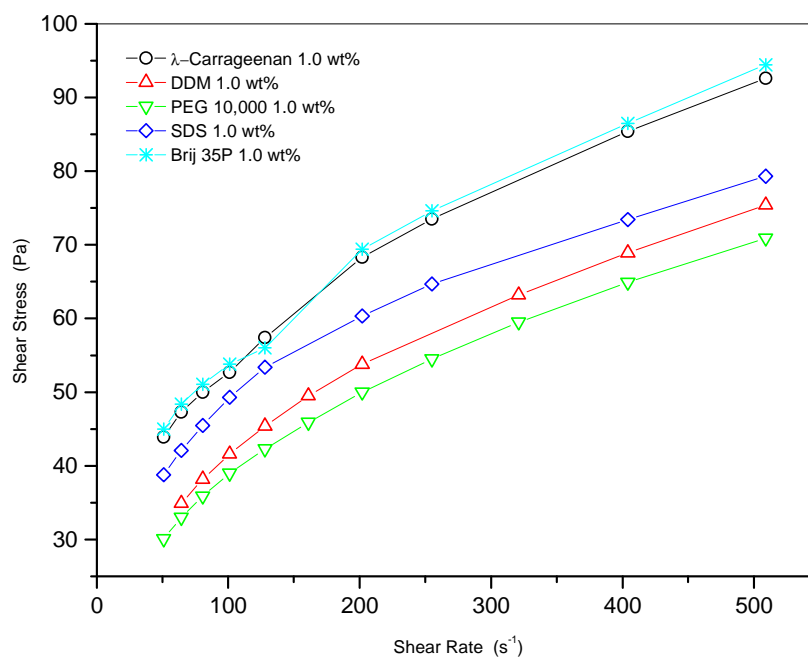
**Figure 3.15:** Shear viscosity profile of different type of based creams.

In addition to degrees of shear thinning, **figure 3.15** also suggests that,  $\lambda$ -Carrageenan and DDM showed greater degree of shear viscosity at all shear rate compared to cream stabilized lower emulsifying agents such as PEG 10,000, SDS and Brij 35P. Which is evident from a slightly higher slope of the line exhibited by  $\lambda$ -Carrageenan and DDM stabilized emulsion at all shear rate domains but slightly change between them it is obvious that  $\lambda$ -Carrageenan stabilized emulsions underwent higher degree of deformation compared to dispersing agents stabilized emulsions respectively. According to Nakarapanich, this in turn suggests that  $\lambda$ -Carrageenan is a more effective emulsifying agent than the others dispersing agents (Nakarapanich et al., 2001). This means degree of shear thinning is an indirect measure of emulsion stability, which is closely related to electrostatic repulsion, degree of dispersion and emulsifying property of surfactant.

It is evident that better structured and more stable creams are produced based on the presence of type of emulsifying agents. This can be probably be ascribed to the fact that, emulsifying property of a homologue series of emulsion with same alkyl tail (DDM, SDS and Brij 35P) and irrespectively for  $\lambda$ -Carrageenan and PEG 10,000 whereas they have differing head group structure or polarity varies strongly with HLB values that influence a good stabilizer. As previous discussed worth note that the lower water solubility of the surfactant the lower its HLB, and the better it acts as an emulsifying agent for an oil-water system (Misni, 2004). Nevertheless, this figure clearly suggests that droplet size distribution plays a strong influence on  $\eta$  of these emulsions and their behavior is in good agreement with that reported previously. The shear viscosity is inversely related to droplet size, and that it increased with decreasing droplet size.

### 3.2.3 Shear stress versus shear rate profiles

**Figure 3.14** exhibits effects of droplet size distribution on  $\sigma-\dot{\gamma}$  profiles of different based creams are shown in **Figure 3.16**. These profiles suggested that shear stress responses are not proportional to shear rate at all shear rate domain. The rate of change of shear stress depends largely on the rate of change of shear rate. From  $\sigma-\dot{\gamma}$  profile, while the  $\sigma$  response does not change linearly with  $\dot{\gamma}$  at low  $\dot{\gamma}$  domain but it changes linearly at high  $\dot{\gamma}$  domain. This means these emulsions showed solid-like viscoelastic property at low  $\dot{\gamma}$  domain and show liquid-like flow behavior at high  $\dot{\gamma}$  domain. This in turn suggests that the emulsions under investigation underwent structural changes past a certain shear rate, called critical shear rate (Almero et al., 2008). This critical shear rate corresponds to the critical shear stress referred to as yield stress. . It means that these emulsions do not flow under the influence of gravity below the critical stress, whereas they deform and flow past that critical yield stress (Bais et al., 2005).



**Figure 3.16:** Shear stress versus shear rate profiles of different type of based creams.

Dispersing Agents	$\lambda$ -Carrageenan	DDM	PEG 10,000	SDS	Brij 35P
Yield Stress (Pa)	>68	65	55	50	45

**Table 3.3:** Values of Yield Stress of different type of based creams.

These flow curves also suggest that  $\lambda$ -Carrageenan showed higher yield stress and stabilized emulsions compared to other dispersing agents respectively (**Table 3.3**), indicating that yield stress largely depends on surfactant type, and in particular, probably on the HLB values of surfactant (Weiss et al., 1997). Also, as shown in this **Figure 3.16**, at zero shear rates, the  $\sigma$  responses are not zero. This means that these emulsions show shear thinning behaviors. In other words, they behave like pseudoplastic material, which

implies that flow can only be induced on these emulsions with the application of a certain minimum amount of stress.

Fitting of these steady shears rheology data into model flow equations proved that these flow profiles data can be best described by Herschel-Bulkley model flow equation. The Herschel-Bulkley is defined;

$$\sigma = \sigma_y + \eta\dot{\gamma} \quad (3.1)$$

where  $\sigma_y$  is yield stress, above the  $\sigma_y$  these samples assume a linear shear stress-shear rate relationship, suggesting the validity of this equation. This suggested that these emulsions do not follow ideal Newtonian flow behavior even at high shear rate domain. By contrast, the shear stress-shear rate relationship increase exponentially at low shear rate domain, suggesting that the flow behaviors of these emulsions switch to pseudoplastic like material at these low shear rate domain.

### 3.2.4 Oscillatory shear rheometry.

Emulsion showing high value of yield stress and high shear viscosity at low shear domain usually show viscoelastic properties. The viscoelastic property of a material is usually accessed with the help of frequency dependence of dynamic moduli, which in turn can be used to describe property of emulsions such as storage stability and ease of spreading (Yasuski et al., 2008). Despite of that, the strain amplitude sweep test, which was performed at a fixed oscillatory shear of 10.0 Hz, suggested that the storage moduli of based creams are independent of applied strain at a wide range of strain amplitude (**Figure 3.17**). The based creams exhibited wide Linear Viscoelastic Region (LVR) showing the ability of emulsion droplets resistance towards external stresses. Deviation from LVR gives a critical strain value which a minimum energy is required to disrupt the structure as well as an indication of dispersion quality (Misni et al., 2004). The greater the critical strain, the more viscoelastic the cream will exhibit.

Although they have the same concentration at 1% wt,  $\lambda$ -Carrageenan has lower critical strain and less viscous (**Table 3.4**), therefore it has better leathering ability. The  $\lambda$ -Carrageenan based creams also exhibits a good viscoelasticity property indicating that the droplets are more stable and resist deformation or rupture as shown by its higher storage and loss moduli.

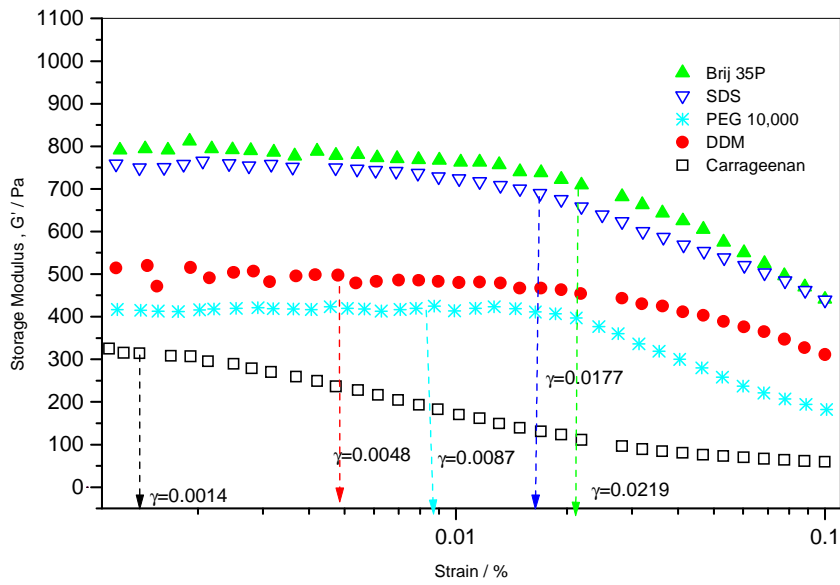
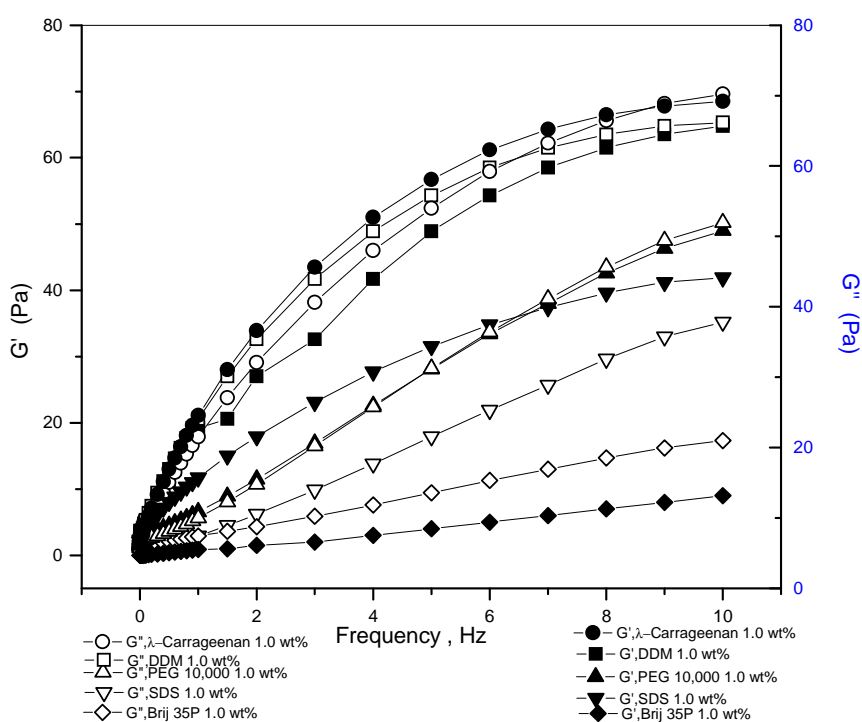


Figure 3.17: Shear rate sweep of different types of based creams.

<b>Dispersing Agents</b>	$\lambda$ -Carrageenan	DDM	PEG 10,000	SDS	Brij 35P
<b>Critical Strain / %</b>	0.0014	0.0048	0.0087	0.0177	0.0219

Table 3.2: Values of Critical Strain of different types of based creams.





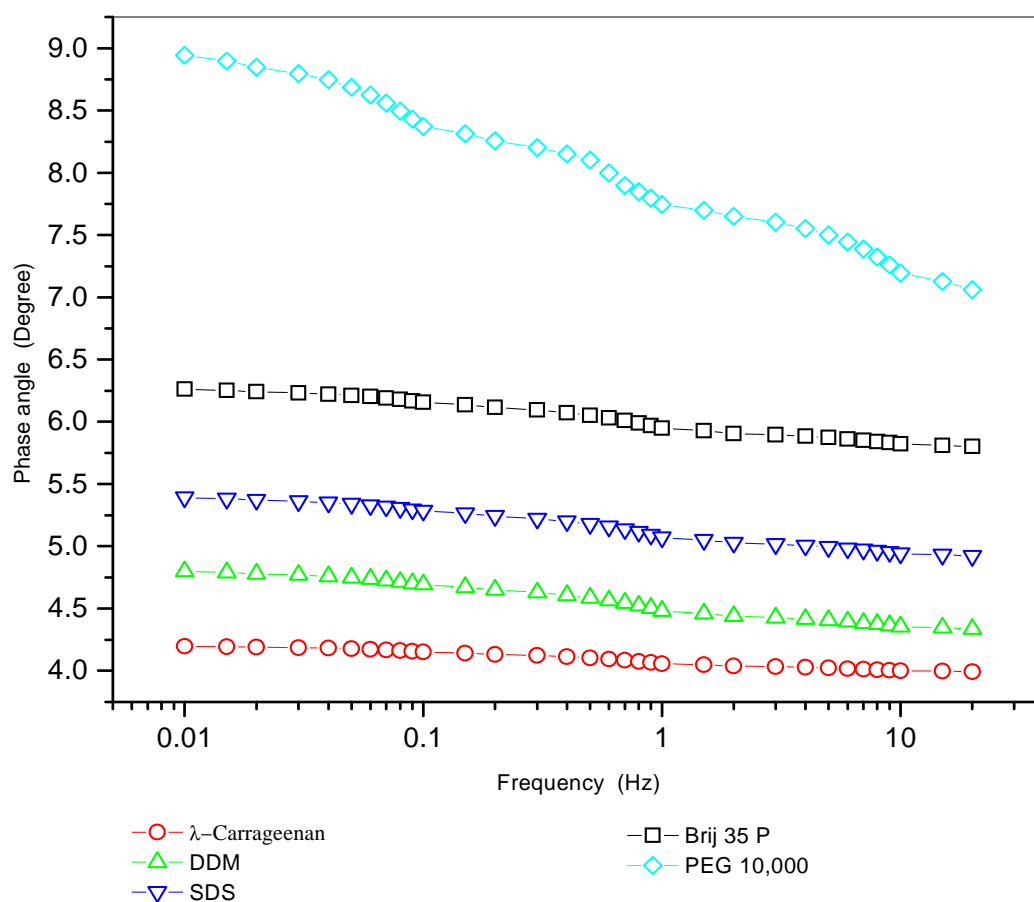
**Figure 3.18:** Dynamic moduli of different type of based creams.

$G'$  and  $G''$  (frequency) profile - For the examination of the viscoelasticity, storage stability and ease of spread dynamic spectra of dispersing agents for stabilized emulsions were scanned in the frequency range 0.1-10 Hz. These profiles, suggest that the emulsion samples under investigation displayed very low visco-elastic moduli, with a noticeable shoulder at low frequencies. According to Capron the appearance of shoulders at low frequencies is related to the relaxation of the droplet shapes, as changes in droplet sizes induce a shift in the characteristic frequencies or relaxation times (Capron et al., 2001; Bousmina, 1999).

As depicted from **Figure 3.18**, the dynamic moduli ( $G'$  and  $G''$ ) are frequency dependent. Both moduli increase exponentially as a function of frequency, exhibiting a typical power-law dependence on frequency, with a comparable exponent. Both moduli increases with frequency, but the slope of the line and trend varied slightly with

surfactant type. As can be seen, within the examined frequency domain,  $G''$  is always greater than  $G'$ , implying that these emulsions are more viscous than elastic at low frequency domain. And what more, irrespective of surfactant type, all emulsions examined here showed higher values of  $G''$  over  $G'$ , suggesting that these emulsions spread easily. As expected,  $\lambda$ -Carrageenan and DDM stabilized emulsions exhibited higher values of both the loss and storage modulus compared to PEG 10,000, Brij 35P and SDS stabilized emulsions, suggesting that it performs better as an emulsifying agent and it is evident that  $\lambda$ -Carrageenan stabilized emulsion is more elastic in nature compared to others which has a good agreement with previous report

These results probably advise much like  $\lambda$ -Carrageenan stabilized emulsions showed Maxwell fluid behavior, which means can be described by simplest mechanical model consisting of a dashpot and spring connected in series of dashpot represents loss/dissipation of energy equivalent to viscosity and spring represents storage energy equivalent to the elasticity (Misni et al., 2000).



**Figure 3.19:** Plot of  $\delta$  against  $\omega$  as a function of different type of surfactant

*$\delta$  dependent  $\omega$  profile* – Frequency dependence of dynamic moduli is not enough to judge whether or not the solid like elastic behavior dominate over liquid like viscous behavior in any emulsion samples. A better picture can be obtained by examining  $\omega$  dependence of phase angle profile. Plot of  $\delta(\omega)$  is given in **Figure 3.19**, which suggests that, while  $\delta$  of these emulsion is independent of  $\omega$ , it depends both on surfactants concentration and alkyl chain length (Moates et al., 2001).. Based on this factors, clearly irrespective with DDM, Brij 35P and SDS because that have same number of carbon in the hydrophobic tail whereas for  $\lambda$ -Carrageenan and PEG 10,000 that totally influenced by alkyl chain length because they have difference number of

carbon. This implies solid like elastic property become enhanced and dominant with increase in concentration of dispersing agents and alkyl chain length mainly because that obviously shows in this profile between  $\lambda$ -Carrageenan and PEG 10,000. Irrespective of concentration of surfactants and alkyl chain length, the value of  $\delta$  of these emulsions was lower than  $45^\circ$ ; it is evident solid like elastic property dominates over liquid like viscous property. These probably explain why  $\sigma_y$  and  $\eta_{low}$  of these samples were high at all dispersing agents' concentration and from this profile alkyl chain length domain.