

CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

Non-ionic and ionic surfactants were supported by HUNTMAN Co.Ltd and Rhodia PPMC (Thailand) Ltd. The list of surfactants are in Table 3.1:

Table 3.1 Properties of the demulsifiers

Non-ionic surfactants:

1. EO/PO Block copolymer of molecular weight 1000-8000									
1.1 Teric series	M.W	EO .no	PO .no	Cloud point (°C)	Viscosity (cP) @ 20 °C	HLB	Solubility		Sp.gr @ 20°C
							Water	Oil	
PE61	1900	6	28	16-18	51	3	I	I	1.017
PE62	2000	17	22	22-24	60	7	S	I	1.032
PE64	2900	25	31	58-61	85	15	S	I	1.051
PE87	7700	12 5	38	>100	-	24	S	I	1.04
305	-	-	-	-	2500	14	-	-	1.14
1.2 Pluronic series	M.W	EO .no	PO .no	Cloud point (°C)	Viscosity (mPa.S) 23°C	HLB	Solubility in water @ 23°C		Density @ 23°C
PE 4300	1750	6	19	40	400	-	S		1.03
PE 6100	2000	3	30	23	350	-	I		1.02
PE 6120	2100	4	30	25	400	-	I		1.02
PE 6200	2450	9	30	33	500	-	S		1.04
PE 6400	2900	20	30	60	1000	-	S		1.05
PE 6800	8000	12 0	30	>100	-	-	S		1.06
PE10500 (solution)	6500	56	56	>100	10	-	S		1.0
RPE 3110	3500	11	45	21	600	-	I		1.02
RPE 2520	3100	5	46	28	600	-	I		1.02

2 Phenolic glycol	M.W	EO no.	PO .no	Cloud point (°C)	Viscosit y (cP) @ 25 °C	HLB	Solubility in water @ 25 °C	Sp.gr.@25 °C
Nonyl Phenol 6	475	6	4	I	250	10.9	D	1.04
Nonyl Phenol 15	-	15	-	>100	-	15	-	-
Nonyl Phenol 30	1535	30	4	>100	1100	17.1	-	1.072

* Solubility : I = insoluble, S = soluble, D = Disperse

Anionic:

1. Suphosuccinate based dihexyl sulphosuccinate, sodium salt					
Trade name	Sodium sulphate%	Acid value	CMC g AS/l	Sp.gr @ 20°C	Application
Disponil SUS IC 680	<1.0	0.5	5	1.10	emulsifiers in polymer
Disponil SUS IC 640	-	-	-	-	-
2. Sulfosuccinate based on fatty alcohol polyglycol ether, disodium salt					
Trade name	Sodium sulphate%	Acid value	CMC g AS/l	Sp.gr @ 20°C	Application
Disponil SUS 87	<1.0	6	1.6	-	Emulsifiers for finely disperse emulsion
3 Fatty alcohol polyglycol ether sulfate, sodium salt					
Trade name	Sodium sulphate%	Sodium Chloride%	CMC g AS/l	Sp.gr @ 20°C	Viscosity mPa.S
Disponil FES 32	<0.8	<0.8	0.22	1.05	<200
Disponil FES 61	0-0.8	0-0.8	0.36	1.10	-
Disponil FES 77	<0.8	<0.8	0.28	1.10	<200
Disponil FES 993	<0.8	<0.8	0.22	1.10	-
Disponil AFX 780	<0.7	<0.8	0.22	1.02	<180
Disponil AFX 1080	<0.7	<0.8	0.30	1.04	<180
Disponil AFX 4060	<0.6	<0.8	0.54	1.10	<200
Disponil AFX 1575	<0.7	<0.8	0.35	1.05	<180
Disponil AFX 2075	<0.7	<0.8	0.38	1.05	<180
Disponil AFX 3070	<0.7	<0.8	0.42	1.05	<180

g AS/l = gram adsorb per liter (mole per liter)

Other demulsifier:

1. Commercial demulsifier PT-5135

3.1.2 Equipment

Bottle test set for determining the efficiency of the demulsifier

Karl Fischer (KF) automatic titrator for determining the amount of remained water in the crude oil. This method was modified from ASTM D 4928 by adding toluene to solubilize the crude oil.

Water bath for temperature controlling

Brookefield viscometer

3.2 Experiments

3.2.1 Characterization of Crude Oil Samples

3.2.1.1 *Water in Crude Samples*

The determination of water by the Karl-Fischer titration method (ASTM D 4928) has been known for a long time (Fischer, 1935). In carrying out this method, a solvent is generally initially taken (in order to remove the water content) and is titrated to the end point with Karl-Fischer solution. A specific amount of the sample to be examined is then dissolved in the solvent and titrated with the Karl-Fischer solution until the end point is reached. The water content is then calculated from the amount of the sample, the consumption of Karl-Fischer solution and the factor of the solution.

The solvents employed are generally low, monohydric alcohols, such as methanol and ethanol. The solvents are employed either on their own or as mixtures, in order to improve the solution properties for certain groups of substances or to suppress interfering side reactions. However, the solubility of nonpolar compounds, such as petroleum fractions or diesel oils in these solvents is very poor. The problem is increased by the fact that these substances often contain very little water and it is therefore necessary to dissolve a fairly large amount of sample. Under these conditions, accurate determination of water by the Karl-Fischer method is not possible without the addition of a solubilizer.

In this work the crude oil became semi-solid when contacted with a bulk solution (methanol). To avoid this problem crude oil was blended with toluene (50% v/v) before being introduced into the methanol solution.

Procedure of KF method:

1. The water content in KF solution reagent (blank or initial water in KF solution) was determined by using a microsyringe to introduce 10 microliters of distilled water into the solution.

2. The crude was blended with toluene at 50% (v/v). 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.

Procedure of Toluene Method (ASTM D4007):

1. Five milliliters of crude oil was poured into the graduated centrifuge tube.
2. Five milliliters of toluene was added into the tube.
3. The crude and toluene mixture were homogenized by hand shaking for 200 times at 2 strokes per second.
4. The mixture in the tube was equilibrated in a controlled temperature bath at 60 degree for three hours.
5. The amount of free water separated out at 0.5, 1, 2 and 3 hour was observed.

3.2.1.2 Determination of Viscosity

The force is applied to the sample through the plate shaft of the equipment. The resistance force at the plate is then measured and converted to viscosity of the sample. A limitation of the method is that a sample must be a Newtonian fluid. However in the case of crude oil sample is a non-Newtonian fluid since it contained water that tends to separate out. A non-Newtonian fluid is broadly defined as one for which the relationship $F'/S = \text{shear stress/shear rate}$ is not a constant. In other words, when the shear rate is varied, the shear stress doesn't vary in the same proportion (or even necessarily in the same direction). The viscosity of such

fluids will therefore change as the shear rate is varied. Thus, the experimental parameters of spindle and speed all have an effect on the measured viscosity of a non-Newtonian fluid. This measured viscosity is called the apparent viscosity of the fluid, it was not the actual viscosity. In this measurement 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 the 56-57 °C with speed 250 rpm of the spindle no. 21.

Viscosity measurement procedure:

1. Assemble and level the rheometer. Select a range of viscosities of samples.
2. Introduce the crude sample to a level of half of the spindle stem.
3. Apply the speed of rotation
4. Record % torque and viscosity.

The exact value of viscosity was achieved when the percentage of torque was exceeded 95% or the rotating speed was adjusted.

3.2.1.3 *Asphaltenes and Sediments*

Asphaltene and sediments were measured by following Nygen *et al.*, (1999) method. Five grams of crude oil sample was dissolved in n-haptane. Asphaltene and sediments after precipitation at the -10 °C for 12 hours was filtrated through a Whatman filter paper (No.40), dried at 30 °C, and weighed for total weight of asphaltene and sediments. Net weight of asphaltene and sediments was obtained by subtracting the weight of blank filter paper which was already rinsed with n-haptane from the total weight. The asphaltene in the mixture was dissolved in toluene and the sediment was left as a residue which was filtered and weighed again. The amount of asphaltene was determined from the weight difference between the asphaltene-sediment mixture and the residue.

3.2.2 Screening of Demulsifiers

Surfactant screening was done by the bottle test method. The concentration of the demulsifier was 1000 ppm. The crude samples with demulsifier were placed in the water bath at 60°C for 3 hours and the amount of free water separated was recorded at 0.5, 1, 2, 3 hours. The best demulsifier efficiency was

selected from the highest amount of water separation after 3 hours.

Bottle test procedure:

1. The test tube was weighed using a 5-digits balance.
2. Crude oil sample was shaken to obtain homogeneous emulsion, then 10 ml the crude was poured into the test tube and weighed again.
3. Demulsifier was weighed and added into the crude oil in the test tube.
4. The total volume was weighed again. The test tube was then covered with a cork.
5. The crude and demulsifier were homogenized by hand shaking for 200 times at 2 strokes per second.
6. The mixture was equilibrated in a controlled temperature bath at 60 °C for three hours.
7. The amount of free water separated out was observed at 0.5, 1, 2 and 3 hour.

The amount of separated water was determined and recorded for each condition. In all experiments, a blank was utilized for comparing the separated water in the absence of demulsifier.

3.2.3 Effects of Temperature, Salinity, pH, and Solvent

3.2.3.1 Effect of Temperature

The demulsification efficiency of selected nonionic surfactants was investigated at three different temperatures (40°C, 60 °C and 80 °C) to match the actual processing temperatures present at the oil fields production. The solution was equilibrated at 60 °C. The free water separation was recorded at 0.5, 1, 2, 3 hours.

3.2.3.2 Effects of Salinity and pH

The effective anionic demulsifier were selected for further study of the effects of salinity and pH. The initial concentrations of metal ions in the crude samples were determined by inductively coupled argon plasma atomic emission spectrometer (ICP-AES). To prepare the salinity solutions, 0.0, 0.2, 0.4, 0.6, and 0.8 and 1.0 M. NaCl corresponding to weights of 11.7, 23.4, 35.1, 46.8, and 58.5 g respectively were dissolved in 1000 ml distilled water. One milliliter of salinity solution was introduced into 10 ml crude oil in a test tube so the total volume

was 11 ml and the solution was shaken until the solution was homogeneous. Then the solution was equilibrated at 60 °C. The free water separation was recorded at 0.5, 1, 2, 3 hours.

For pH-value, the pH values of buffer solution were 4.01, 7.00, and 10.01. The method was conducted by injecting 0.5 ml of buffer solution in the test cells which were already contained crude oil from those 6 wells. The testing conditions were using 1000 ppm of demulsifiers at 60 °C. The free water separation was recorded at 0.5, 1, 2, 3 hours.

3.2.3.3 *Effect of Solvent*

Solvent was used to dissolve solid or reduce viscosity of demulsifiers. Also, the solvent depress pour point of demulsifiers and facilitates the use of demulsifiers at lower temperature. The solvent also can be used as a co-demulsifier in assistance to break emulsion. The solvent used in this study were methanol, toluene, xylene. The volume of the solvent was 0.5 ml, injected in the test cells containing crude sample and demulsifier after that the amount of free water separated out was measured. The testing condition was 1000 ppm of demulsifier at 60 °C for 3 hours.

3.2.4 Mixed Crude Oil

The crude from 6 wells, i.e., A 07T, C 10T, D 12T, F 09T, F 10T, and W 05T were mixed together and test with demulsifier to measure the water removal. Mixing crude oil together was based on some criteria. Firstly, the water content in the mixed crude oil will be in the range of 30% to 40%, and the water in the mixed crude oil should not separate at room temperature by itself. The weight proportional of each well was calculated based on percent water. Data from PTTEP revealed the water content of those 6 crude oil wells which are 12, 80, 38, 10, 70, and 12 respectively. Mixing crude oil in the proportional of 1:1:1:1:1:1 was exhibited 37% water content.

New crude oil was received on 11/12/05. After tested for water content by KF method, the crude oil would be mixed based on the water content in order to achieve 30%-40% water content. The mixed crude oil would be justified if only the phase separation was not happened after leave out at room temperature.

Teric 61, Teric 62, AFX 780, Pluronic PE6100, and mix demulsifiers between Teric 61 and Pluronic PE6100 were used to test their demulsification efficiency with mixed crude oil by bottle test method then the water remaining will be conduct by KF method to check whether it can remove until the water content less than 0.5% or not.

3.2.5 Analysis of Metal Ion

Cations in crude sample were analyzed by using atomic adsorption spectroscopy by following the step below.

3.2.5.1 *Preparation of Standard*

Standard stock solutions of 1000 ppm were diluted to 10 ppm and then to a measuring range for preparing calibration curve.

3.2.5.2 *Preparation of Sample*

Firstly, the water was extracted from the crude oil by using the bottle test method then free water was pipetted accurately and placed into 25 ml volumetric flask. Secondly, hydrochloric acid (conc.) 1-1.5 ml was added to dissolve all metal ions. The solution was shaken until clear (if not, addition of conc. HNO_3 was needed and shaken again until the solution was clear). Finally, make volume to 25 ml by distilled water.

3.2.5.3 *Measuring Step*

The concentration of metal ions was obtained by comparing its absorbance with the calibration curve of the standard solution. A. Varian Spectra AA-300 was employed to determine the concentration of metal ions by fitted with the standard curve. Calculation curves were needed to find the actual concentration of the metal ion