

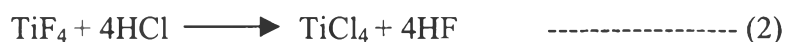
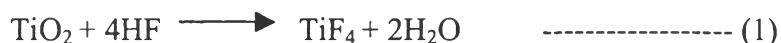
## CHAPTER III EXPERIMENTAL

### 3.1 Chemicals

High purity (98%) anionic surfactant, sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol OT, AOT) obtained from Fluka (Switzerland) was used to prepare microemulsion solutions. The analytical reagent (AR) grade consisted of 99% n-heptane as an oil phase, 99% sodium chloride (NaCl) for salinity scan of microemulsion formation, and 99.5% acetone for rinsing the titanium dioxide precipitate (Lab-Scan, Bangkok, Thailand).

Ammonium hydroxide (NH<sub>4</sub>OH, AR grade) was purchased from J.T.Baker (N.J., U.S.A.). 99.5% Titanium dioxide (TiO<sub>2</sub>, P-25) was obtained from Degussa-Hüls (Frankfurt, GmbH) and 40% Hydrofluoric acid (HF) from Riedel-de Haën AG (GmbH). 56% Perchloric acid (HClO<sub>4</sub>) was purchased from Carlo Erba (Italy). Water used throughout the experiments was deionized water.

Titanium tetrachloride solution (TiCl<sub>4</sub>) in concentrated HCl was prepared by dissolving and heating TiO<sub>2</sub> in concentrated aqueous HF and the combined solutions heated until a clear solution was obtained (Barksdale, 1996 and Kirk and Othmer, 1981). The clear solution was concentrated, then a few milliliters of HClO<sub>4</sub> was added to remove excess HF from the solution, and finally concentrated HCl was added. The reactions are shown below



## 3.2 Experimental Methods

### 3.2.1 Formation of Microemulsion

#### 3.2.1.1 Phase behavior of microemulsion

Experiment on microemulsion preparation involves studying the phase behavior of the system AOT/n-heptane/TiCl<sub>4</sub>/NaCl brine solution at 30°C. Mass fractions of AOT ( $\gamma$ ), oil ( $\alpha$ ), and salt ( $\varepsilon$ ) in the microemulsion system are defined as follows,

$$\alpha = \frac{W_{oil}}{W_{brine} + W_{oil}} \quad \text{----- (3)}$$

$$\gamma = \frac{W_{AOT}}{W_{brine} + W_{oil} + W_{AOT}} \quad \text{----- (4)}$$

$$\varepsilon = \frac{W_{NaCl}}{W_{NaCl} + W_{aqueous}} \quad \text{----- (5)}$$

Where  $W_{AOT}$ ,  $W_{oil}$ ,  $W_{NaCl}$ ,  $W_{aqueous}$ ,  $W_{brine}$  were weights of AOT, n-heptane, NaCl, TiCl<sub>4</sub>, and brine solutions, respectively. The mass fraction of oil ( $\alpha$ ) and the mass fraction of AOT ( $\gamma$ ) were kept constant at 50 wt% and 6.0 wt% respectively. The mass fraction of salt ( $\varepsilon$ ) was varied at 0.1-8.0 wt%.

Preparation of microemulsion by mixing on a Vortex mixer, (Genie-2 G560E, Scientific Industries, N.Y., U.S.A.) the 6.0% weight AOT in n-heptane solution with the aqueous solution of 0.3 M TiCl<sub>4</sub> and NaCl salt. The solution was left in a temperature controlled water bath (Heto DT2, Scandinavia) at 30°C for 2 days until it reached equilibrium, and a microemulsion was observed.

#### 3.2.1.2 Effects of salt on micellar size and water content

The microemulsion type I and II with varying the concentration of NaCl from 0.1-8.0 wt% was used to study the effects of salt on micellar size and amount of water in the microemulsion phase. Micellar size was estimated from dynamic light scattering. Water was determined using acoulometer.

### *3.2.1.3 Effects of $TiCl_4$ concentration*

Microemulsions were prepared by varying the concentration of  $TiCl_4$  at 0.1 M, 0.2 M, and 0.3 M. The effects of  $TiCl_4$  concentration on the micellar size and amount of water were measured as described above.

### *3.2.1.4 Effects of weight ratio of oil to aqueous phases*

The microemulsion was prepared by varying the weight ratio of oil phase to aqueous phase from 0.8 to 1.2. The effect of the weight ratio on the micellar size and the amount of water in the microemulsion phase were measured as described above.

## 3.2.2 Characterization of Microemulsions

### *3.2.2.1 Dynamic light scattering (DLS)*

The apparent hydrodynamic diameter ( $D_h$ ) of microemulsion was determined using dynamic light scattering (Coherent, CA., U.S.A.) at constant angle  $90^\circ$ , pinhole 100, wavelength 514.3 nm, and constant temperature at  $30^\circ C$ . The 3 ml of microemulsion solution filled in a quart cell was measured with DLS. The viscosity and the refractive index of water at  $30^\circ C$  of microemulsion type I are 0.7977 cP and 1.3319, respectively. For microemulsion type II the viscosity and the refractive index of n-heptane at  $30^\circ C$  are 0.3850 cP and 1.3878, respectively.

### *3.2.2.2 Coulometer*

Amount of water in microemulsion phase was determined using coulometer (Metrohm 737 KF, Switzerland). 50.0  $\mu L$  of microemulsion solution was titrated with hydramal coulomat solution. The amount of water reported was an average of three runs.

## 3.2.3 Preparation of Titanium Dioxide Particles in Microemulsion

### *3.2.3.1 Synthesis of titanium dioxide particles in microemulsions*

The microemulsion was prepared by varying the concentration of NaCl from 0.4 to 8.0% by weight and the microemulsion phase was separated from the excess phases for subsequent precipitation. Ammonia gas obtained by bubbling the air through concentrated  $NH_4OH$  solution at the constant

flow rate of 20 ml/min was transferred into the microemulsion to precipitate titanium dioxide at pH 3.0 to 8.0. The optimum pH for the titanium precipitation was at pH 6.0. The precipitate was separated by a high speed and low temperature centrifuge (Sorvall super T21, DuPont, U.S.A.) at 10,000 rpm for 10 min, washed two times with ethanol and acetone to remove the oil and the surfactant from the precipitate particles, dried at 80°C for 24 h to remove water, and calcined for 5 h prior to characterization of the nanoparticles. The calcination temperature was varied from 100 to 600°C. The nanoparticles were characterized using x-ray diffraction, scanning electron microscope, transmission electron microscope and BET surface area analyzer.

### 3.2.4 Characterization of Titanium Dioxide Particles

#### *3.2.4.1 X-ray diffraction (XRD)*

The phase analysis of titanium dioxide particles was done by x-ray diffractometer (Rigaku D/max-2200, Tokyo, Japan) at room temperature. X-ray diffraction patterns of all titanium dioxide particles were obtained by using a Phillips PW 1830/00 No. SY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (wavelength 1.5406 Å). The particles were spread on a glass slide specimen holder and its diffraction angles were examined between 5-90° at a scanning rate of  $2\theta$  of 1.5° per minute with 0.02° increments. CuK $\alpha$  radiation of the x-ray source at  $\lambda = 0.154$  nm was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional x-ray detector and the goniometer angle measurements were sent to an online microcomputer for storing the data and the data were analyzed by PC-APD version 3.5B. Peak positions were compared with the standard files to identify crystalline phases.

X-ray diffraction is based on the fact that an x-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns were used for the average particle diameter (T) estimation by line broadening measurements in the Debye-Scherrer equation:

$$T = K\lambda / \beta \cos\theta \quad \text{----- (6)}$$

where

- $\lambda$  = the wave length (nm)
- K = the Debye-Scherrer constant (assume equal to 0.9)
- $\beta$  = the full width at half maximum (FWHM) of the broadened peak
- $\theta$  = the Bragg angle of the reflection (degree)
- T = the crystal size (nm)

#### 3.2.4.2 Electron microscopes (SEM and TEM)

The size, shape, and morphology of titanium dioxide particles were observed using a transmission electron microscope or TEM (Joel 2010, Tokyo, Japan) and a scanning electron microscope or SEM (Joel JSM-5200, Tokyo, Japan) at room temperature.

The precipitate titanium dioxide was placed on a copper stub and coated with gold at 40 mA for 4 minutes. The precipitate titanium dioxide was measured using the scanning electron microscope at constant accelerating voltage 25 kV.

The specimen for the transmission electron microscope was prepared by placing a small amount of sonicated precipitate titanium dioxide sample dispersed in acetone solution on a 300-mesh carbon film coated copper grid. The particle size of precipitate titanium dioxide was determined at constant accelerating voltage 100 kV.

#### 3.2.4.3 Surface area analyzer

The surface areas of all titanium dioxide particles were determined by measuring the quantity of gas adsorbed onto or desorbed from their

solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature below the critical temperature of the adsorbate. An adsorption or desorption causes the change in the pressure of the sample cell until the equilibrium is established. This volume-pressure data are used to calculate the BET surface area.

The BET surface area of TiO<sub>2</sub> was done by using surface area analyzer (Autosorb I, Quanta Chrom, U.S.A). The titanium dioxide particles was first outgased to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 300 °C for three hours before starting the analysis to determine the surface area. Autosorb ANYGAS Version 2.10 was used to analyze the results.

The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1) P}{V_m c P_0} \quad \text{----- (7)}$$

where

V = the volume of gas adsorbed

P = the pressure of gas

P<sub>0</sub> = the saturated vapor pressure of the liquid at the operating temperature

V<sub>m</sub> = the volume equivalent to an adsorbed monolayer

c = the constant related to the energy of adsorption in the first adsorbed layer, the magnitude of adsorption in the first adsorbed layer, and the magnitude of adsorbate/adsorbent interaction, which is given by:

$$c = \exp \frac{H_1 - H_L}{RT} \quad \text{----- (8)}$$

where

H<sub>1</sub> = the fixed heat of adsorption

H<sub>L</sub> = the latent heat of evaporation

R = the gas constant

T = the temperature

The surface area can be determined by the following equation:

$$S_g = \frac{V_m}{0.0224} (6.02 \times 10^{23})(A) \quad \text{----- (9)}$$

where

$S_g$  = the specific surface area ( $\text{m}^2/\text{g}$ )

A = the area occupied by each adsorbate molecule ( $\text{m}^2$ )