CHAPTER III
EXPERIMENTAL SECTION

In this chapter, the preparation method of silica particle was overviewed. It also included the colloidal solution for hosting all of the formation mechanisms, the chemical constituents required, and the controlled conditions used in this studied system. Moreover, the techniques used to characterize the morphology (i.e., dimension) were described, and the fundamental kinetics of silica particle formation in W/O microemulsion system was mentioned.

3.1 Materials

The high purified and qualified nonionic surfactant, Polyoxyethylene dodeylphenyl ether (POE), was used to prepare W/O microemulsion solution. POE has an average of six oxyethylene groups per molecule (DP6, CH_3-(CH_2) $_{11}$—◯—$(OC_2H_4)_6OH$) and its molecular weight is approximately 526. This surfactant was a complementary from RHONE-POULENC Chemical Company, which has commercial number of Igepal RC520. The HPLC grade of n-heptane (oil media) and 1-butanol (co-surfactant) were obtained from Fisher Chemical Company, Chicago. Aldrich Chemical Company supplied HPLC grade of 28% aqueous ammonia and 98% tetrabuthyl orthosilicate (TBOS, Si $(OC_4H_9)_4$, M.W. 320.55) that utilized as a base catalyst and initial reagent, respectively. The water used was deionized at 18 Mohm by utilizing DI-water generating machine that was manufactured by Fisher Chemical Company.

3.2 Experimental Methods

3.2.1 Phase Diagram Study

The single-phase boundaries of the W/O microemulsion known as the solubilization limit were determined by titration with aqueous component into the premixed stock solution. This solution that provided from the mixture containing DP6/heptane was placed in 20-ml screw-capped vials. Titration was carried out by gradually adding aqueous component, drop-by-drop, into the premixed solution. After each addition of the aqueous component, the sample was shaken gently and kept at constant temperature of 22°C. Once the sample turned transparent bluish, it indicated the reaction already reached the soluble equilibrium.

3.2.2 Silica Particles Preparation in W/O Microemulsions

There were two experiments being carried out, the first experiment was the study of kinetics of silica particle formation in W/O microemulsions from TBOS; the second experiment was to determine the effect of butanol on the size distribution of silica particles. Prior to the preparation of samples for both experiments, all the chemicals used (n-heptane, 1-butanol, and deionized water) were filtered by using 50 μm in pore size filter papers in order to remove all contaminants.

For the preparation of W/O microemulsions or reverse micelle solution, the given amounts of aqueous ammonium and DI water were added into the premixed solution of DP6/n-heptane. The mixture was then shaken vigorously till it became homogeneously transparent. After that, the defined amount of TBOS was applied to the solution. The silica particles occurred immediately through the hydrolysis and condensation reactions of TBOS. The entire reaction was carried out in a 20 ml tightly capped Teflon vial. The

temperature was also kept constant at 22 °C throughout the experiment. The occurrence of bluish-white-opalescence color was used to indicate the presence of silica particles formed.

To control the size distribution of silica particles, the defined amount of butanol was added into the solution containing 50 g DP6/n-heptane. The further steps and operating conditions were performed under the same operating conditions used in the above experiment. The detail of all procedures is shown schematically in the Figure3.1.

3.3 Characterization Techniques

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy was used to study the kinetics of TBOS hydrolysis in the microemulsion solution. The location and the intensity of IR spectra absorption bands were used to quantify the concentration of TBOS. The IR spectra locating at wavenumber of 805 and 905 nm^{-1} are Si-O-Si stretching. The intensities of each band are differed considerably from the absorption background that contributed by heptane and DP6 surfactant. The transmission FTIR spectra of microemulsion solutions were determined by using a single-beam Mattson CYGNUS 100 FTIR spectrophotometer equipped with a wide-band mercury-cadmium-telluride (MCT) detector. The scattering of the incident beam by silica particles was considered negligible for two reasons: 1) there was diluted amount of silica particles and the silica particles; 2) the diameter of 40-50 nm was much smaller than the wavelength of infrared light. A triangular apodization method was employed for Fourier transforming the interferogram. The sample solution was accommodated with a pair of zinc selenide (ZnSe) windows with spacer, a 0.2 mm thickness.
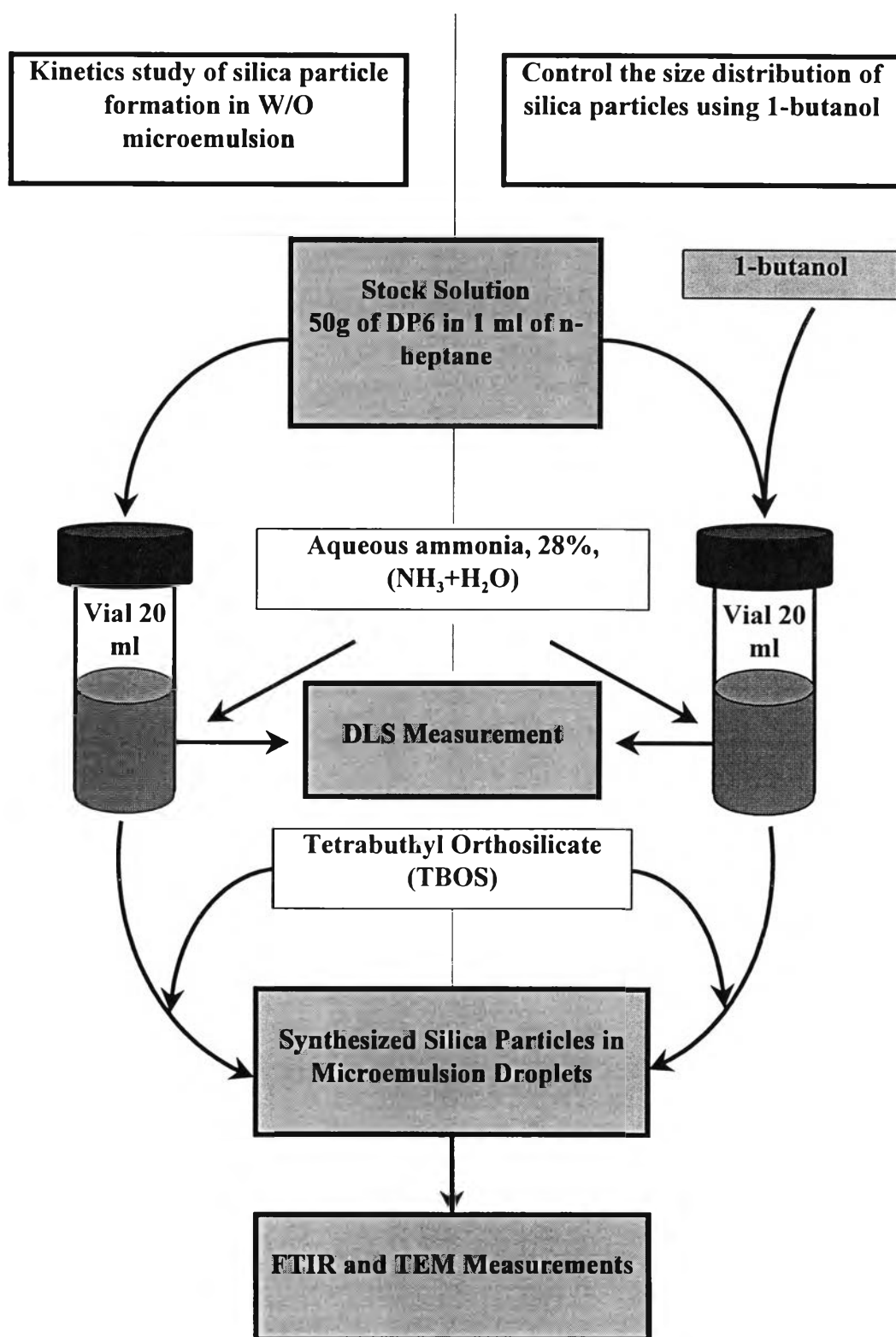
Figure 3.1 Schematic diagram of overall experiments

3.3.2 Transmission Electron Microscopy (TEM)

The size and morphology of the silica particles synthesized in W/O microemulsions were investigated by using a JEOL 200 FX transmission electron microscope. The specimen for TEM measurement was prepared by placing a small amount of sonicated sample solution on a 300-mesh carbon-coated copper grid (Structure Probe, 3520C) supported on filter paper. Since drying oven cannot potentially evaporate the residual DP6 surfactant that remained on the copper grid, dichloromethane was added to wash it off. The diameter of silica particle was measured from the enlarged image of the TEM micrographs by View Capture Apparatus. The average diameter of the silica particle was determined from the measured values of 200 particles. For the particle-size distribution, the standard deviation, σ, were computed using the average diameter, $<D>$, as

$$\sigma = \left[\langle D^2 \rangle - \langle D \rangle^2 \right]^{\frac{1}{2}} \tag{3.1}$$

3.3.3 Dynamic Light Scattering (DLS)

Dynamic light scattering was employed to estimate the apparent hydrodynamic diameter (D_h) of W/O microemulsion droplet entities in the sample solution. For colloidal entities that randomly move in liquid media, their second order autocorrelation function (g_2) measured by DLS is given as

$$g_2 - 1 = \exp\left(-2q^2 D\tau\right) \tag{3.2}$$

where τ is the correlation time, q is the magnitude of the scattering vector and θ is the scattering angle of incident light. The term of g_2 is also expressed as:

$$g_2 = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{3.3}$$

where λ is the wavelength of light in vacuum, and n is the refractive index of solution.

D is the diffusion coefficient of colloidal entities in solution, which relates to the apparent hydrodynamic diameter, D_h, of colloidal can be calculated by the following Stokes-Einstein relation:

$$D = \frac{kT}{3\pi\mu D_h} \qquad (3.4)$$

where k is the Boltzmann constant, T is the absolute temperature of solution, and μ is the viscosity of solution.

The DLS instrument used in this study contained a photon multiplier tube connected with a 136-channel digital correlator (COHERENT, INNOVA 70). A laser source was equipped with the 2-W argon bulb which produces a light with a wavelength of 514.5 nm. The temperature was carried out at 295 K. Since the microemulsion solution contains heptane, which is a good solvent for any plastic materials, a round quartz cell was needed to accommodate the specimens for DLS measurement.

3.4 Kinetic Analysis of Silica Particles Formation

The concentration of TBOS obtained from the FTIR spectroscopic measurement was used to examine the kinetics of TBOS hydrolysis. Excessive amount of water was used to stabilize silica particles in microemulsion solution. Due to the constant of water concentration in the initial stage, the rate of TBOS hydrolysis can be assumed as a pseudo-first order reaction. This rate equation with respect to the concentration of TBOS can be described as follows:

$$\frac{[TBOS](t)}{[TBOS](0)} = \exp(-k_h t) \qquad (3.5)$$

where k_h is the apparent rate constant for TBOS hydrolysis, $[TBOS](t)$ and $[TBOS](0)$ are the concentrations of TBOS at reaction time t and at the start of reaction, respectively.

The rate of silica particle growth can be observed by the enlarged photographs of TEM. The pictures show the increment in volume of silica particles (i.e., diameter). The rate of silica particle growth can be also assumed to be a first order reaction, that can be presented as:

$$1 - \frac{V_p(t)}{V_p(\infty)} = \exp(-k_c t) \qquad (3.6)$$

For a fairly mono-disperse particle, it can be approximated in terms of average diameter, $<Dp>$ as follows:

$$1 - \frac{\langle D_p \rangle^3 (t)}{\langle D_p \rangle^3 (\infty)} = \exp(-k_c t) \qquad (3.7)$$

where k_c is the apparent rate constant for silica condensation (i.e., silica particle growth); $V_p(t)$ and $V_p(\infty)$ are the volumes of silica particles at time t and at the end of reaction, respectively.