

CHAPTER III METHODOLOGY

3.1 Materials

CP mineral oil and Milli-Q water were used as oil and water phase to prepare oil-in-water emulsion. Laboratory-grade Triton X-100 (OmniPur, EMD Chemicals) was used as a surfactant. Methylene blue trihydrate was used to dye the oil phase for visual observation. Wax deposition experiments were performed using paraffin wax. n-Octacosane (n-C₂₈H₅₈) purchased from Aldrich, was used to pre-coat the cold finger surface prior to wax deposition experiments.

Solvents purchased from Fischer, including toluene and acetone, were used to clean the homogenizer probe as well as the cold-finger surface. The list of chemicals and their purities is shown in Table 3.1.

Table 3.1 List of chemicals used in the emulsion preparation and wax deposition experiments

Chemical name	Formula	Purity (%)
Triton X-100	C ₁₄ H ₂₂ O(C ₂ H ₄ O) ₉	Laboratory-grade
Methylene blue trihydrate	C ₁₆ H ₁₈ ClN ₃ S·3H ₂ O	95
n-Octacosane	C ₂₈ H ₅₈	99
Toluene	C ₇ H ₈	99+
Acetone	C ₃ H ₆ O	99+

3.2 Equipments

Pulsing vortex mixer from Fisher Scientific was used to dissolve Triton X-100 in deionized water prior to emulsion preparation. Emulsification was performed using homogenize (SCIOGEX D-160). The prepared emulsions were characterized using an optical microscope (Nikon, model Eclipse E600).

Cold finger apparatus was used to generate a waxy deposit under various operating conditions. The microcentrifuge (Eppendorf, model 5418) was also used to separate water from the deposit sample prior to characterizations of wax content. The wax content was characterized by gas chromatograph (Agilent 6890N).

3.3 Softwares

The droplet size distribution (DSD) and volume-based mean diameter (VMD) were analyzed and calculated using Image J and MATLAB software.

3.4 Experimental Procedures

3.4.1 Oil-in-Water Emulsion

Mineral oil-in-water emulsions were prepared using nonionic surface active agent, Triton X-100, which can be completely dissolved in water. In order to make an oil-in-water emulsion, 5 wt% of surfactants based on total mass of oil-in-water emulsion were dissolved in water. Oil-in-water emulsions with different oil fractions varying from 10 vol% to 50 vol% were prepared and characterized using the following procedures under room temperature;

3.4.1.1 *Emulsion Preparation*

5 wt% of Triton X-100 was dissolved in water in a 4mL vial stirred by vortex mixer at 3000 rpm. Then, the vial of clear homogeneous solution of Triton X-100 in water was installed to the homogenizer stand, and homogenized while mineral oil was gradually added over a duration of 6 minutes. After addition of oil, the emulsion was further vortex mixed for 30 seconds using vortex mixer at 3000 rpm.

3.4.1.2 *Macroscopic Stability of Emulsion*

The variation of separated water height of prepared oil-in-water emulsion was observed over 48 hours in order to evaluate the macroscopic or bulk stability of emulsion. The separated water volume fraction was defined as a clear phase separated after a period of time, settling at the bottom of containing vial.

The total height of prepared emulsion was defined as the height of the whole solution including separated water and milky phase.

3.4.1.3 *Emulsion Characterization*

The DSD and VMD of emulsion needed to be observed twice; after finishing the preparation and after 48 hours regarding the evaluation of microstructure stability of prepared oil-in-water emulsion. The samples taken from original prepared oil-in-water emulsion were considered as “dense sample”, which need to be diluted by deionized water before proceeding micrograph analysis. Dense samples could not be used for these analyses owing to overlapping of oil droplets on the micrograph.

Micrographs were then analyzed by image processing program (Image J) for determining the area of each droplet captured in the micrograph, this information acquired from image processing program was further processed using MATLAB software to obtain the DSD and VMD of prepared emulsion.

3.4.2 Verification of Non-existence of Free Oil

Methylene blue trihydrate, a water soluble dye, was dissolved in water (approximately 0.24 wt%) and in order to identify the oil droplets dispersed in oil-in-water emulsion. Moreover, the mixture of oil/water was also prepared without surfactant using blue dye solution to observe any appearance of free oil layers. These experiments indicated and ensured that none of free oil existed in the prepared emulsion.

3.4.3 Cold Finger Experiments

Cold finger apparatus was set-up for simulating the cold wall of a subsea pipeline in the presence of warm waxy oil-in-water dispersed flow as shown in Figure 3.1. This apparatus consisted of a temperature-controlled cold steel cylindrical finger submerged in a jacketed reactor of warm waxy oil-in-water emulsion (Singh, 2001).

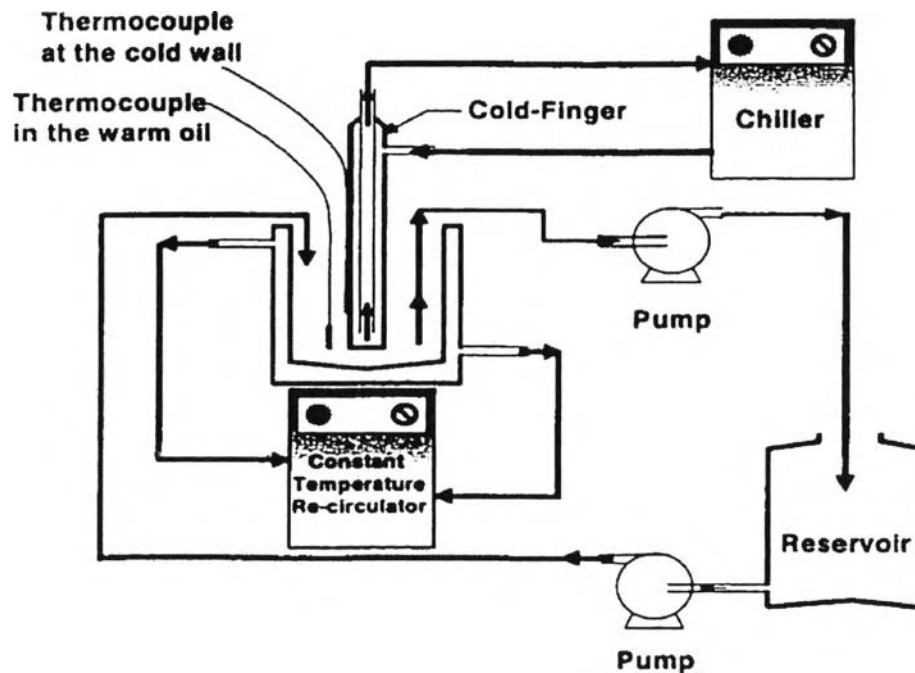


Figure 3.1 Cold finger apparatus (Singh, 2001).

The cold finger experiments were conducted to assess the possibility of wax deposition and also wax deposition rate on different surface characteristics by waxy mineral oil-in-water emulsion. Oil dispersed phase of oil-in-water emulsion was substituted by 10 wt% of waxy model oil. The experiments were separated into two parts: an un-coated and a coated cold finger surface under various operating conditions;

3.4.3.1 Waxy Oil-in-Water Emulsion Preparation

Wax was dissolved in mineral oil (10 wt%) under stirring and heating. The water continuous phase containing 5 wt% Triton X-100 (based on total mass of emulsion) was brought to the desired temperature with a temperature-controlled jacketed reactor. In order to make well-dispersed oil-in-water emulsion, the waxy mineral oil solution was gradually added into stirred water continuous phase.

3.4.3.2 *Wax Deposition on Un-coated Cold Finger Surface*

The cold finger at controlled temperature was inserted into the well-stirred waxy oil-in-water emulsion. The cold finger and oil-in-water emulsion reservoir temperature were set at 5°C and 45°C, respectively at various operating timing: 10 seconds, 30 seconds, 2 minutes, 15 minutes, 30 minutes, 2 hours, 12 hours, and 24 hours. After finishing the experiments, the appearance of the deposit was photographed. Deposit weight and wax content were characterized.

3.4.3.3 *Wax Deposition on Coated Cold Finger Surface*

To coat the surface of cold finger, temperature of the coolant was set at 15°C. The cold finger was then dipped into stock coating solution of 4 wt% Octacosane at 45°C in mineral oil for 30 minutes. Coated cold finger was then inserted into the prepared waxy oil-in-water emulsion as previous procedures for wax deposition on the un-coated cold finger surface.

3.4.4 Wax Deposition Characterization: Wax Content

Deposits on the cold finger had to be analyzed for their carbon number distribution. To collect the deposit sample, the deposit on cold finger was dipped into methyl ethyl ketone (MEK) instantaneously in order to remove the residual oil and water attached to the deposit before sampling in a micro-centrifugal tube and further wax content characterization using gas chromatography.

The centrifuged sample was analyzed for carbon number distribution by GC-FID with initial temperature of 325°C and 9.5 atm. To proceed characteristic analysis the sample, collected sample was firstly multiple-dissolved by toluene, the final concentration was approximately 0.7 to 0.9 g/L. Then, stirred by vortex mixer at 3000 rpm for 30 seconds and centrifuged at 14000 rpm for 5 minutes (toluene blank had to be put opposite to the sample in the centrifuge). Afterward, the GC micro-syringe was rinsed by toluene for 10 times, followed by the sample for 10 more times. Eventually 1.8 µL of sample was injected into the preset GC-FID.