CHAPTER III
EXPERIMENTAL

3.1 Material

    3.1.1 The main surfactant used is Sodium lauryl ether sulfate (SLES.1EO) provided by Unilever as a 28%w/w aqueous solution and was used as received without further purification.

$$CH_3 (CH_2)_{10}CH_2 (OCH_2CH_2)_n OSO_3 Na$$

Figure 3.1 Chemical structure of sodium lauryl ether sulfate consist of C12 chain length with average one ethoxylation (n=1).

    3.1.2 The polyeletcrolyte used is a commercial cationic guar, Jaguar C13 supplied by Rodia and was used as received without further purification
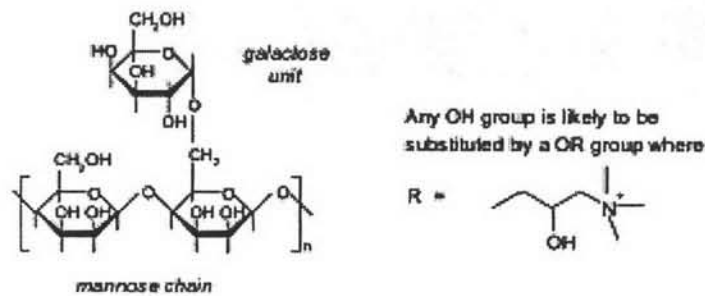

Figure 3.2 Structure of cationic guar.

    3.1.3 Sodium chloride was supplied by Carlo Erba with 99.9% purity minimum and it was used as received without any further purification

    3.1.4 Reversed osmosis water was used for the whole study.

    3.1.5 Virgin Thai hair supplied locally were used as substrate in friction measurement

3.2 Experimental

3.2.1 Surface Tension

In order to determine at which concentration of surfactant the interactions between the polyelectrolyte and the SLES began to take place, surface tension measurement was conducted. The measurement was performed using the wilhelmy plate method on a Dataphysic tensiometer (DCAT II). The surface tension profiles were recorded for sample with and without added Jaguar (at 0.1 and 1 gl $^{-1}$) as a function of SLES concentration.

3.2.2 Phase Diagram

The phase diagram was constructed in order to obtain the information about the phase separation boundary. Solutions of Jaguar and surfactant were mixed together in a test tube to achieve the desired concentrations. The tubes were tumbled for 1 h and then left to stand for two days and the evidence for flocculation and phase separation should be obtained visually. Flocculation and subsequent phase separation should be observed and completed after two days. The minimum concentration of surfactant necessary to observe the phase changed from a clear phase to turbid phase is called the critical flocculation (CFC) concentration and the (higher) concentration of surfactant required to obtain a one-phase region again is called the critical re-solubilization (CRC).

3.2.3 Weight Measurement and Composition of Flocs

Weight measurements were carried out on different systems of SLES / Jaguar known as phase separation (or flocculate) in a total volume of 150 ml. These samples were prepared and left to reach equilibrium over 5 days. The flocs could be seen as a deposit at the bottom of the sample chamber with a resulting supernatant. The procedure for preparing the samples for isolation of the flocs was as followed.

The solution containing the flocs was put in a centrifuge tube then centrifuged for 20 minutes at 8000 rpm. After this initial centrifugation the top phase of the sample was removed and water added again before another centrifugation process was carried out. These centrifugation processes were repeated for 3 times.

After these centrifugations the flocs should be seen to be 'grouped' together. The wet mass was extracted, weighed and then placed in an oven set at 40°C under vacuum for around 24 hours. The wet mass sample was also freeze-dried so as to acquire some Scanning Electron Microscopy (SEM) micrographs of the flocs.

In order to confirm that the isolated flocs consisted of anionic SLES and cationic polymer Jaguar C13S. FTIR spectra of isolated flocs were conducted on a Nicolet Nexus 670 FTIR spectrometer.

The chemical composition of the flocs was determined using an elemental analysis CHNS 932 determinator (Leco VTF-900 series). Sulphur (one atom in each surfactant molecule) and nitrogen (one atom for each cationic centre on the polymer) levels of the flocs was determined. The ratio between the molar percentage of sulphur and nitrogen can then be calculated to obtain the average number of surfactant molecules bound per cationic polymer centre in the floc.

3.2.4 Size Distribution of the Flocs

The size distribution of flocs was determined by using the Malvern Mastersizer X Version 2.18, Serial number 6389 which allows measurement of the particle in the range from 0.1-1000 micron. This machine is based on laser scattering particle sizer comprised of an optical measurement unit which forms the basic particle size sensor, and a computer which manages the measurement and performs result analysis and presentation. When the particle scatters light it produces a unique light intensity characteristic dependent on the angle of observation. The particle scatters light so that the measured energy on the detector has a peak at a favored scattering angle which is related to its diameter. Large particles have peak energies in small angles of scatter and vice versa, as illustrated in Figure 3.3.
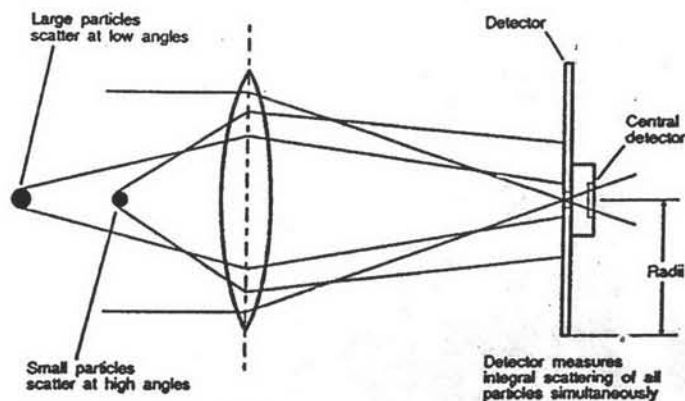
Figure 3.3 Properties of the scattered light (Manual machine operation 0073).

In order to understand the meaning of the results, it is important to note that the instrument is based on a number of fundamental concepts, such as the result is volume based and expressed in term of equivalent spheres. Moreover, results are reported in derived diameters i.e. D(3,2) is called the Sauter mean diameter, D(4,3) is the mean diameter over volume distribution or is sometimes called Herdan diameter and D(V,0.5) is a median diameter.

The procedure to prepare the sample for measurement was as followed; the solution of Jaguar and surfactant were mixed together, stirred for 5 minutes to ensure homogeneous. The flocs solution were then transferred to the sample presentation bath and measurement was taken 10 minutes after sample preparation (10 minute flocculation time), ensured that the minimum obscuration level is met. The instrument required obscuration range between 10-30%. The median particle size, D(V,0.5) was collected and plotted.

3.2.5 Electrophoresis Mobility

In order to estimate the particle charge, the electrophoretic mobility of flocs was performed using zeta-meter system 3.0^+. The Smoluchoeski equation shows a direct relation between zeta potential (ZP) and electrophoresis mobility (EM) as

$$ZP = \frac{4\pi \times V_t}{D_t} \times EM$$

Where   ZP   =   Voltage in electrostatic units

                EM   =   Electrophoretic mobility at actual temperature

                V_t =   Viscosity of suspending liquid

                D_t =   Dielectric constant

In this study, we measured electrophoresis mobility but did not convert the mobility values to zeta potentials because of the difficulty in applying a suitable model for the polyelectrolyte–surfactant particles.

The instrument measures the movement of charged particles relative to the liquid it is suspend in, whist under the influence of an applied electric field. Theoretically, the development of a net charge at the particle surface affects the ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ion of opposite charge to that of the particle) close to the surface. Thus an electrical double layer exists around each surface (DLVO theory). The liquid layer surrounding the particle exists as two part; an inner region called the Stern layer, where the ion are strongly bound and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a national boundary inside which the ions and particles form a stable entity. When the particles moves, ions within the boundary move with it but any ion beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane and the potential that exist at this boundary is related to the mobility of the particle and is called zeta potential. Figure 3.4 shows the diagram of electrical double layer
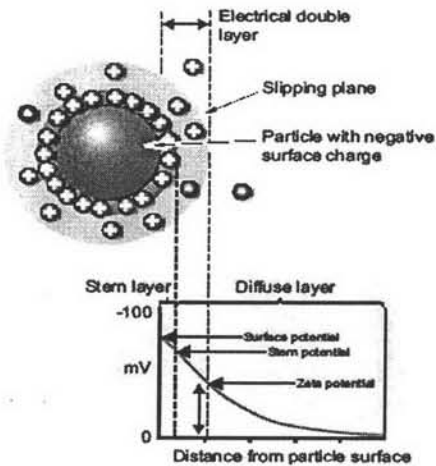
Figure 3.4 Diagram of electrical double layer.

The procedure to prepare the sample for measurement was as follows; flocs were prepared by mixing the solution of SLES and Jaguar together. The samples were then left to reach equilibrium over 5 days. The flocs could be seen as a deposit at the bottom of the sample chamber with a resulting supernatant. The solution containing the flocs was put in a centrifuge tube then centrifuged for 20 minutes at 3000 rpm. This light centrifuge was used to avoid the flocs grouped together in a dense form which would be difficult for further re-dispersion. The centrifuged process was repeated to ensure no excess surfactant presented in the solution, the wet flocs were then obtained. The wet flocs were then re-dispresed in water and left for 1 day before measuring. The dispersed flocs were transferred to an electrophoretic cell of a zeta meter equipped with microscope. After applying a suitable voltage according to the solution conductivity, the mobility values were then recorded.

3.2.6 Surface Analysis

3.2.6.1 Friction Measurement

Standard hair switch of 2.5 gram, 6 inches long and 1.5 inches wide. Friction tests using Texture analyser were performed after treatment. Details of method for hair preparation and cleaning were explained in appendix E. The standard method was as followed; a quick release clamp mechanism is used to fix the sample to the bed. To acquire friction data the friction probe, which weighs 500 g is

placed on the mounted sample and friction loops are recorded at total distance of 80 mm (2 × 40 mm) and a speed of 10 mms^{-1}. The friction probe is a steel cylinder covered with the grey tube rubber material. A data capture rate of 500Hz typically reveals a hysteresis plot as shown in Figure 4 below. For each sample, two measurements are carried out, turning the probe over after the first run. The area of each friction loop is calculated and is a proportional measure of hair friction and is typically reported in the unit of g.mm. A data reveals a hysteresis plot as shown in Figure 3.5 below.
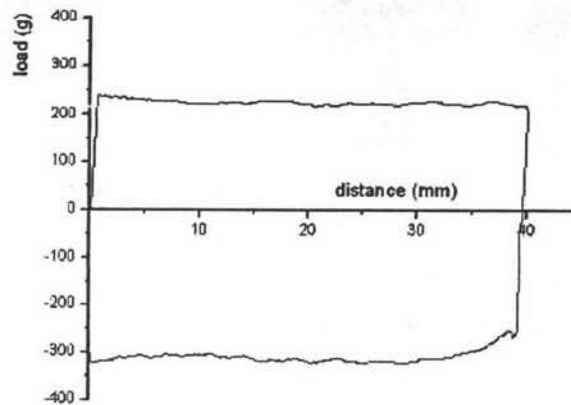

Figure 3.5 Typical friction hyteresis plot.

3.2.6.2 Friction as a Function of Applied Floc Mass

In order to compare the property of each floc characteristic from each point on the phase diagram on the hair frictional property, it was suggested that a constant mass of floc should be used. Therefore, the dose response experiment had to be conducted in order to determine an appropriate dose of floc to be used in the constant mass experiment. In this experiment, the wet isolated flocs was used and the method of preparing the wet isolated flocs was as follow

The solution containing the flocs was put in a centrifuge tube then centrifuged for 20 minutes at 3000 rpm. This light centrifuge was used to avoid the flocs grouping together in a dense form which would be difficult for further re-dispersion. The centrifuge process was repeated to ensure no excess surfactant was

present in the solution. The wet flocs were then separated from the solution. The procedure to prepare the sample for friction measurement was as follow:

The isolated wet flocs were weighted according to the dose range from 0 to 150 mg of dry floc, 20 ml of water to re-disperse the flocs was added. The beakers containing the flocs solution were then stirred for one week to ensure a good dispersion. The re-dispersed flocs solutions were then poured on the hair switches and rubbed for 2 minutes. The hair switches were then left overnight to dry naturally in a temperature and humidity controlled room (22 °C, 50%RH) before measuring the friction using the Texture analyser, procedure as descript above.

3.2.6.3 Friction under Constant Floc Mass

From the dose response experiment, 50 mg of isolated wet flocs was proposed to use in this experiment. The procedure to prepare the sample for friction measurement was as follow:

The isolated wet flocs of each studied point in the phase diagram were weighted at 50 mg, added 20 ml of water to re-disperse the flocs. The beakers containing the flocs solution were then stirred for one week to ensure a good dispersion. The re-dispersed flocs solutions were then poured on the hair switch and rubbed for two minutes. The hair switches were then left for overnight natural dry in a temperature and humidity controlled room (22 °C, 50%RH) before measuring friction using Texture analyser, procedure as described above.