

CHAPTER III METHODOLOGY

3.1 Materials

Polyoxyethylene tert-octylphenyl ether or Triton X-100 (nonionic surfactant) and n-hexanol were purchased from Fluka. Polyethyleneglycol dipolyhydroxystearate (Arlacel P-135, nonionic surfactant) was supplied by East Asiatic Company Ltd. The structures of surfactants are shown in Table 3.1. Cyclohexane, acetone, ethanol, and methanol were purchased from Labscan (Thailand). Ammonium hydroxide was purchased from Merck. Tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Purum) was purchased from Aldrich.

3.2 Experimental Methods

3.2.1 Microemulsion Preparation

The microemulsion system consisted of non-ionic surfactant/n-hexanol/cyclohexane/aqueous phase of tin (IV) chloride. The concentration of Triton X-100 (TX-100) was 10 %wt (0.126 molar) and 3 % wt (0.011 molar) for the system of Arlacel P-135 (AP-135). Both systems were prepared at different concentration due to the different HLB numbers. The microemulsion was prepared by varying the molar ratio of water to surfactant (W_o) and the amount of water expressed in equation (3.1). Weights of surfactant and co-surfactant were fixed for studying the effect of water content and temperature. The molar ratio of water to surfactant was varied between 2 and 6 for the system of AP-135 and between 2 and 3 for the TX-100 system. The effect of temperature on micellar size was varied between 30 and 60 °C.

$$W_o = \frac{[\text{H}_2\text{O}]}{[\text{surfactant}] + [\text{co - surfactant}]} \quad (3.1)$$

The effect of co-surfactant was studied by fixing the W_o equal 2 and amount of surfactant (0.126 M. for system of TX-100 and 0.011 M. for the system of AP-135).

Amount of co-surfactant was varied between 10 and 50 % wt at 30 °C. The effect of metal salt precursor concentration was studied by fixing the W_o value, amount of water, amount of co-surfactant and amount of surfactant while the concentration of metal salt precursor was varied in the range of 0.1-0.5 M. The compositions of microemulsion are shown in the appendix A.

Table 3.1 The structures of surfactants

Properties	Arlacel P-135	Triton X-100
Chemical formula	$\text{RCO}(-\text{CH}_2-\underset{\text{OH}}{\text{HC}}-)_{30}\text{OOCR}$	$\text{C}_8\text{H}_{17}\langle\bigcirc\rangle\text{O}(\text{CH}_2-\text{CH}_2-\text{O})_{9.5}\text{H}$
Molecular weight	1,976	646.85
HLB	5.5	13.4
Type of tail	2 tail	1 tail

The solution was stirred for 30 min and settled for 2 days. The apparent hydrodynamic diameter (D_h) of micellar size was determined by dynamic light scattering (DLS) at different temperature.

3.2.2 Precipitation Method

Ammonia (NH_3) gas generated by bubbling air into an ammonium hydroxide aqueous solution was introduced into the reverse micelle microemulsion to precipitate tin hydroxide. The precipitate was rinsed orderly by cyclohexane, ethanol, acetone and distilled water and the precipitate was dried at 110 °C. The precipitate was calcined at various calcination temperatures from 550 to 900 °C for 2 hours to complete the conversion of hydroxide to SnO_2 particles.

3.2.3 Sensing Application

Tin oxides from two different emulsions (0.1 M. and 0.7 M. SnCl_4) were used to prepare for sensing test. The SnO_2 sensing material was mixed with printing oil that has the duty as a glue. The slurry was pasted on a sensing substrate

and fired at high temperature (550 °C) to remove the organic solvent of printing oil from the substrate. The powders formed a thick film on the substrate. The test of sensor was started with application of the 1.5 volt of direct electricity to the sensing layer. The reducing gas carbon monoxide was introduced over the sensing material with varying concentration of 0 to 1000 ppm. The effect of the temperature on the sensing response was varied between 300 and 400 °C. The sensitivity of the sensor to the probing gas was measured by monitoring the changes of the resistance of the sensor using an electrometer. The sensitivity of a sensor was expressed as the ratio of the resistance of the sensor in air to that in the reducing gas ($S = R_{air} / R_{gas}$, where R_{air} is the resistance of the sensor in air and R_{gas} is the resistance in reducing gas).

3.3 Characterization

3.3.1 Characterization of Microemulsion

Dynamic Light Scattering (DLS)

The apparent hydrodynamic diameter (D_h) of microemulsions was determined using dynamic light scattering (Coherent, CA., U.S.A.) at constant angle 60 °, pinhole 200, and wavelength 514.3 nm. The 5 ml of microemulsion solution filled in a quart cell was measured with DLS.

3.3.2 Characterization of Tin Dioxide Particles

X-ray diffraction (XRD)

The phase analysis of tin dioxide particles was done by x-ray diffractometer (Rigaku D/max-2200, Tokyo, Japan) at room temperature. X-ray diffraction patterns of all tin 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 2θ of 1.5° per minute with 0.02° increments. CuK α 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 was sent to an online microcomputer for storing the data and

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 could be found between the pattern of an unknown and reference, chemical identity could be assumed. It is also possible to make a relatively semi-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 pattern is used for the average particle diameter (T) estimation by line broadening measurements in the Debye-Scherrer equation:

$$T = K\lambda / \beta \cos\theta \quad (3.2)$$

Where

λ = the wavelength (nm)

K = the Debye-scherrer constant (assume equal to 0.9)

β = the full width at half maximum (FWHM) of the broadened peak

θ = the Bragg angle of the reflection (degree)

T = the crystal size (nm)

Electron microscopes (SEM and TEM)

The size, shape and morphology of tin dioxide particles were observed using a transmission electron microscope or TEM and a scanning electron microscope or SEM at room temperature.

The morphology of tin dioxide was characterized by SEM. The precipitate tin dioxide was placed on a copper stub and coated with gold at 10 mA for 4 minutes. The precipitate tin dioxide was measured using the scanning electron microscope (SEM) at constant accelerating voltage of 25 kV.

The size, shape and morphology of tin dioxide particles were observed using a transmission electron microscope or TEM. The specimens for the transmission electron microscope were prepared by placing a small amount of

sonicated precipitated tin dioxide sample dispersed in acetone solution on a 300-mesh carbon film coated copper grid. The particle sizes of tin dioxide were determined at constant accelerating voltage of 100 kV.

Surface area analyzer (BET)

The surface areas of all tin 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 caused the change in the pressure of the sample cell until the equilibrium was established. This volume-pressure data were used to calculate the BET surface area.

The BET surface area of SnO₂ was done by using surface area analyzer (Autosorb I, Quanta Chrom, U.S.A.). The tin dioxide particles were first outgased to remove the humidity and volatile adsorbates adsorbed on the surface under vacuum condition at 250°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 is calculated by using the Brunauer-Emmett-Teller (BET) equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P_0} \quad (3.3)$$

Where

V = the volume of gas adsorbed

P = the pressure of gas

P₀ = the saturated vapor pressure of the liquid at the operating temperature

V_m = 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 adsorption layer, and the magnitude of adsorbate/adsorbent interaction, which is given by:

$$c = \exp \frac{H_1 - H_L}{RT} \quad (3.4)$$

where

H_1 = the fixed heat of adsorption

H_L = the latent heat of evaporation

R = the gas constant

T = the temperature

The surface area can be determined by the following equation:

$$S_g = \frac{V_m}{0.0224} (6.02 \times 10^{23})(A) \quad (3.5)$$

where

S_g = the specific surface area (m^2/g)

A = the area occupied by each adsorbate molecule(m^2)