

CHAPTER III EXPERIMENTAL

3.1 Materials and Chemicals

Phet crude oil samples with low water content, A15T, C09T, D12T, F09T, and W05T and high water content, W09T, A02T, X09T, B15T, X12T, B02T, and B24T were obtained from Lankrabue Oilfield.

Non-ionic surfactants supplied by Huntman Co., Ltd. were EO-PO block copolymers, Teric PE 61 consisting of 6 ethylene oxides and 28 propylene oxides and Teric PE 62 with 17 ethylene oxides and 22 propylene oxides. The surfactants obtained from Clariant Co., Ltd. were oxoalcohol EO-PO adduct (Genapol EP 2584) and ethylenediamine EO-PO block copolymers (Genapol ED 3060). The properties of the surfactants are shown in Table 3.1 and the molecular structures are shown in Figure 3.1.

Table 3.1 Properties of the surfactants**

| 1. EO/PO block copolymers | | | | | | | | | |
|---|------|--------|--------|------------------|--------------------------|-----|------------|-----|---------------|
| | M.W | EO No. | PO No. | Cloud point (°C) | Viscosity (cP) @ 20 °C | HLB | Solubility | | Sp.gr. @ 20°C |
| | | | | | | | Water | Oil | |
| Teric PE 61 | 1900 | 6 | 28 | 16-18 | 51 | 3 | I | I | 1.017 |
| Teric PE 62 | 2000 | 17 | 22 | 22-24 | 60 | 7 | S | I | 1.032 |
| 2. Oxoalcohol EO-PO adduct | | | | | | | | | |
| | M.W | EO No. | PO No. | Cloud point (°C) | Viscosity (mPas) @ 50 °C | HLB | Solubility | | Sp.gr. @ 20°C |
| | | | | | | | Water | Oil | |
| Genapol EP 2584 | 791 | 8 | 4 | 39-42 | 20-30 | 12 | S | I | 0.99 |
| 3. Ethylenediamine EO-PO block copolymers | | | | | | | | | |
| | M.W | EO No. | PO No. | Cloud point (°C) | Viscosity (mPas) @ 50 °C | HLB | Solubility | | Sp.gr. @ 20°C |
| | | | | | | | Water | Oil | |
| Genapol ED 3060 | 4856 | 30 | 60 | 28-30 | 230-330 | N/A | S | I | 1.03 |

* Solubility : I = insoluble, S = soluble

** From product specification of Huntman Co., Ltd. and Clariant Co., Ltd.

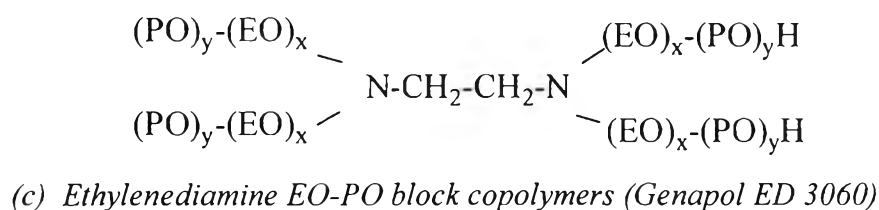
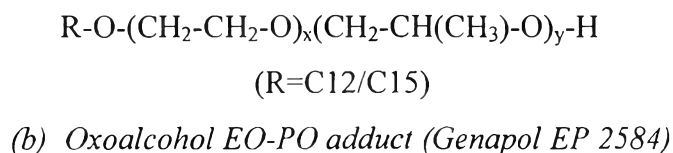
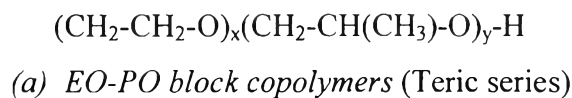


Figure 3.1 Molecular structures of the surfactants used in demulsification tests.

Carbon disulphide (synthesis grade) was supplied by Merck KGaA Co. (Germany), used for diluting crude oil sample to identify hydrocarbon components by Sim-Dist GC. n-Heptane 99% purity (AR grade) was obtained from Lab-Scan Asia Co. (Bangkok, Thailand), used in Nguyen method (Nguyen *et al.*, 1999) to dissolve crude oil sample and to determine amount of asphaltenes and sediments. Toluene (AR grade) was supplied by Lab-Scan Asia Co. (Bangkok, Thailand), used to dissolve crude oil sample before determining water content in the crude by Karl-Fischer titrator. Methanol (AR grade) was obtained from Lab-Scan Asia Co. (Bangkok, Thailand) and hydranol-composite-5 (AR grade) from Sigma-Aldrich (Germany) was used as a titrate solution for Karl-Fischer titrator.

3.2 Experimental Procedures

3.2.1 Characterization of Crude Oil Samples

Water Content in Crude Oil Samples. The water content in crude oil sample was determined following ASTM D 4928 by the Karl-Fischer 720 KFS automatic titrator (Metrohm, Switzerland).

Water content as a blank in the KF reagent was initially determined by introducing 10 μl of distilled water by using a microsyringe to the solution. Then water content in crude samples were determined, the crude was blended with toluene to 50% by volume. Then 25-30 microliters of the crude solution withdrawn by a microsyringe was weighed and injected into the methanol bulk solution in a KF titrator and the microsyringe was weighed again. The amount of sample injected was determined from the weight difference of the microsyringe. Water was determined from the volume of KF solution used to reach the end point. The amount of water content was automatically calculated and reported on the display panel of KF titrator.

Viscosity of Crude Oil Samples. The viscosity of crude oil samples was determined by Brookfield DV III viscometer (Brookfield engineering labs, USA.). The crude oil was shaken for 200 times at 2 strokes/sec to achieve a homogeneous emulsion, and then the viscosity measurement was conducted at 30-47°C with the spindle no. 21. The crude sample was introduced to a level of half of the chamber and then the spindle was placed into the chamber. The speed of rotation was applied and percent torque and viscosity were recorded. The exact value of viscosity was achieved when the percentage of torque was exceeded 95% or the rotating speed was adjusted.

Density of Crude Oil Samples. The density of crude oil sample was determined following ASTM 1298-85 by using a hydrometer. The crude oil sample was warmed at 48°C until it became sufficiently fluid and then was transferred to a hydrometer cylinder. The fluid was stirred using a combination of vertical and rotational motions of a stirring rod to ensure uniform temperature and density throughout the hydrometer cylinder and then the temperature was recorded. A hydrometer was settled slowly in the crude. The crude density was recorded when the hydrometer has come to rest floating freely away from the walls of the cylinder.

Asphaltenes and Sediments. The crude oil was measured for its asphaltenes and sediments content by following modified Nguyen's method (Nguyen *et al*, 1999). Crude oil sample (2.5 grams) was dissolved in n-haptane (ratio of crude oil sample : n-heptane = 1 : 10). Asphaltenes and sediments after precipitation at 0°C for 24 hours was filtered through a Whatman filter paper (No.40), dried at 60°C, and weighed. Net weight of asphaltenes and sediments was obtained by subtracting the

total weight from the weight of the blank filter paper. The asphaltenes in the mixture was dissolved in toluene and the sediment was left as a residue. The amount of asphaltenes was determined from the weight difference between the asphaltenes-sediments mixture and the residue.

Simulation Distillation Gas Chromatograph. A Varian GC-3800 simulated distillation gas chromatograph (Sim-Dist GC, Holland) was used to identify hydrocarbon distillation by following ASTM D 2887. The crude oil sample was homogenized at 48°C, dissolved in carbon disulfide (CS₂) in the volume ratio of 1:200. Then the crude solution was filtered and kept in a vial. One microliters of crude in carbon disulfide solution was auto sampling injected at 295°C injector temperature with helium carrier gas at the flow of 18 ml/min. The GC column was Chrompak capillary column (CP 7512) with length of 10 m, diameter of 0.53 mm, and thickness of 0.88 µm. The column was operated with temperature program at 20°C for 5 min and increasing the temperature with the rate of 20°C/min for 14.5 min until reaching the final temperature of 320°C and held for 8.5 min. The chromatographic peaks were detected by flame ionization detector (FID) at temperature of 320°C.

3.2.2 Experimental Design Study

The factors and levels were selected to vary in the experiment. In this study, three factors (temperature, demulsifier concentration and demulsifier type) each at two levels (high and low) were selected, which is called a 2³ factorial design. Then the response variable (% water separation) was selected for the experiments. Table 3.2 shows factors and levels in the experimental design.

Table 3.2 Factors and levels in experimental design

| Factors | Levels | |
|-------------------------------------|-------------|-----------------|
| | Low (-) | High (+) |
| A = Temperature (°C) | 55 | 60 |
| B = Demulsifier concentration (ppm) | 25 | 50 |
| C = Demulsifier type | Teric PE 61 | Genapol ED 3060 |

The main and the interaction effects between each factor were studied. A capital letter is used to denote the effect of each factor. Thus, “A”, “B”, “C” and “AB” refer to the effects of temperature, demulsifier concentration, demulsifier type, and interaction between A and B, respectively. In the 2^3 factorial design, the low and high levels of A and B are denoted by “-” and “+”, respectively.

The eight treatment combinations in the design are represented by lowercases letters. The high and low levels of any factor in the treatment combination are denoted by the corresponding lowercase letter and the absence of the letter. For example, “a” represents the treatment combination of A at high level, B and C at low level. “b” represents the treatment combination of B at the high level, and A and C at low level, and “ab” represents the treatment combination of A and B at the high level, and C at the low level. In addition, (1) denote all factors at the low level, the treatment combination with corresponding to the experimental condition shown in Table 3.3.

The eight runs in the 2^3 design are listed as shown in Table 3.4. This is sometimes called the design matrix. It is often convenient to write down the treatment combinations in the order of (1), a, b, ab, c, ac, bc, and abc. This is referred to as standard order (Douglas, 1997).

Table 3.3 All treatment combinations corresponding to the experimental condition

| Treatment combination | Temperature (°C) | Demulsifier Concentration (ppm) | Demulsifier Type |
|-----------------------|------------------|---------------------------------|------------------|
| (1) | 55 | 25 | Teric PE 61 |
| a | 60 | 25 | Teric PE 61 |
| b | 55 | 50 | Teric PE 61 |
| ab | 60 | 50 | Teric PE 61 |
| c | 55 | 25 | Genapol ED 3060 |
| ac | 60 | 25 | Genapol ED 3060 |
| bc | 55 | 50 | Genapol ED 3060 |
| abc | 60 | 50 | Genapol ED 3060 |

Table 3.4 Total number of run and label in the 2^3 design

| Run | A | B | C | Label |
|-----|---|---|---|-------|
| 1 | - | - | - | (1) |
| 2 | + | - | - | a |
| 3 | - | + | - | b |
| 4 | + | + | - | ab |
| 5 | - | - | + | c |
| 6 | + | - | + | ac |
| 7 | - | + | + | bc |
| 8 | + | + | + | abc |

3.2.3 Demulsification Study

Demulsifier preparation. The demulsifiers were diluted by xylene in order to reduce their viscosity. The ratio of demulsifier to xylene was equal to 1.5 : 1 (Pena *et.al.*, 2005). In addition, the mixed demulsifiers of Teric PE 61 and Genapol ED 3060 were prepared at different weight ratios of Teric PE 61 to Genapo ED 3060 equal to 0 : 100, 20 : 80, 40 : 60, 60 : 40, 80 : 20, and 100 : 0. The weight ratio of demulsifier to solvent was 1.5 : 1 (Appendix B).

Mixed crude preparation. The two crudes of W05T and B02T were mixed at 6 different ratios to obtain water contents of 0.50%, 14.7%, 28.8%, 43.0%, 57.1%, and 71.3% in the study of the effect of water-to-oil ratio on viscosity. Three levels of water cut of low (14.7%), medium (43.0%), and high (71.3%) were selected for study the effect of temperature, demulsifier concentration, separation time, and mixed surfactants. Furthermore, four-mixed crude (B15T : X12T : B02T : B24T = 1 : 1 : 2 : 2) with water content of 70.24% was used for study the effect of separation time, mixed surfactants, and large scale test (Appendix B).

Screening of demulsifiers. The bottle test was carried out to measure free water separation. The crude oil sample as received was shaken to obtain homogeneous emulsion. Then 10 ml of crude was poured into a centrifuge tube. A

demulsifier was added into the crude oil centrifuge tube with a concentration of 1000 ppm (wt/wt). Four demulsifiers used were EO-PO block copolymers with 6 and 17 ethylene oxides (Teric PE 61 and 62), oxoalcohol EO-PO adduct (Genapol EP 2584), and ethylenediamine EO-PO block copolymers (Genapol ED 3060). The crude oil and demulsifier were homogenized by hand shaking and vortex mixture for 200 times at 2 strokes per second and placed in a temperature controlled bath at 60°C for 3 hours. The amount of free water separated out was observed at 0.5, 1, 2, and 3 hour. In all experiments, a blank was utilized for comparing the separated water in the absence of the demulsifier.

Effect of Water-to-oil Ratio. The two crudes of W05T and B02T were mixed at 6 different weight ratios of 0.50%, 14.7%, 28.8%, 43.0%, 57.1%, and 71.3%. The mixed crudes were demulsified at 60°C for 3 hours and using 1000 ppm of demulsifier concentration. The water separated out was determined and the free water separation was recorded at 0.5, 1, 2, 3 hours.

Effect of Temperature. The demulsification efficiency of the 3 mixed crudes at three different levels of water cut were investigated by using demulsifier concentration of 500 ppm for 3 hours and varying the temperature, namely, 45, 50, 55 and 60°C. The emulsion was equilibrated at the desired temperature and the free water separation was recorded at 0.5, 1, 2, 3 hours.

Effect of Demulsifier Concentration. The mixed crudes with three different levels of water cut were used. Concentration of demulsifier was varied, namely, 20, 50, 100, 250, and 500 ppm. The water separated out was determined at the best condition from studying the effect of temperature (55°C) for 3 hours. The free water separation was recorded at 0.5, 1, 2, 3 hours.

Effect of Separation Time. The mixed crudes with three different levels of water cut were used. The demulsification efficiency was determined at the best conditions at 55°C, and demulsifier concentration of 20 and 50 ppm. Separation time was varied from 0.5, 1, 2, and 3 hours.

Mixed Surfactants. The mixed crudes with three different levels of water cut were used and the four-mixed crude (B15T : X12T : B02T : B24T = 1 : 1 : 2 : 2) with water content of 70.24% were selected. These crudes were demulsified by using the optimum conditions at water-to-oil ratio at least 40%, temperature at 55°C,

demulsifier concentration of 50 ppm, and separation time of 2-3 hours. The synergistic effect was studied by varying the weight ratios of Teric PE 61 and Genapol ED 3060 equal to 100 : 0, 80 : 20, 60 : 40, 40 : 20, 20 : 80, and 0 : 100.

3.2.4 Preliminary Test for Large Scale

The mixture of 4 crudes (B15T : X12T : B02T : B24T = 1 : 1 : 2 : 2) with water content of 70.24% were demulsified and the demulsification efficiency was determined in a large scale of centrifuge tube (250 ml) using the optimum conditions of demulsifier concentration of 50 ppm, temperature of 55°C, and separation time of 2-3 hours.