CHAPTER TWO:

EXPERIMENTAL AND INSTRUMENTATION TECHNIQUES

2.1　INSTRUMENTATION

The prepared samples were characterized using various techniques. Among which are Dynamic Light Scattering, Zeta Potential Measurements, Kruss Tensiometer K122, Bohlin VOR rheometer and light microscope.

2.1.1　Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were performed using a Malvern 4800 Autosizer employing 7132 digital correlator. The light source was Ar-ion laser operated at 514.5 nm with maximum power output of 2W. Measurements were made at five different angles ranging from 50 to130°. All the measurements were taken at 25 °C.

2.1.2　Zeta potential measurements

The zeta potential was calculated by measuring the electrophoretic mobility, using the Smoluchowsky approximation:

$$u = \frac{\varepsilon \zeta}{\eta} \qquad\qquad (2.1)$$

Where ζ = zeta potential, ε = dielectric constant, η = viscosity and μ = electrophoretic mobility.

The zeta potentials were determined without dilution by a Zetasizer 3000 (Malvern instruments; internal He-Ne laser) and taken as a mean value from 6-7 measurements.

2.1.3   Kruss Tensiometer K122

The surface tension of surfactant solutions is carried out using a KRÜSS tensiometer with a K122 program software. It interfaces with a computer with K122 software installed to control both test routines and data evaluation. This tensiometer has two measuring methods, i.e., Du Nouy ring method and plate method.

The ring method is known since 19th century. The description of a ring tensiometer by Lecomte Du Nouy in 1919 makes the method well-known all over the world. The measurements are done with a horizontal hanging platinum ring of exactly known geometry. The ring geometry is determined by its mean radius R and the radius of the wire cross-section r. It determines the wetted length l_w. The platinum ring is dipped into liquid (to be measured) and pulled out again afterward.

The maximum force needed to pull the ring through the interface is measured. The force σ_s is:

$$\sigma_s = \sigma^* \, F = \frac{P}{2\pi(R_i + R_0)} F \qquad\qquad (2.2)$$

whereas σ_s is real surface tension value, σ^* is measured surface tension value, F is correction factor, P is maximum force at the ring, R_i is radius at inner side of the ring and R_0 is radius at outer side of the ring. The correction factor F includes the weight of liquid that is lifted by the ring.

The observed values obtained with the Du Nouy ring method are always too high. When the ring is pulled above the level of the liquid surface, the measured force of the surface tension includes the forces, created by the weight of the lifted liquid lamella. The correction factor F was determined experimentally by Harkins and Jordon in 1930 and is available in extensive tables. The correction factor is a non-linear function which depends on the density difference (D-d) of the involved phases, the proportions $\dfrac{R}{r}$ and $\dfrac{R^3}{V}$ and form the value of surface tension, where R is the mean radius of the ring and V is the lifted liquid volume.

2.1.4   Rheometer

A Bohlin C-VOR strain and stress controlled Rheometer with a cone plate measuring geometry CP4 / 40 was used in this work. This geometry with a cone of 40 mm diameter, cone angle 4.0°, and with a measurement gap of 150 μm. The temperature control unit help run rheology experiments at any given temperature with an accuracy of 0.1 °C. In this work, all rheological measurements were carried out at 25.0 °C.

The advantage of using this instrument is that it can be configured to measure a variety of rheology characteristics within a wide range of shear rate and oscillation frequencies. It covers 5 orders of magnitude in shear rate from 10^{-3} to 1.5×10^3, which allows measuring a wide range of shear stress ranging from 10 to 10^4 Pa. The accessible range of viscosities is being 10^{-2} to 10^4 Pas. Oscillation experiments can be run from 10^{-3} to 20 Hz, covering shear strain rate values from 0.01 to 20 s^{-1}.

While the steady state shear sweep experiments were run to monitor $\eta(\dot{\gamma})$ and $\sigma(\dot{\gamma})$ profiles, the oscillatory shear sweep experiments were run to monitor ω dependence of dynamic moduli profiles. As the $\eta(\dot{\gamma})$ profile did not show an apparent Newtonian plateau at low $\dot{\gamma}$ domain, the estimation of zero shear viscosity (η_0) was not possible. For this same reason, instead of η_0, $\eta(\dot{\gamma})$ was monitored at a $\dot{\gamma}$ of 0.01 s^{-1} and it is referred to as low shear viscosity (η_{low}). While the σ_Y was obtained from $\sigma(\dot{\gamma})$ profiles through the extrapolation of the stress towards zero-shear rate.

It should be noted that, before running any oscillatory shear tests, a strain sweep test was carried out for the estimation of optimum strain amplitude so that each sample is examined below its linear viscoelastic region. In these cases, the lower limit is usually automatically set by built-in transducer, whilst the upper limit was set within the limit of the linear viscoelastic regime of samples under investigation. Because these emulsions did not show an apparent plateau modulus within the measured frequency range, the liquid-like entanglement storage modulus (G_N^o), could not be estimated. In such situations G_N^o is usually estimated from the on-set of plateau region at high frequency $G^{'}$ ($\omega = 100\ Hz$).

It is also worth noting here that all results shown in this work are within the sensitivity range of the Rheometer, whereas data collected below Rheometer sensitivity of 20 mPa were discarded.

2.1.4   Polarizing Microscope

The optical microscopy consists of a high voltage beam source, a polarizing unit and a detector unit. Images were focused between cross polarizers both at the dark field and bright field modes. Objectives with long working distance and magnifications of 20×, 50× (oil immersion) and 100× were used for these purposes. The detector unit was interfaced with a personal computer equipped with image analysis Leica QWin Standard version 2.6 software. This software is designed to help capture and import optical images of the samples from the microscope detector filed into the personal computer, whereby they can be processed further electronically.

2. 2   EXPERIMENTAL AND CHEMICALS

2. 2.1   Materials

All emulsions and surfactant solutions used in this work were prepared in deionized water with an ionic conductivity of 2.8 µS/cm. All chemicals, including oil and surfactants used in this work were of at least TLC grade with a purity of 98%, at least. Parafin oil used in this work was of 0.84-0.86 mg/ml density , Sodium Dodecyl Sulfate (SDS), Polyethylene Glycol (PEG), n-Dodecyl β-D-Maltoside (DDM), λ-Carragenan and Brij 35P was purchased from Fluka. These were used as they were received, without any purification similar with paraffin oil. The titania powder used was of cosmetic grade with a purity of ≥98%. It was purchased from Erocham. To make it moisture free, before its use titania was placed in vacuum oven at an ambient temperature of 25 °C and for a period of 24 hours. A 15 mmHg vacuum was employed for this purpose

2.2.2   Sample Preparation

All chemicals were used with different preparations to examine stability of dispersing agents which is to enhance stability of emulsion when blended with various dispersing agents.

Concentration $\times$ (10^{-3} M)	Dispersing Agents				
5	λ-Carrageenan	DDM	SDS	PEG 10,000	Brij 35P
2.5					
1					
0.5					
0.25					
0.10					
0.05					
0.025					
0.01					
0.005					

Table 2.1: Several of concentration dispersing agents to examine stability of solution

2.2.3 Examination of settle volume

A series of titanium oxide solutions of 0.04 g titanium was prepared by dispersing it in a surfactant solution of varying concentration (**Table 2.1**). These solutions were transferred to culture tubes and sonicated to give homogeneous dispersions. Size of the particles in these dispersions was determined by Submicron Particle Size Analyzer. Stability was measured as the ratio of settled particle volume to total suspension volume over a period of time. Beside gravity settling sizes of the particles were measured over time in order to monitor whether or not they underwent changes

$$Settle\ Volume\ \%\ Height = Height\ 2\ (mm)/Height\ 1\ (mm) \dots\dots\dots\dots\dots\dots\dots..(2.1)$$
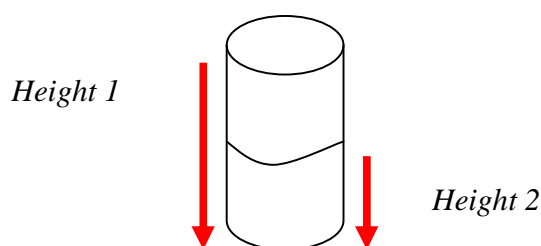

Figure 2.1: Diagram culture tubes to determine settle volume % height

2.2.4   Examination of size distribution by volume and zeta potential

Both the zeta potential and the particle size of the titanium dioxide were determined with the help of a Zetasizer 3000 (Malvern instruments; internal He-Ne laser) in which the dynamic light scattering technique was applied for determination of these quantities. For each suspension sample, 7 measuring runs with 4 cycles in each run were taken. All these experiments were carried out at $20 \pm 0.1 \,^{\circ}\text{C}$ and repeated two or three times. The zeta potentials of TiO_2 particles were calculated from the electrophoretic mobility using the Smoluchowski equation, which was appropriate for most of the systems studied. This is because the ionic strength of the solution was 10^{-3} mol dm^{-3} and the particle size of TiO_2 ranged from 0.2 to 21 µm (aggregated), as determined by dynamic light scattering

2.2.5   Preparation of emulsion

Various ratio of emulsions in 1.0 wt% concentration of dispersing agent and 0.01% of titanium oxide were prepared according to the aqueous and oil phases proportion, such as 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9 (aqueous phase : oil phase).Behaviors of emulsions stabilized with ionic surfactant, non-ionic surfactant and Glycolipids are shown in **Figure 2.2**, **Figure 2.3** and **Figure 2.4** respectively. These behaviors are the results of varying the aqueous to oil ratio and the effect of surfactants on one another.
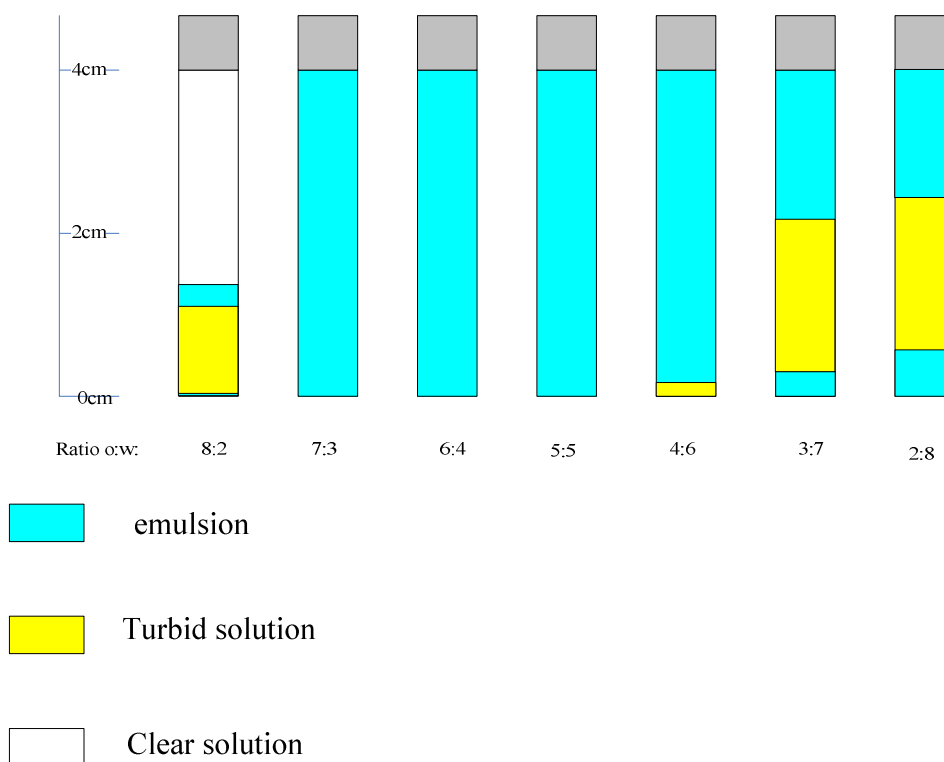
Figure 2.2:   Behaviors of λ-Carrageenan stabilized emulsion blended with titania for 8 months preparation.
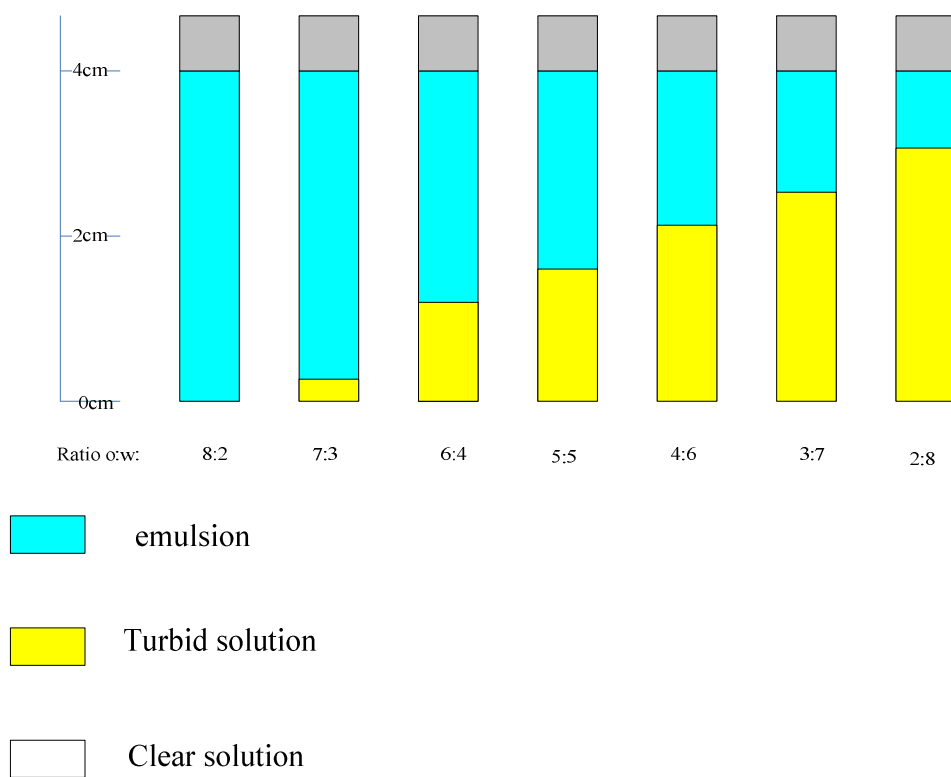
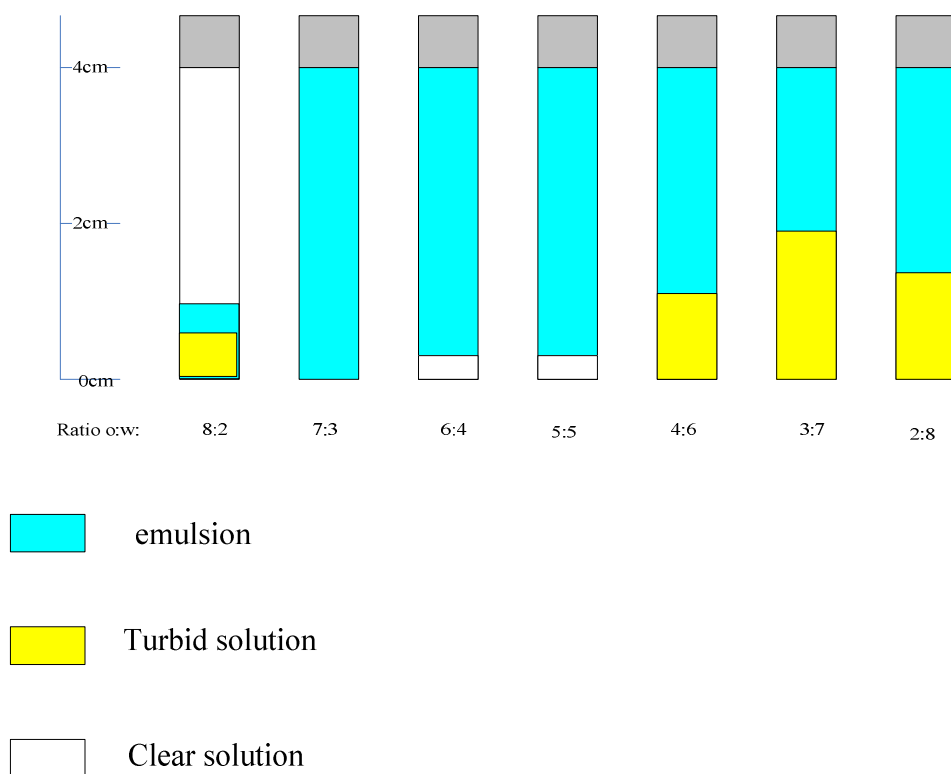**Figure 2.3:**   Behaviors of DDM stabilized emulsion blended with titania for 8 months preparation.

Figure 2.4:   Behaviors of PEG 10,000 stabilized emulsion blended with titania for 8 months preparation.
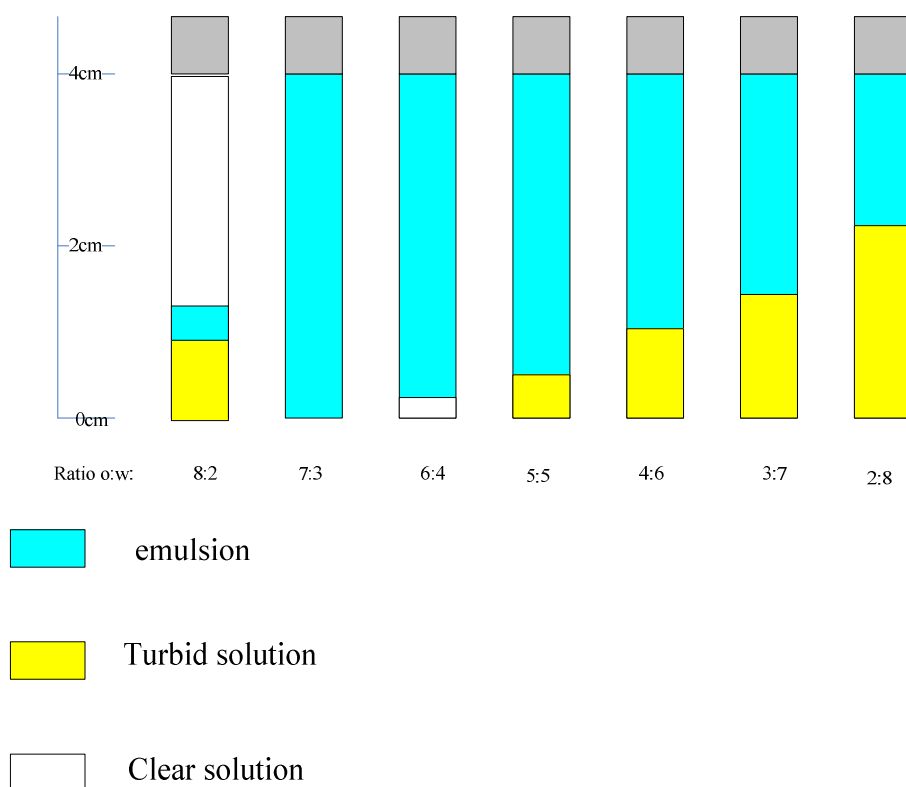
Figure 2.5:   Behaviors of SDS stabilized emulsion blended with titania for 8 months preparation.
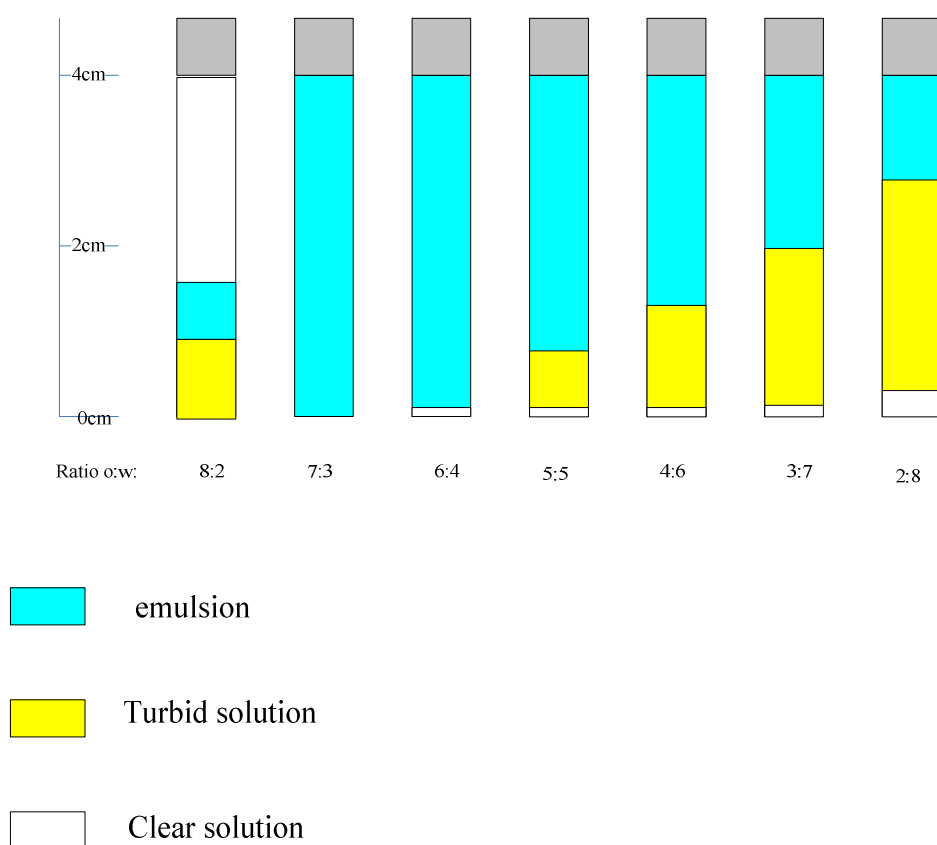
Figure 2.6: Behaviors of Brij 35P stabilized emulsion blended with titania for 8 months preparation.