# CHAPTER III

# EXPERIMENTAL

## 3.1 Materials

### 3.1.1 Chemicals

Aerosol-OT or AOT (sodium bis(2-ethyl-1-hexyl) sulfosuccinate, 98% purity, batch no. MKBJ6637V) and Tween 20 (polyoxyethylene (20) sorbitan monolaurate, BioXtra, batch no. SLBD2600V) were purchased from Sigma-Aldrich. The structures of these surfactants are shown in Figure 3.1. All surfactants were used as received.
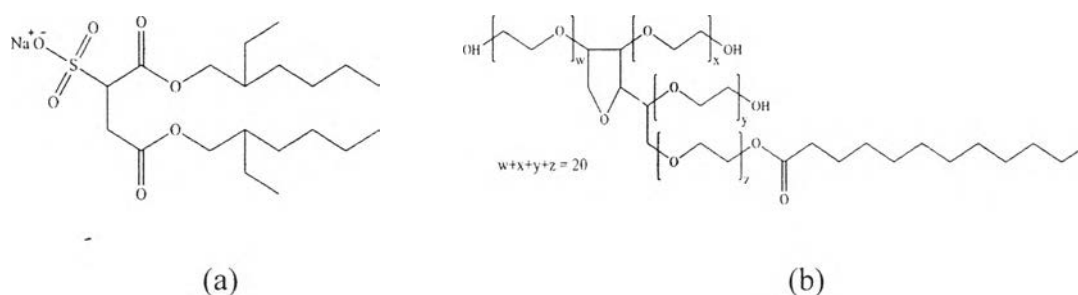


(a)                                      (b)

**Figure 3.1** The chemical structures of (a) anionic surfactant - Dioctyl sodium sulfosuccinate and (b) nonionic surfactant - Polyoxyethylene (20) sorbitan monolaurate.

### 3.1.2 Sensor Crystal

Gold sensor crystals (QSX 301) was purchased from Q-Sense, Biolin Scientific Inc. The layer structure and sensor layout was shown in Figure 3.2 and the sensor specifications was shown in Table 3.1.

Figure 3.2 The structures of (a) gold layer and (b) sensor layout of gold crystal.

Table 3.1 The specifications of gold crystal.

| ·Properties | Specifications |
| --- | --- |
| Description | QSX 301 Gold |
| Top coating material | AT- cut, fundamental frequency 5 MHz |
| Thickness | 100 nm |
| Coating method | PVD (Physical Vapor Deposition) |
| Operating temperature range | 4 – 260 °C |

## 3.2 Equipment

These following equipment were used in this work, such as,

　　1. Quartz crystal microbalance with dissipation (QCM-D), Model E4, from Q-Sense, Biolin Scientific Inc.

　　2. Plasma cleaner (PCD-32G) from Harrick Plasma Inc.

　　3. Syringe pump (NE-1000) from Pump Systems Inc.

　　4. Dynamic contact angle analyzer (DCA-322) from Cahn Scientific Inc.

　　5. Ultrasonic cleaner with heater (EW-08855-10) from Cole-Parmer Instrument Company

　　6. Stirring hot plate (PC-420D) from Corning Inc.

　　7. Barnstead NANOpure II instrument

## 3.3 Methodology

### 3.3.1 Preparation of Surfactant Stock Solutions

AOT and Tween 20 were used as received. A 25 mM stock solution of AOT and a 3.91 mM stock solution of Tween 20 were prepared with the raw surfactant and pure water (Resistivity = 18.2 M$\Omega$·cm, obtained from a Millipore Milli-Q system of ion exchange and activated carbon cartridges).

### 3.3.2 Critical Micelle Concentration Measurements

To measure the critical micelle concentration (CMC) for the individual surfactant, CMCs were obtained from the surface tension using a dynamic contact angle analyzer (DCA-322) at ambient temperature. The Wilhelmy Plate Method was applied. Glass slides (25 x 25 cm) were used to measure surface tension. The graph of log concentration plot as the intersection point of the two best linear fitting for low and high concentrations. The CMCs were measured three times for surfactant and the average values are reported.

### 3.3.3 Cleaning Procedure for Gold Surface

Before inserting each crystal into the flow modules, the crystals were cleaned following Q-Sense protocol (Q-Sense) in order to remove organic and biological material and obtain reproducible measurements as follows:

1. The surfaces were first placed for 10 min within the plasma cleaner (PCD-32G) at a medium rf level.

2. The surfaces were immersed for 5 min in an ammonia-peroxide "base piranha" mixture (APM) (5:1:1 pure water, 25% ammonium peroxide, and 30% hydrogen peroxide, respectively) at 75 °C.

3. The surfaces were rinsed with nanopure water and dried with flowing $N_2$.

4. Surfaces again were placed in the plasma cleaner at a low rf level for 5 min.

### 3.3.4 Adsorption Isotherm Measurements

Measurements was performed using a Q-Sense E4 instrument, Figure 3.3, composed of three parts: the chamber platform which contains the 4 flow modules containing each one a sensor crystal, the Ismatec peristaltic pump that allows to force the solution through the modules, and the electronics unit which connects the whole instrument to the computer for the data acquisition to monitor the different signals. All results are obtained at 25 °C with typical temperature variations in the range of ± 0.05 °C.



**Figure 3.3** QCM-D instrument purchased from Q-Sense.

After the cleaned crystals were achieved, the gold crystals were inserted into the flow modules. Before starting a measurement, a baseline for each gold crystal in the modules with nanopure water, that is, no surfactant was required. Nanopure water was fluxed through the modules using the Ismatec peristaltic pump until the stable baseline was obtained. The baseline was obtained by recording the frequency (and eventually the dissipation) values. A reliable baseline can be obtained when the baseline was flat at the frequency equal to zero or does not drift by more than 0.5 Hz for at least 30 minutes. If it was not the case, we restarted the pump for a few minutes and then proceed to a new acquisition. Once the baseline was sufficiently stable, the experiments began as follows:

1. Individual surfactants adsorption: a series of surfactant concentrations increments from 0 to 2.5(CMC) was flowed through the modules at a

rate of 0.1 mL/min. The steps were of ~ 0.1(CMC), 0.2(CMC), and 0.5(CMC) for concentration ranges from 0 to 0.6(CMC), 0.6(CMC) to 2.0(CMC), and 2.0(CMC) to 2.5(CMC), respectively. At each surfactant concentration sufficient time was allowed until the frequency reached a plateau before increasing the surfactant concentration further. The plateaus were identified as regions in which the frequency did not change more than 0.1 Hz a minute. This procedure required 30-60 minutes for each surfactant concentration, depending on the concentration and properties of the surfactants.

2. Competitive surfactant adsorption: To quantify competitive surfactant adsorption, the effect of sequential addition was studied. The sensing element was first covered by one surfactant layer. Then the other surfactant was added according to the fractional CMC increments described above. Specifically, 1.4(CMC) concentration of either AOT or Tween 20 was first injected to QCM-D. Sufficient time was allowed for a constant adsorption to be reached before further injection of a solution of either Tween 20/1.4(CMC) of AOT or AOT/1.4(CMC) of Tween 20 mixture respectively from 0.1(CMC) to 2.5(CMC). A mixture of surfactants was used instead of pure surfactant to reduce pre-adsorbing surfactant on gold desorbing due to a concentration driving force for surfactants.

### 3.3.5 Dynamics of Adsorption Measurements

To study the kinetics of adsorption, the oscillation resonance frequency was recorded as a function of time when the bulk surfactant concentration was increased.

To understand the role of mixed micelles in the adsorption mechanism, the bulk surfactant concentration was increased from zero to a very small concentration 0.1(CMC) as well as a large concentration 1.4(CMC) on a clean surface (i.e., no surfactant pre-adsorbed).